

CrossMark
click for updatesCite this: *Chem. Sci.*, 2015, 6, 5506Received 30th April 2015
Accepted 12th June 2015

DOI: 10.1039/c5sc01578b

www.rsc.org/chemicalscience

A hexanuclear gold carbonyl cluster†‡

Sonia Martínez-Salvador,^a Larry R. Falvello,^b Antonio Martín^a and Babil Menjón^{*a}

The hexanuclear gold carbonyl cluster [PPh₄]₂[Au₆(CF₃)₆Br₂(CO)₂] (**4**) has been obtained by spontaneous self-assembly of the following independent units: CF₃AuCO (**1**) and [PPh₄][Br(AuCF₃)₂] (**3**). The cyclo-Au₆ aggregate **4**, in which the components are held together by unassisted, fairly strong aurophilic interactions (Au⋯Au ~310 pm), exhibits a cyclohexane-like arrangement with chair conformation. These aurophilic interactions also result in significant $\nu(\text{CO})$ lowering: from 2194 cm⁻¹ in the separate component **1** to 2171 cm⁻¹ in the mixed aggregate **4**. Procedures to prepare the single-bridged dinuclear component **3** as well as the mononuclear derivative [PPh₄][CF₃AuBr] (**2**) are also reported.

Introduction

There is much current interest in the study of gold carbonyls, mainly because of both the intriguing nature of the [Au]–CO bond and their involvement in gold-catalyzed transformations of CO, including its low-temperature oxidation by molecular oxygen as well as water-gas shift reaction.³ Direct unambiguous information on the active species in the latter processes is still lacking.⁴ IR spectroscopy is a powerful tool helping to assign the oxidation state of the active sites on the catalyst surface as well as to evaluate the influence of the chemical environment.^{4,5} Well-established gold carbonyls for appropriate comparison are therefore valuable species, although they still remain scarce.⁶ Aside from the following dinuclear derivatives: Cl₃Au(μ-Cl)AuCO,⁷ (tBu^FO)₃Al(μ-Cl)AuCO and [Cl(AuCO)₂][Al(OtBu^F)₄],⁸ the handful of currently isolated gold carbonyls are all mononuclear, either neutral XAuCO (X = Cl,⁹ CF₃,¹⁰ OSO₂F,¹¹ HB(pz*)₃,¹²) or cationic LAuCO⁺ species (L = CO,^{11,13} SIDipp,^{14,15} IDipp,¹⁵ PMes₃,^{14,16} DPCh¹⁷). Additionally, some oligomers of unknown nuclearity have been suggested to form in frozen concentrated solutions of ClAuCO in CH₂Cl₂.¹⁸

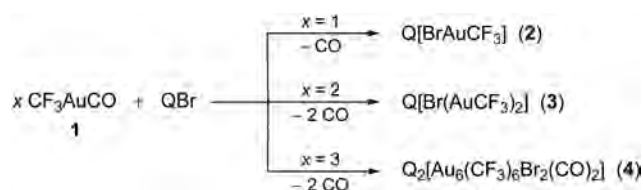
To the best of our knowledge, discrete polynuclear gold carbonyl compounds featuring both the Au–CO and Au⋯Au

interactions are still lacking. Such species, if experimentally available, might illustrate two key interactions occurring on the catalyst surface: (1) CO coordination to an exposed gold center, and (2) cohesive bonding interaction of this active site with the bulk catalyst support. Here we report on a discrete hexanuclear gold carbonyl cluster formed by spontaneous self-assembly of independent Au₁ and Au₂ units, which are held together by *unassisted* aurophilic interactions alone.^{§19–21} It is further shown that such aurophilic interactions have a distinct effect on the vibrational properties of the highly sensitive [Au]–CO unit, which can therefore act as a fine probe of the molecular environment.

Results and discussion

The gold carbonyl compound CF₃AuCO (**1**) has already proven to be a useful synthon of the 'AuCF₃' fragment toward neutral ligands.¹⁰ We have found now that the 1:1 reaction of compound **1** with [PPh₄]Br proceeds in a similar way giving rise to CO replacement (Scheme 1) with formation of the mononuclear anionic derivative [PPh₄][CF₃AuBr] (**2**). This air- and moisture-stable compound shows a typical linear arrangement (Fig. 1).

The coordination of bromide results in significant lengthening of the Au–C distance (211.9(4) pm) with respect to that observed in both the neutral parent species **1** (204.7(14) pm)¹⁰



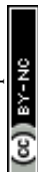
Scheme 1 Synthetic procedures affording the trifluoromethyl-gold derivatives 2–4. In all cases Q⁺ = [PPh₄]⁺.

