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Co_5C and Co_4C carbido carbonyl clusters stabilized by $[AuPPh_3]^+$ fragments

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ABSTRACT

The synthesis and structural characterization of $[Co_5C(CO)_{11}(AuPPh_3)_3]$, **1-A** and **1-B**, $[Co_5C(CO)_{11}(AuPPh_3)_2]^-$, **2**, $[Co_5C(CO)_{10}(PPh_3)_2(AuPPh_3)]$, **3**, $[Co_5C(CO)_{12}(AuPPh_3)]$, **4**, $[Co_5C(CO)_{11}(PPh_3)(AuPPh_3)]$, **5**, and $[Co_4C(CO)_{10}(AuPPh_3)_2]$, **6**, is herein reported. Compounds **1–6** have been obtained whilst studying the reactivity of $[Co_6C(CO)_{15}]^{2-}$ with $[Au(PPh_3)Cl]$ under different experimental conditions, even if better alternative syntheses have been, then, found for some of these new clusters. **1–6** contain the electron precise $[Co_5C(CO)_{12}]^-$, $[Co_5C(CO)_{11}]^{3-}$ and $[Co_4C(CO)_{10}]^{2-}$ clusters, or their PPh_3 derivatives, stabilized by $[AuPPh_3]^+$ fragments. Two different isomers of **1**, *i.e.*, **1-A** and **1-B**, have been found in the solid state due to solvation effects and weak d^{10}–d^{10} Au(I)···Au(I) aurophilic interactions. **1-A** and **4** have been previously described in the literature.

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1. Introduction

Several fully interstitial carbide clusters are known, due to the stabilizing effect of interstitial C-atoms [1–6]. Conversely, semi-interstitial carbide clusters are less common and this is likely to be a consequence of the greater reactivity of exposed or semi-exposed carbides. Almost all of the known carbonyl clusters containing semi-interstitial carbides belong to two categories: (a) square pyramidal M_5C clusters possessing 74 Cluster Valence Electrons (CVE) such as $[M_5C(CO)_{15}]$ [7], $[M_5C(CO)_{14}]^{2-}$ (M = Fe, Ru, Os) [8], $[Fe_4MC(CO)_{14}]^-$ (M = Co, Rh) [9], and $[HRe_5C(CO)_{16}]^{2-}$ [10]; (b) butterfly M_4C clusters possessing 62 CVE such as $[HFe_4C(CO)_{12}]^-$ [11], $[Fe_4C(CO)_{12}]^{2-}$ [12], $[Fe_3RhC(CO)_{12}]^-$ [13], $[Os_3MnC(CO)_{13}]^-$ [14]. Most of these clusters are based on Group VIII Metals, whereas as free species they are unknown for Group IX Metals.

We have recently reported the $[\{Co_5C(CO)_{12}\}Au\{Co(CO)_4\}]^-$, $[\{Co_5C(CO)_{12}\}_2Au]^-$ and $[Co_5C(CO)_{12}(AuPPh_3)]$, **4**, clusters which contain a square pyramidal 74 CVE $[Co_5C(CO)_{12}]^-$ fragment stabilized by coordination to miscellaneous Au(I) centers, as well as $[Co_5C(CO)_{11}(AuPPh_3)_3]$, **1-A**, comprising a 74 CVE $[Co_5C(CO)_{11}]^{3-}$ core stabilized by three $[AuPPh_3]^+$ fragments [15]. In addition, $[Co_4C(CO)_{10}\{[CpRu(CO)]Hg[CpRu(CO)_2]\}$ is the only example of a butterfly 62 CVE $[Co_4C(CO)_{10}]^{2-}$ cluster stabilized by interaction with a $\{[CpRu(CO)]Hg[CpRu(CO)_2]\}^{2+}$ fragment [16]. These are the only Co_5C and Co_4C carbonyl clusters containing semi-exposed carbides, and all of them do not exist as free species but require coordination to cationic fragments in order to be stable. A possible explanation is that in the case of Group VIII metals the M_5C and M_4C frames are stabilized by 14–16 and 12–13 CO ligands respectively, which saturate the surface of the clusters and ensure steric protection. Conversely, the hypothetical $[Co_5C(CO)_{12}]^-$, $[Co_5C(CO)_{11}]^{3-}$ and $[Co_4C(CO)_{10}]^{2-}$ clusters contain fewer CO ligands which do not guarantee steric protection resulting in an enhanced reactivity. Thus, it is not surprising that the free clusters are not known, whereas it has been possible to obtain them upon coordination to cationic metal centers. Indeed, this might result in crowding the metal surface with concomitant steric protection as well as electronic stabilization.

