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# A comparative experimental and computational study of heterometallic Fe-M (M = Cu, Ag, Au) carbonyl clusters containing N-heterocyclic carbene ligands

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**Abstract:** The  $[\text{Fe}(\text{CO})_4\{\text{M}(\text{NHC})\}]^-$  (M = Cu, NHC = IMes, **1**; M = Cu, NHC = IPr, **2**; M = Ag, NHC = IMes, **3**; M = Ag, NHC = IPr, **4**; IMes =  $\text{C}_3\text{N}_2\text{H}_2(\text{C}_6\text{H}_2\text{Me}_3)_2$ ; IPr =  $\text{C}_3\text{N}_2\text{H}_2(\text{C}_6\text{H}_3\text{Pr}_2)_2$ ) mono-anions were obtained from the reaction of  $\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot 2\text{thf}$  with one equivalent of  $\text{M}(\text{NHC})\text{Cl}$  (M = Cu, Ag; NHC = IMes, IPr) in dmso. Furthermore, the reaction of  $\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot 2\text{thf}$  with two equivalents of  $\text{M}(\text{NHC})\text{Cl}$  in thf afforded the neutral compounds  $\text{Fe}(\text{CO})_4\{\text{M}(\text{NHC})\}_2$  (M = Cu, NHC = IMes, **11**; M = Cu, NHC = IPr, **12**; M = Ag, NHC = IMes, **13**; M = Ag, NHC = IPr, **14**). **2** and **4** further reacted with one equivalent of  $\text{M}(\text{IPr})\text{Cl}$  (M = Cu, Ag, Au) resulting in the trimetallic clusters  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}\{\text{Ag}(\text{IPr})\}$  (**18**),  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}\{\text{Au}(\text{IPr})\}$  (**19**), and  $\text{Fe}(\text{CO})_4\{\text{Ag}(\text{IPr})\}\{\text{Au}(\text{IPr})\}$  (**20**). **1-4**, **11-14** and **18-20** have been spectroscopically characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR techniques. The molecular structures of **2**, **12**, **18**, **19** and **20** have been determined through single crystal X-ray diffraction. The structure, bonding and stability of the copper and silver IMes derivatives were compared to the related Fe-Au clusters previously reported on the basis of theoretical calculations. Stability of the Fe-M bonds decreases in the order  $\text{Au} > \text{Cu} > \text{Ag}$ , and the same trend was found for what concerns the M-IMes interactions. The decomposition products of **1-4**, **11-14** and **18-20** have been studied allowing, among the others, the structural characterization of the new species  $[\text{Fe}_2(\text{CO})_8\{\text{Ag}(\text{IPr})\}]^-$  (**10**) and  $\text{Fe}(\text{CO})_4(\text{CH}_2\text{IMes})$  (**21**).

**Keywords:** Heterometallic clusters / Carbonyl / Coinage metals / Iron / N-Heterocyclic carbene

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## Introduction

Heterometallic complexes and clusters containing coinage metals in the +1 oxidation state were very attractive since they presented heterometallic bonds and metallophilic interactions, that is, attractive interactions between the closed shell  $d^{10}$  centres.<sup>[1-8]</sup> Auophilicity was investigated at first, in relation also to relativistic phenomena,<sup>[9-12]</sup> followed by argentophilicity and cuprophilicity.<sup>[13,14]</sup> Several homoleptic and heteroleptic carbonyl clusters containing 2-8 coinage metals (also mixed ones) supported by Fe, Co, Mo, V and Ru carbonyl moieties were reported.<sup>[1,3,15-17]</sup> These allowed to study the effects of the coinage metal, heterometal and ancillary ligands on the bonding within such heterometallic clusters.