^aInstituto de Síntesis Química y Catálisis Homogénea (iSQCH), CSIC – Universidad de Zaragoza, C/Pedro Cerbuna 12, E-50009 Zaragoza, Spain. E-mail: menjon@unizar.es

^bInstituto de Ciencia de Materiales de Aragón (ICMA), CSIC – Universidad de Zaragoza, C/Pedro Cerbuna 12, E-50009 Zaragoza, Spain

† Dedicated to Prof. Dr Pablo Espinet on the occasion of his 65th birthday. Abbreviations are defined prior to the Acknowledgements section. As defined in ref. 1, “clusters are molecular units which may contain small or large numbers of similar atoms where there are several short internuclear distances between atom pairs.” This definition is fully compatible with that originally given by F. A. Cotton (ref. 2).

‡ Electronic supplementary information (ESI) available: Experimental procedures, comments on the X-ray structure determinations and 3D Hirschfeld surfaces for the ions constituting the crystal of **4**. CCDC 1049919–1049921. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc01578b



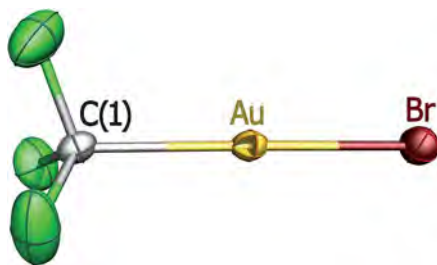


Fig. 1 Displacement-ellipsoid diagram (50% probability) of the mononuclear $[\text{CF}_3\text{AuBr}]^-$ anion as found in single crystals of **2**. Selected bond lengths (pm) and angles ($^\circ$) with estimated standard deviations: Au–Br 240.5(1), Au–C(1) 211.9(5), av. C(1)–F 132.1(7); C(1)–Au–Br 177.64(15), av. Au–C(1)–F 110.7(4), av. F–C(1)–F' 108.2(5).

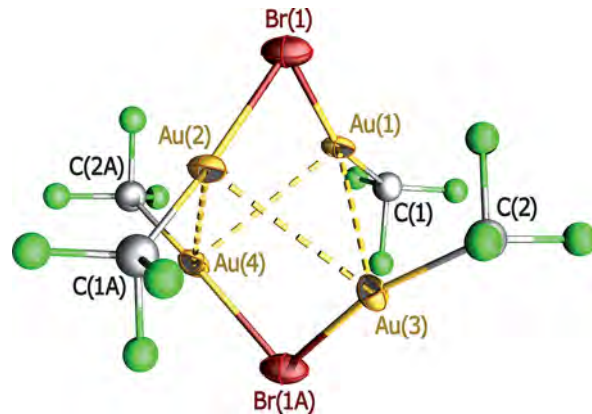


Fig. 2 Structure drawing of one of the two crystallographically independent pairs of dinuclear $[\text{Br}(\text{AuCF}_3)_2]^-$ anions in disordered state as found in crystals of $\mathbf{3} \cdot \text{CH}_2\text{Cl}_2$. Displacement ellipsoids (50% probability) are given only for the heavy atoms. Selected bond lengths (pm) and angles ($^\circ$) with estimated standard deviations: av. Au–Br 244.2(3), av. Au–C 194(2), av. C–F 138(2), av. intramolecular Au \cdots Au' 367.6(2), av. intermolecular Au \cdots Au' 325.9(2); av. Au–Br–Au' 97.6(1), av. C–Au–Br 168.6(7), av. Au–C–F 118(2), av. F–C–F' 99(2).

and the homoleptic anionic derivative $[\text{NBu}_4][\text{Au}(\text{CF}_3)_2]$ (203.3(2) pm).^{10a} The Au–Br distance (240.5(1) pm) is, in turn, comparable to that found in the homoleptic complex halide $[\text{NBu}_4][\text{AuBr}_2]$ (237.6(3) pm).²² In the crystal lattice of compound **2**, the anions are separated by the cations resulting in large intermetallic separations (>0.7 nm).