As an extension and generalization of our previous work, we herein report the synthesis and structural characterization of $[Co_5C(CO)_{11}(AuPPh_3)_3]$, **1-B**, $[Co_5C(CO)_{11}(AuPPh_3)_2]^-$, **2**, $[Co_5C(CO)_{10}(PPh_3)_2(AuPPh_3)]$, **3**, $[Co_5C(CO)_{11}(PPh_3)(AuPPh_3)]$, **5**, and $[Co_4C(CO)_{10}(AuPPh_3)_2]$, **6**. One isomer of **1** (**1-A**) has been previously reported, and a second isomer **1-B** will be herein described. Clusters **3** and **5** will be compared to the isostructural **4** reported in a previous paper [15]. **1–6** contain $[Co_5C(CO)_{12}]^-$, $[Co_5C(CO)_{11}]^{3-}$ and $[Co_4C(CO)_{10}]^{2-}$ cores stabilized by the interaction to $[AuPPh_3]^+$ fragments, which further confirm their ability to coordinate to anionic metal carbonyl clusters and stabilize unprecedented species [17–23].

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2. Results and discussion

2.1. Synthesis of compounds 1–6

The neutral $[Co_5C(CO)_{11}(AuPPh_3)_3]$, 1 (isomer **1**-**A**), cluster has been previously isolated in very low yields as **1**-**A**·thf·0.5C_6H_{14} whilst studying the reaction of $[\{Co_5C(CO)_{12}\}_2Au]^-$ with four equivalents of $[Au(PPh_3)Cl]$ (Scheme 1) [15]. At the same time, we have reported that $[Co_6C(CO)_{15}]^{2-}$ reacts with 2–3 equivalents of $[Au(PPh_3)Cl]$ resulting in $[Co_6C(CO)_{12}(AuPPh_3)_4]$ [24]. In the search for a better synthesis of **1**, we have studied the latter reaction using increasing amounts of $[Au(PPh_3)Cl]$ and found out that the target compound can be obtained in moderate yields by using four equivalents of the Au(I) reagent per mole of $[Co_6C(CO)_{15}]^{2-}$ (Scheme 1).

Two different isomers of **1** (**1**-**A** and **1**-**B**) showing significant structural differences (see Section 2.3), may be obtained depending on the crystallization conditions. Thus, crystals of the previously reported 1-A·thf·0.5C_6H_{14}, containing isomer **1**-**A**, have been obtained, after work-up, by slow diffusion of *n*-hexane on its thf solutions. Conversely, crystals of **1**-**B**·CH_3CN, containing the new isomer **1**-**B**, have been obtained by slow diffusion of *n*-hexane and di-isopropyl-ether on a CH_3CN solution. In view of the different structures of isomers **1**-**A** and **1**-**B**, they show different IR spectra in solid as Nujol mulls (see Experimental). These crystals are almost insoluble in all organic solvents hampering further studies, such as solution NMR investigations. It is likely that the almost insoluble compounds **1**-**A** and **1**-**B** are formed during crystallization starting from a soluble precursor which undergoes a chemical transformation upon crystallization. For the same reason, the nature of this precursor is, at the moment, unknown.