In this sense, we recently reported that the thermal decomposition of the heterometallic  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IMes})\}_2$  complexes ( $\text{IMes} = \text{C}_3\text{N}_2\text{H}_2(\text{C}_6\text{H}_2\text{Me}_3)_2$ ;  $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$ ) resulted in the triangular  $[\text{M}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  clusters.<sup>[18]</sup> Furthermore, the direct reaction of  $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 2\text{thf}$  with  $\text{M}(\text{I})$  salts afforded the same triangular  $[\text{Cu}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  cluster in the case of Cu,<sup>[19]</sup> whereas the square species  $[\text{M}_4\text{Fe}_4(\text{CO})_{16}]^{4-}$  were obtained for Ag and Au.<sup>[20,21]</sup> These results indicated a significant effect of the ancillary ligands on the synthesis and reactivity of heterometallic clusters. The scope of this work was further widened, in the case of Au, to other ligands and stoichiometric combinations of Au and Fe. Thus, the syntheses and thermal reactions of  $[\text{Fe}(\text{CO})_4\{\text{Au}(\text{NHC})\}]^-$  ( $\text{NHC} = \text{IMes}$ ;  $\text{IPr} = \text{C}_3\text{N}_2\text{H}_2(\text{C}_6\text{H}_3\text{Pr}_2)_2$ ),  $\text{Fe}(\text{CO})_4\{\text{Au}(\text{NHC})\}_2$  ( $\text{NHC} = \text{IMes}, \text{IPr}$ ),  $\text{Fe}(\text{CO})_4\{\text{Au}(\text{IMes})\}\{\text{Au}(\text{IPr})\}$  and  $\text{Fe}(\text{CO})_4\{\text{Au}(\text{NHC})\}\{\text{Au}(\text{PPh}_3)\}$  ( $\text{NHC} = \text{IMes}, \text{IPr}$ ) were systematically investigated.<sup>[22,23]</sup> As a result, the higher nuclearity clusters  $[\text{Fe}_2(\text{CO})_8\{\text{Au}(\text{NHC})\}]^-$  ( $\text{NHC} = \text{IMes}, \text{IPr}$ ),  $[\text{Au}_3\text{Fe}_2(\text{CO})_8(\text{IMes})_2]^-$ ,  $[\text{Au}_3\{\text{Fe}(\text{CO})_4\}_2(\text{PPh}_3)_2]^-$  and  $[\text{Au}_{16}\text{S}\{\text{Fe}(\text{CO})_4\}_4(\text{IPr})_4]^{n+}$  were obtained.<sup>[24]</sup>

In order to complete our study, we herein report a detailed investigation on related species containing Cu and Ag. In particular, the syntheses, spectroscopic and structural characterization of mono-anionic  $[\text{Fe}(\text{CO})_4\{\text{M}(\text{NHC})\}]^-$  ( $\text{M} = \text{Cu}$ ,  $\text{NHC} = \text{IMes}$ , **1**;  $\text{M} = \text{Cu}$ ,  $\text{NHC} = \text{IPr}$ , **2**;  $\text{M} = \text{Ag}$ ,  $\text{NHC} = \text{IMes}$ , **3**;  $\text{M} = \text{Ag}$ ,  $\text{NHC} = \text{IPr}$ , **4**), neutral bimetallic  $\text{Fe}(\text{CO})_4\{\text{M}(\text{NHC})\}_2$  ( $\text{M} = \text{Cu}$ ,  $\text{NHC} = \text{IMes}$ , **11**;  $\text{M} = \text{Cu}$ ,  $\text{NHC} = \text{IPr}$ , **12**;  $\text{M} = \text{Ag}$ ,  $\text{NHC} = \text{IMes}$ , **13**;  $\text{M} = \text{Ag}$ ,  $\text{NHC} = \text{IPr}$ , **14**), and neutral trimetallic  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IPr})\}\{\text{M}'(\text{IPr})\}$  ( $\text{M} = \text{Cu}$ ,  $\text{M}' = \text{Ag}$ , **18**;  $\text{M} = \text{Cu}$ ,  $\text{M}' = \text{Au}$ , **19**;  $\text{M} = \text{Ag}$ ,  $\text{M}' = \text{Au}$ , **20**) clusters is described. Within this context, the terms "bimetallic" and "trimetallic" are referred to the fact that the former species contain Fe and a coinage metal, whereas the latter contain Fe and two different types of coinage metal. The structure, bonding and stability of the resulting