The 2 : 1 reaction of compound **1** with $[\text{PPh}_4]\text{Br}$ gives rise (Scheme 1) to the dinuclear species $[\text{PPh}_4][\text{Br}(\text{AuCF}_3)_2]$ (**3**) containing single-bridging bromide. In the crystal, the dinuclear anions are self-assembled in pairs (Fig. 2) showing significant intermolecular auriphilic interactions (av. Au \cdots Au' \sim 326 pm), which apparently counteract Coulomb repulsion between the constituent anions in the dimer. The intramolecular intermetallic separation within each dinuclear $[\text{Br}(\text{AuCF}_3)_2]^-$ anion is, in turn, too long to denote any bonding interaction: av. Au \cdots Au' \sim 368 pm. Similar structural patterns have been found in certain halonium $[\text{X}(\text{AuPR}_3)_2]^+$ salts.²³ Recent theoretical studies on the model halonium monocations $[\text{X}(\text{AuPH}_3)_2]^+$ (X = F, Cl, Br, I) at the $X\alpha$ level conclude that they should also undergo self-assembly against Coulomb repulsion to form tetranuclear $[\text{X}(\text{AuPH}_3)_2]_2^{2+}$ clusters, whereby the intermolecular interaction energy for each Au \cdots Au pair was estimated to be 85.0 kJ mol⁻¹ on average.²⁴ It has also been suggested that such type of associations might be counterion-mediated.²⁵ With regard to this possibility, it is interesting to note that no pairwise association was, in fact, observed in several other $[\text{X}(\text{AuL})_2]^+$ salts,²⁶ including the recently reported chloronium gold carbonyl derivative $[\text{Cl}(\text{AuCO})_2][\text{Al}(\text{OtBu})_4]^-$.⁸

The av. Au–C distance in compound **3** (194(2) pm) is significantly shorter than in the mononuclear derivative **2** (211.9(5) pm), whereas the av. Au–Br distance in the single-bridging system of compound **3** (244.2(3) pm) is just slightly longer than that found in the terminal Au–Br bond of **2** (240.5(1) pm). The geometry of the Au–Br–Au unit in the anionic compound **3** is very similar to that found in the cationic derivative $[\text{Br}(\text{AuPPh}_3)_2][\text{SbF}_6]$, which is also associated in pairs in the solid state.²³ The relationship between these cationic $[\text{X}(\text{AuPR}_3)_2]^+$ and anionic $[\text{Br}(\text{AuCF}_3)_2]^-$ species illustrates the already pointed functional similarity between the corresponding cationic 'AuPR₃⁺' and neutral 'AuCF₃' fragments, regardless of their different global charge.^{10a}

We considered whether the strong electrophilic 'AuCF₃' neutral fragment would enable to build a trinuclear $[(\mu_3\text{-Br})(\text{AuCF}_3)_3]^-$ derivative. To this aim, compound **1** was reacted with $[\text{PPh}_4]\text{Br}$ in 3 : 1 ratio. However, instead of the targeted trinuclear species, a hexanuclear compound with formula $[\text{PPh}_4]_2[\text{Au}_6(\text{CF}_3)_6\text{Br}_2(\text{CO})_2]$ (**4**) was obtained (Scheme 1). The reaction outcome makes it clear that the residual nucleophilicity of bridging bromide, $\mu_2\text{-Br}$, in component **3** is not sufficient to expel the extremely labile CO ligand in component **1**. Attempts to force the release of CO resulted in extensive decomposition.

The precise nature of compound **4** was established by X-ray diffraction methods. The crystal lattice is formed by large cations and anions with little polarizing effect on each other and showing no sign of significant extra covalent interactions between them.^{¶27–32} The anion (Fig. 3) is, in fact, an aggregate of the following components: the anion of compound **3** and the neutral precursor species **1**. The components are held together solely by auriphilic interactions of similar strength: Au \cdots Au \sim 310 pm. The six gold(i) atoms exhibit a cyclohexane-like arrangement with chair conformation, *cyclo*-Au₆, of which just a single precedent is known.³³ Upon aggregation, the Au–Br–Au angle in component **3** closes from 97.6(1) to 90.28(3) $^\circ$, probably to favor the auriphilic interaction with component **1**. All these interactions are broken in solution, since the ¹⁹F NMR signals of aggregate **4** dissolved in CH₂Cl₂ correspond to the separate components **1** + **3** in the appropriate 1 : 1 ratio (see Experimental in ESI[†]). Solid samples of **4** at room temperature show no sign of luminescent behavior by UV irradiation.

The stereochemistry of hexanuclear gold clusters is largely dominated by a planar arrangement of the six gold centers in the metal core. For instance, the most simple neutral Au₆ and charged (Au₆)[±] bare clusters³⁴ as well as different $[\text{Au}_6(\text{CO})_n]^-$ adsorbates ($n = 1\text{--}3$)³⁵ and even Au₆H_n ($n = 1\text{--}6$) binary