The closely related mono-anion $[Co_5C(CO)_{11}(AuPPh_3)_2]^-$, **2**, which formally derives from **1** upon dissociation of one $[AuPPh_3]^+$ fragment, has been obtained in moderate yields by reacting $[Co_6C(CO)_{15}]^{2-}$ in thf with two equivalents of $[Au(PPh_3)Cl]$ and one equivalent of PPh_3. The latter, probably, is needed in order to help the elimination of one Co-atom from the cluster. After workup (see Experimental), crystals of $[NEt_4][Co_5C(CO)_{11}(AuPPh_3)_2]\cdot 2CH_2Cl_2$, $[NEt_4]$[**2**]·$2CH_2Cl_2$, have been obtained by slow diffusion of *n*-hexane on a CH_2Cl_2 solution of the cluster. Compound **2** is soluble in organic solvents such as CH_2Cl_2 and acetone, allowing further spectroscopic studies in solution (see Experimental). In particular, the ^{31}P NMR spectrum of **2** displays a singlet at δ_P 44 ppm at all temperatures, indicating a fluxional behavior which makes equivalent the two PPh_3 ligands (Fig. 1). Apparently, **2** does not react with one equivalent of $[Au(PPh_3)Cl]$, whereas decomposition to unknown species is observed by using an excess of the Au(I) reagent.

In the search of new Co–Au carbido carbonyl clusters, we have investigated the reaction of $[Co_6C(CO)_{15}]^{2-}$ with $[Au(PPh_3)Cl]$ under different experimental conditions, such as the addition of free PPh_3 and/or $AgNO_3$. The latter has been employed in order to enhance the reactivity of $[Au(PPh_3)Cl]$.

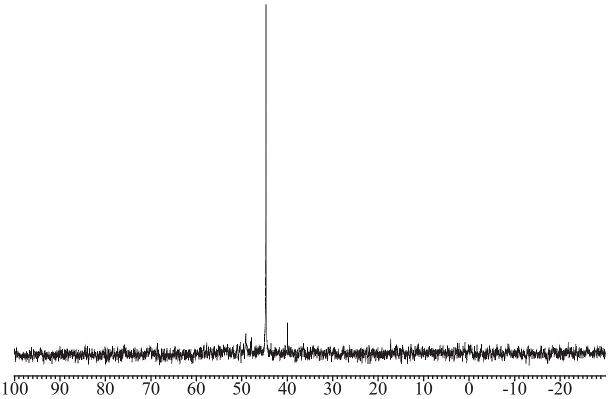
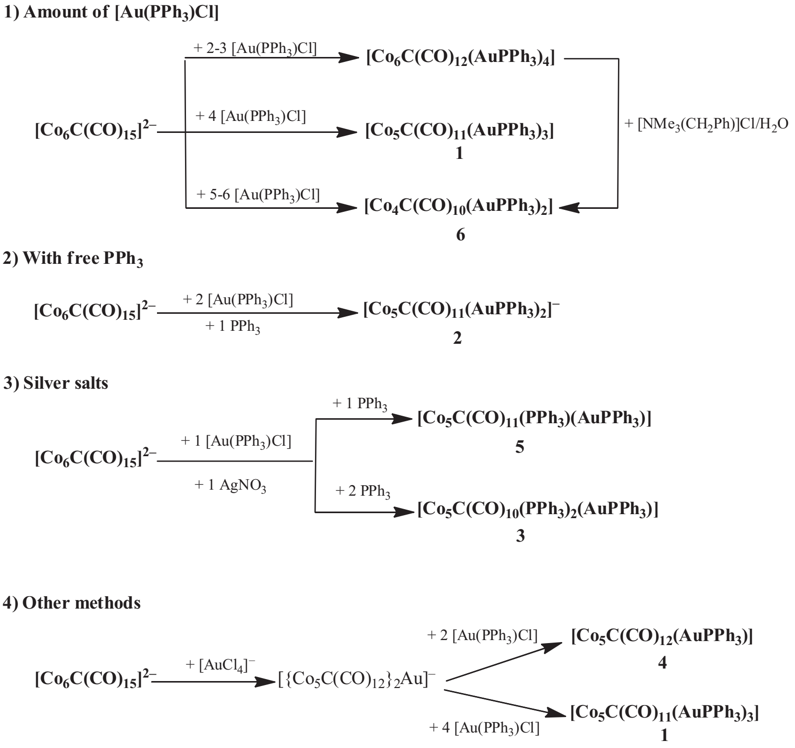


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[Co_5C(CO)_{11}(AuPPh_3)_2]^-$, 2, in CD_2Cl_2 (298 K).



Scheme 1. Syntheses of complexes 1–6.

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