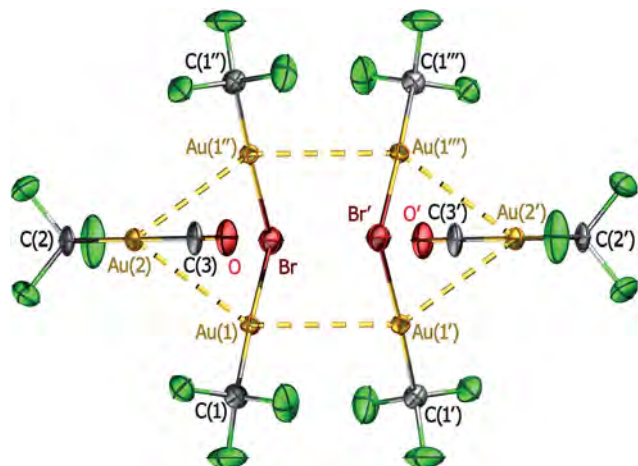


Fig. 3 Displacement-ellipsoid diagram (50% probability) of the hexanuclear $[\text{Au}_6(\text{CF}_3)_6\text{Br}_2(\text{CO})_2]^{2-}$ anion as found in single crystals of **4**. Selected bond lengths (pm) and angles ($^\circ$) with estimated standard deviations: (a) $\text{Au}(1)\text{--Br}$ 245.30(7), $\text{Au}\text{--C}(1)$ 201.1(6), av. $\text{C}(1)\text{--F}$ 136.5(8), $\text{Au}(2)\text{--C}(2)$ 204.5(9), $\text{Au}(2)\text{--C}(3)$ 201.2(11), $\text{C}(3)\text{--O}$ 108.3(11), av. $\text{C}(2)\text{--F}$ 136(1), $\text{Au}(1)\cdots\text{Au}(2)$ 314.83(3), $\text{Au}(1)\cdots\text{Au}(1')$ 307.24(4); $\text{Au}(1)\text{--Br}\text{--Au}(1')$ 90.28(3), $\text{C}(1)\text{--Au}(1)\text{--Br}$ 177.9(2), av. $\text{Au}(1)\text{--C}(1)\text{--F}$ 115.0(4), av. $\text{F}\text{--C}(1)\text{--F}$ 103.4(5), $\text{C}(2)\text{--Au}(2)\text{--C}(3)$ 175.8(3), $\text{Au}(2)\text{--C}(3)\text{--O}$ 179.2(8), av. $\text{Au}(2)\text{--C}(2)\text{--F}$ 114.6(6), av. $\text{F}\text{--C}(2)\text{--F}$ 103.8(7).

hydrides³⁶ all have been assigned triangular planar structures following theoretical calculations. Cyclic planar arrangements of the gold centers were experimentally found in the homoleptic neutral compounds $[\text{Au}_6(\text{SMes})_6]$,³⁷ $[\text{Au}_6(\text{P}^t\text{Bu}_2)_6]$ and $[\text{Au}_6(\text{PCy}_2)_6]$,³⁸ as well as in the heteroleptic $[\text{Au}_6\text{Cl}_4(\text{dppm})_2]^{2+}$ cation containing double-bridging tetraphosphine ligands.³⁹ The precise arrangement of gold centers in hexanuclear gold clusters, however, can be imposed by the presence of heteroatoms and/or additional centers that may exert a template effect. Thus, whereas the six gold(i) atoms in the heterometallic $[\text{Ag}(\text{AuMes})_6]^+$ cation build a planar hexagonal ring around the central Ag^+ ion,⁴⁰ they were found to nucleate in an octahedral fashion around the hyperaurated C atom in the $[\text{C}(\text{AuPPh}_3)_6]^{2+}$ cation.⁴¹ Even the nature of the ancillary ligands is known to play a key role on the stereochemistry of hexanuclear gold clusters. As an example, a standard planar metal core was experimentally found in $[\text{Au}_6(\text{S}_2\text{CR})_6]$ ($\text{R} = o\text{-tolyl}$),⁴² whereas a unique chair conformation was observed in $[\text{Au}_6(\text{S}_2\text{CNR}_2)_6]$ ($\text{R} = \text{aza-15-crown-5}$).³³ The latter arrangement was considered exceptional and it was attributed to the steric effect of the bulky R substituent. Moreover, it has also been noted that “sometimes, the geometry is not imposed by the nature of the bridging ligand(s) but by aurophilicity”.^{20e} Compound **4** is a nice example of this particular behavior whereby, in the absence of significant steric constraints, the structure of the metal core is driven by aurophilic interactions. Recently, the effect of both aurophilic interactions and the nature of ancillary ligands on the self-assembly of complex molecular systems, as well as on the rich structural diversity found in the family of Au^{I} thio-derivatives, has been studied in detail.⁴³

Compound **4** provides a unique opportunity to compare the structural and spectroscopic properties of a gold carbonyl

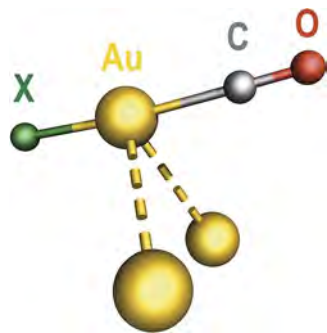
molecule, namely CF_3AuCO , in two different and well defined chemical environments: (a) in isolated pure form (**1**), and (b) adsorbed onto a gold framework (**4**). None of the structural parameters of component **1** are substantially modified in aggregate **4**. However, the $\nu(\text{CO})$ vibration undergoes a significant frequency decrease upon aggregation. In the separate component **1**, each CF_3AuCO molecule is surrounded by three identical neighbors with trigonal symmetry, resulting in an extended three-dimensional network of *weak* aurophilic interactions ($\text{Au}\cdots\text{Au}$ 345.9(1) pm).¹⁰ In solid samples of component **1**, $\nu(\text{CO}) = 2194\text{ cm}^{-1}$, whereas in the *cyclo-Au*₆ aggregate **4** featuring *substantially stronger* aurophilic interactions ($\text{Au}\cdots\text{Au} \sim 310\text{ pm}$) the value drops to $\nu(\text{CO}) = 2171\text{ cm}^{-1}$. Recent theoretical calculations on CF_3AuCO and related systems predicted that aurophilic interactions might have an impact on the vibrational properties of the $[\text{Au}]\text{--CO}$ unit.^{14,44} We now provide experimental support for this prediction, as it is found that aurophilic interactions do have a distinct effect on the $\nu(\text{CO})$ frequency. The experimentally observed trend is, however, opposite to the theoretical predictions: the stronger the interaction, the lower the $\nu(\text{CO})$ frequency.

It is well known that $[\text{Au}(\text{L})]^+$ and ‘ AuX ’ fragments—both having single vacant coordination sites—are isolobal with the simplest Lewis acid, proton H^+ .⁴⁵ This isolobal relationship enables to establish a formal comparison between our CF_3AuCO molecule and the formyl cation HCO^+ . The $\nu(\text{CO})$ frequency of this protonated carbonyl is known to lower from 2184 cm^{-1} in the gas phase⁴⁶ to 2110 cm^{-1} in the condensed phase, namely in superacidic $\text{HF}(\text{l})/\text{SbF}_5$ medium.⁴⁷ Such a large decrease was attributed to interaction of the HCO^+ cation with SbF_5 or anionic species derived thereof. This frequency lowering by interaction of HCO^+ with extremely weak nucleophiles|| is in keeping with our experimental finding with the isolobal CF_3AuCO molecule, where the $\nu(\text{CO})$ frequency drops from 2194 cm^{-1} in the separate component **1** to 2171 cm^{-1} in the *cyclo-Au*₆ aggregate **4** owing to fairly strong aurophilic interactions.

Conclusions

Compound **4**, formed by spontaneous self-assembly of smaller pre-existing units (Scheme 1), is the first polynuclear gold carbonyl derivative to have been structurally characterized (Fig. 3). A cyclohexane-like arrangement in chair conformation was found for the *cyclo-Au*₆ metal core even in the absence of significant conformational locks. In compound **4**, the neutral gold carbonyl molecule CF_3AuCO appears to be adsorbed onto a gold framework without the need of any kind of assistance. Since aurophilic interactions are the only cohesive forces holding together this supramolecular aggregate, it can be taken as a model for the local environment of gold carbonyl species adsorbed onto gold layers (Scheme 2). Compound **4** is a unique species because of its high nuclearity and also because it enables to check the influence of the strength of aurophilic interactions on the properties of the highly sensitive $[\text{Au}]\text{--CO}$ unit. We have now experimentally established that aurophilic interactions, although weak in nature, are able to produce significant changes in the $\nu(\text{CO})$ value of gold carbonyls, as had





Scheme 2 Model for local coordination environment of a [Au]–CO unit of an exposed gold site on a gold surface (X stands for any monodentate substituent).

been theoretically predicted.^{14,44} This result should be taken into account when considering the properties of [Au]–CO units on the surface of supported gold catalysts.

Abbreviations

av.	Average
Cy	Cyclohexyl
DPCb	1,2-Bis(diaminophosphino)-1,2-dicarba- <i>closo</i> -dodecaborane
dpmppm	<i>meso</i> -Bis[(diphenylphosphinomethyl)phenylphosphino]methane
IDipp	1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene
Mes	2,4,6-Trimethylphenyl (mesityl)
Mes'	2,4,6-Tris(isopropyl)phenyl
pz*	3,5-Bis(trifluoromethyl)pyrazolyl
SIDipp	1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene
<i>t</i> Bu ^F	Perfluoro- <i>tert</i> -butyl

Acknowledgements

This work was supported by the Spanish MINECO/FEDER (Project CTQ2012-35251), and the Gobierno de Aragón (Grupo Consolidado E21: *Química Inorgánica y de los Compuestos Organometálicos*).

Notes and references

§ Auophilic interactions are among the most important secondary interactions currently known in chemistry.¹⁹ Although usually weak in nature, they are instrumental in shaping a most stunning variety of clusters, polynuclear compounds and supramolecular frameworks.²⁰ Auophilic interactions also have a marked influence on the electronic properties of the chemical entity, thus enabling the fine-tuning of the energy levels and hence of the optical properties thereby involved.²¹ The effect on other fundamental spectroscopic properties, however, is by far less known.

¶ Three-dimensional Hirschfeld surfaces (HSs) have been calculated for each ion constituting the crystal of **4** (Fig. S3 and S4 in ESI†).²⁷ These HSs are unique to each constituent unit and provide a convenient way for comparison of intermolecular contacts relative to van der Waals radii through a simple red–white–blue colour scheme.²⁸ It becomes clear that the ions constituting the crystal lattice of **4** are virtually non-interacting. Just a few small, red spots of poor intensity are to be

located in the corresponding HS, which have been specifically analyzed and considered of little (if any) significance as justified in what follows. In particular, the interatomic distances associated with the few, seeming H-bonds are at the long end of the commonly admitted range,²⁹ and the angles between the atoms involved deviate significantly from linearity (<135°). These geometric parameters jointly indicate extremely poor interactions. The possibility of significant F⋯CO interactions of both intra- and inter-molecular character was also considered. Such interactions are known to be favored in some salts of superelectrophilic metal carbonyl cations [M(CO)_x]^{q+} with fluorinated [SbF₆]ⁿ⁻ anions—*n*, *q* and *x* being integers—and have been thoroughly studied.³⁰ F⋯CO contacts at >300 pm, as found in compound **4**, are well within the 10% safety margin of the sum of the corresponding van der Waals radii, *r*_{vdw}(F) + *r*_{vdw}(C) = 317 pm,³¹ and have been previously considered as of just marginal importance.^{30,32}

|| Anions such as [SbF₆][−] or [Sb₂F₁₁][−] typically behave as extremely poor nucleophiles. Nevertheless, they are known to interact with sufficiently strong electrophilic centers, as for instance, in (PF₃)₂Pt(SbF₆)₂ and (P[∧]P)Pt(Sb₂F₁₁), where P[∧]P = (CF₃)₂PCH₂CH₂P(CF₃)₂.⁴⁸ This is most probably the case of the HCO⁺ cation in HF(*l*)/SbF₅ medium.⁴⁷

- 1 *Encyclopedia of Inorganic Chemistry*, ed. R. B. King, John Wiley & Sons, Chichester, 2nd edn, 2005, p. 926, DOI: 10.1002/0470862106.id150.
- 2 F. A. Cotton, in *Metal Clusters in Chemistry*, ed. P. Braunstein, L. A. Oro and P. R. Raithby, Wiley-VCH, Weinheim, 1999, vol. 1, ch. 1, pp. 2–7 and ref. given therein.
- 3 T. Takei, T. Akita, I. Nakamura, T. Fujitani, M. Okumura, K. Okazaki, J. Huang, T. Ishida and M. Haruta, *Adv. Catal.*, 2012, **55**, 1; M. Haruta and M. Daté, *Appl. Catal.*, A, 2001, **222**, 427; G. C. Bond and D. T. Thompson, *Gold Bull.*, 2000, **33**, 41; A. I. Kozlov, A. P. Kozlova, H. Liu and Y. Iwasawa, *Appl. Catal.*, A, 1999, **182**, 9; G. C. Bond and D. T. Thompson, *Catal. Rev. Sci. Eng.*, 1999, **41**, 319; M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 1989, **115**, 301; M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett.*, 1987, 405.
- 4 R. Meyer, C. Lemire, S. K. Shaikhutdinov and H.-J. Freund, *Gold Bull.*, 2004, **37**, 72.
- 5 F. Zaera, *Chem. Soc. Rev.*, 2014, **43**, 7624; F. Zaera, *ChemCatChem*, 2012, **4**, 1525; M. Mihaylov, H. Knözinger, K. Hadjiivanov and B. C. Gates, *Chem. Ing. Tech.*, 2007, **79**, 795.
- 6 D. B. dell'Amico, L. Labella, F. Marchetti and S. Samaritani, *Coord. Chem. Rev.*, 2010, **254**, 635; J. J. Rack and S. H. Strauss, *Catal. Today*, 1997, **36**, 99; D. B. dell'Amico and F. Calderazzo, *Gold Bull.*, 1997, **30**, 21.
- 7 D. B. dell'Amico, F. Calderazzo, P. Robino and A. Segre, *J. Chem. Soc., Dalton Trans.*, 1991, 3017.
- 8 J. Schaefer, A. Kraft, S. Reininger, G. Santiso-Quiñones, D. Himmel, N. Trapp, U. Gellrich, B. Breit and I. Krossing, *Chem.–Eur. J.*, 2013, **19**, 12468.
- 9 D. B. dell'Amico, F. Calderazzo, H. H. Murray and J. P. Fackler, *Inorg. Synth.*, 1986, **24**, 236; P. G. Jones, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 1982, **37**, 823; D. B. dell'Amico, F. Calderazzo and G. dell'Amico, *Gazz. Chim. Ital.*, 1977, **107**, 101; D. B. dell'Amico, F. Calderazzo and F. Marchetti, *J. Chem. Soc., Dalton Trans.*, 1976, 1829; D. B. dell'Amico and F. Calderazzo, *Gazz. Chim. Ital.*, 1973, **103**, 1099; M. S. Kharasch and H. S. Isbell, *J. Am. Chem. Soc.*, 1930, **52**, 2919; W. Manchot and H. Gall, *Ber. Dtsch. Chem. Ges. B*, 1925, **58**, 2175.



- 10 (a) S. Martínez-Salvador, L. R. Falvello, A. Martín and B. Menjón, *Chem.–Eur. J.*, 2013, **19**, 14540; (b) S. Martínez-Salvador, J. Forniés, A. Martín and B. Menjón, *Angew. Chem., Int. Ed.*, 2011, **50**, 6571.
- 11 H. Willner and F. Aubke, *Inorg. Chem.*, 1990, **29**, 2195.
- 12 H. V. R. Dias and W. Jin, *Inorg. Chem.*, 1996, **35**, 3687.
- 13 R. Küster and K. Seppelt, *Z. Anorg. Allg. Chem.*, 2000, **626**, 236; C. Wang, S. C. Siu, G. Hwang, C. Bach, B. Bley, M. Bodenbinder, H. Willner and F. Aubke, *Can. J. Chem.*, 1996, **74**, 1952; H. Willner, J. Schaebs, G. Hwang, F. Mistry, R. Jones, J. Trotter and F. Aubke, *J. Am. Chem. Soc.*, 1992, **114**, 8972; M. Adelhalm, W. Bacher, E. G. Höhn and E. Jacob, *Chem. Ber.*, 1991, **124**, 1559.
- 14 M. A. Celik, C. Dash, V. A. K. Adiraju, A. Das, M. Yousufuddin, G. Frenking and H. V. R. Dias, *Inorg. Chem.*, 2013, **52**, 729.
- 15 C. Dash, P. Kroll, M. Yousufuddin and H. V. R. Dias, *Chem. Commun.*, 2011, **47**, 4478.
- 16 H. V. R. Dias, C. Dash, M. Yousufuddin, M. A. Celik and G. Frenking, *Inorg. Chem.*, 2011, **50**, 4253.
- 17 M. Joost, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune and D. Bourissou, *Angew. Chem., Int. Ed.*, 2014, **53**, 14512.
- 18 O. Elbjeirami, S. Yockel, C. F. Campana, A. K. Wilson and M. A. Omary, *Organometallics*, 2007, **26**, 2550.
- 19 H. G. Raubenheimer and H. Schmidbaur, *J. Chem. Educ.*, 2014, **91**, 2024; H. Schmidbaur, *Gold Bull.*, 2000, **33**, 3; H. Schmidbaur, *Gold Bull.*, 1990, **23**, 11.
- 20 (a) H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2012, **41**, 370; (b) R. J. Puddephatt, *Chem. Soc. Rev.*, 2008, **37**, 2012; (c) H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2008, **37**, 1931; (d) M. J. Katz, K. Sakaib and D. B. Leznoff, *Chem. Soc. Rev.*, 2008, **37**, 1884; (e) J. Vicente, M. T. Chicote, I. Saura-Llamas, M. C. Lagunas, M. C. Ramírez de Arellano, P. González-Herrero, M. D. Abrisqueta and R. Guerrero, in *Metal Clusters in Chemistry*, ed. P. Braunstein, L. A. Oro and P. R. Raithby, Weinheim, 1999, vol. 1, ch. 1.26, pp. 493–508; (f) H. Schmidbaur, *Chem. Soc. Rev.*, 1995, **24**, 391.
- 21 E. R. T. Tiekink and J.-G. Kang, *Coord. Chem. Rev.*, 2009, **253**, 1627; V. W.-W. Yam and E. C.-C. Cheng, *Chem. Soc. Rev.*, 2008, **37**, 1806; V. W.-W. Yam and E. C.-C. Cheng, *Top. Curr. Chem.*, 2007, **281**, 269.
- 22 P. Braunstein, A. Müller and H. Bögge, *Inorg. Chem.*, 1986, **25**, 2104.
- 23 H. Schmidbaur, A. Hamel, N. W. Mitzel, A. Schier and S. Nogai, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4916; A. Hamel, N. W. Mitzel and H. Schmidbaur, *J. Am. Chem. Soc.*, 2001, **123**, 5106.
- 24 H. Fang, X.-G. Zhang and S.-G. Wang, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5796.
- 25 M. A. Carvajal, S. Alvarez and J. J. Novoa, *Theor. Chem. Acc.*, 2006, **116**, 472.
- 26 Y. Zhu, C. S. Day, L. Zhang, K. J. Hauser and A. C. Jones, *Chem.–Eur. J.*, 2013, **19**, 12264; A. Homs, I. Escofet and A. M. Echavarrén, *Org. Lett.*, 2013, **15**, 5782; A. Bayler, A. Bauer and H. Schmidbaur, *Chem. Ber.*, 1997, **130**, 115; P. G. Jones, G. M. Sheldrick, R. Usón and A. Laguna, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, **36**, 1486; R. Usón, A. Laguna and M. V. Castrillo, *Synth. React. Inorg. Met.-Org. Chem.*, 1979, **9**, 317.
- 27 M. A. Spackman and D. Jayatilaka, *CrystEngComm*, 2009, **11**, 19.
- 28 J. J. McKinnon, D. Jayatilaka and M. A. Spackman, *Chem. Commun.*, 2007, 3814; M. A. Spackman and J. J. McKinnon, *CrystEngComm*, 2002, **4**, 378.
- 29 T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48; G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, 1997.
- 30 H. Willner and F. Aubke, *Organometallics*, 2003, **22**, 3612; H. Willner and F. Aubke, *Chem.–Eur. J.*, 2003, **9**, 1668; H. Willner and F. Aubke, in *Inorganic Chemistry Highlights*, ed. G. Meyer, D. Naumann and L. Wesemann, Wiley-VCH, Weinheim, 2002, ch. 11, pp. 195–212; H. Willner and F. Aubke, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2402.
- 31 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
- 32 B. von Ahsen, M. Berkei, G. Henkel, H. Willner and F. Aubke, *J. Am. Chem. Soc.*, 2002, **124**, 8371.
- 33 J. Arias, M. Bardaji and P. Espinet, *Inorg. Chem.*, 2008, **47**, 1597.
- 34 P. Pykkö, *Annu. Rev. Phys. Chem.*, 2012, **63**, 45.
- 35 H.-J. Zhai, B. Kiran, B. Dai, J. Li and L.-S. Wang, *J. Am. Chem. Soc.*, 2005, **127**, 12098.
- 36 S. Baishya and R. C. Deka, *Comput. Theor. Chem.*, 2012, **1002**, 1.
- 37 D. J. LeBlanc and C. J. L. Lock, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 1765; I. Schröter and J. Strähle, *Chem. Ber.*, 1991, **124**, 2161.
- 38 D. M. Stefanescu, H. F. Yuen, D. S. Glueck, J. A. Golen and A. L. Rheingold, *Angew. Chem., Int. Ed.*, 2003, **42**, 1046.
- 39 Y. Takemura, H. Takenaka, T. Nakajima and T. Tanase, *Angew. Chem., Int. Ed.*, 2009, **48**, 2157.
- 40 E. Cerrada, M. Contel, A. D. Valencia, M. Laguna, T. Gelbrich and M. B. Hursthouse, *Angew. Chem., Int. Ed.*, 2000, **39**, 2353.
- 41 F. Scherbaum, A. Grohmann, B. Huber, C. Krüger and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1544.
- 42 J. A. Schuerman, F. R. Fronczek and J. Selbin, *J. Am. Chem. Soc.*, 1986, **108**, 336.
- 43 M.-R. Azani, O. Castillo, M. L. Gallego, T. Parella, G. Aullón, O. Crespo, A. Laguna, S. Alvarez, R. Mas-Ballesté and F. Zamora, *Chem.–Eur. J.*, 2012, **18**, 9965.
- 44 Z.-F. Li, X.-P. Yang, L. Hui-Xue and Z. Guo, *Organometallics*, 2014, **33**, 5101; O. Elbjeirami, S. Yockel, C. F. Campana, A. K. Wilson and M. A. Omary, *Organometallics*, 2007, **26**, 2550.
- 45 H. G. Raubenheimer and H. Schmidbaur, *Organometallics*, 2012, **31**, 2507.
- 46 P. B. Davies, P. A. Hamilton and W. J. Rothwell, *J. Chem. Phys.*, 1984, **81**, 1598; S. C. Foster, A. R. W. McKellar and T. J. Sears, *J. Chem. Phys.*, 1984, **81**, 578.
- 47 P. J. F. de Rege, J. A. Gladysz and I. T. Horváth, *Science*, 1997, **276**, 776.
- 48 R. Friedemann and K. Seppelt, *Eur. J. Inorg. Chem.*, 2013, 1197.