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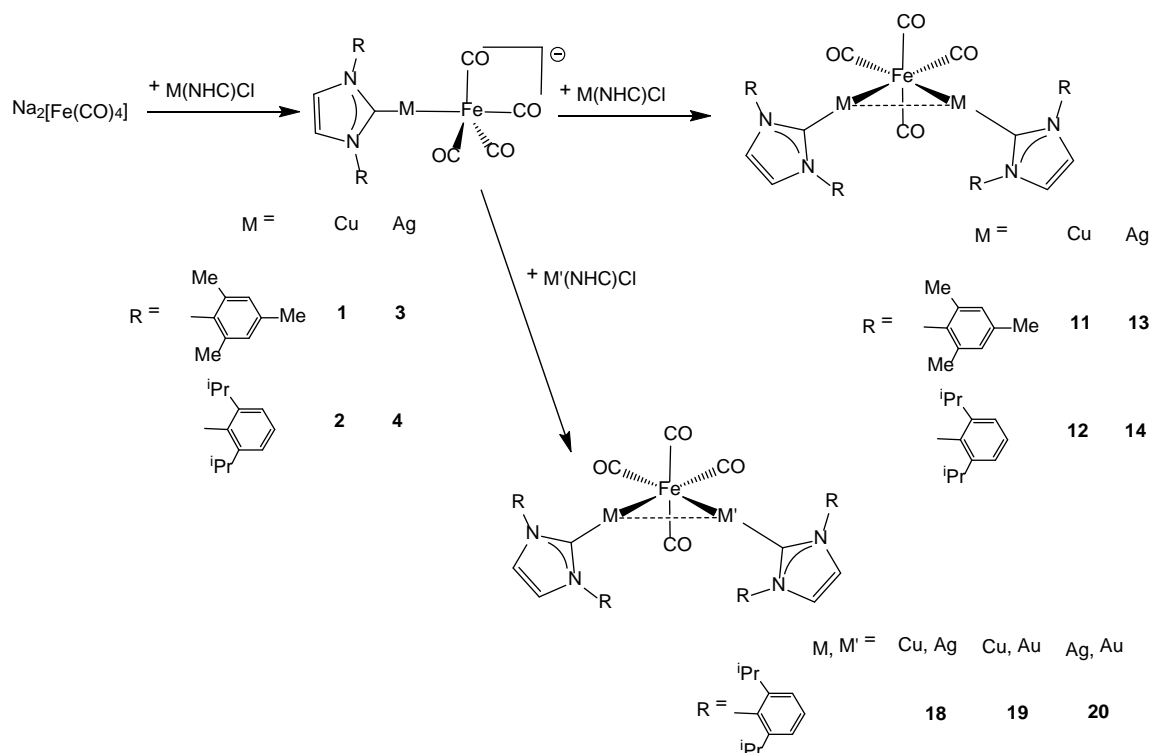
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species are compared to the related Fe-Au clusters previously reported, also on the basis of computational simulations. This allows a comparative study of the different coinage metals within the same organometallic environments.

## Results and Discussion

### Synthesis and characterization of mono-anionic $[\text{Fe}(\text{CO})_4\{\text{M}(\text{NHC})\}]^-$ complexes ( $\text{M} = \text{Cu}, \text{Ag}$ , $\text{NHC} = \text{IMes}, \text{IPr}$ )

The reaction of Collman's reagent  $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 2\text{thf}$  with one equivalent of  $\text{M}(\text{NHC})\text{Cl}$  ( $\text{M} = \text{Cu}, \text{Ag}$ ;  $\text{NHC} = \text{IMes}, \text{IPr}$ ) in dmsO resulted in the  $[\text{Fe}(\text{CO})_4\{\text{M}(\text{NHC})\}]^-$  ( $\text{M} = \text{Cu}, \text{NHC} = \text{IMes}$ , **1**;  $\text{M} = \text{Cu}, \text{NHC} = \text{IPr}$ , **2**;  $\text{M} = \text{Ag}, \text{NHC} = \text{IMes}$ , **3**;  $\text{M} = \text{Ag}, \text{NHC} = \text{IPr}$ , **4**) mono-anions in accord to Scheme 1. At difference with the related gold-containing species  $[\text{Fe}(\text{CO})_4\{\text{Au}(\text{NHC})\}]^-$  ( $\text{NHC} = \text{IMes}$ , **5**;  $\text{IPr}$ , **6**),<sup>[23]</sup> the copper and silver compounds **1-4** displayed a limited stability which, in most of the cases, prevented their isolation and crystallization. Thus, **1-4** were characterized directly in the crude reaction mixtures by means of IR,  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopies (Figures S5-S12 in the Supporting Information.  $^1\text{H}$  NMR spectra of  $\text{M}(\text{NHC})\text{Cl}$  ( $\text{M} = \text{Cu}, \text{Ag}$ ;  $\text{NHC} = \text{IMes}, \text{IPr}$ ) were included for comparison as Figures S1-S4 ).



Scheme 1. Syntheses of the complexes

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The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR data of **1-4** were in keeping with the proposed structures and similar to those previously reported for **5** and **6**.<sup>[23]</sup> Compounds **1-4** displayed two  $\nu_{\text{CO}}$  bands in dmso solution, that is a sharp band at 1909-1913(s) and a broader band at 1796-1801(vs)  $\text{cm}^{-1}$  (Figures S39-S40 in the Supporting Information), significantly shifted towards lower wavenumbers compared to the Au-congeners **5** and **6** ( $\nu_{\text{CO}}$  1924(s) and 1820(vs)  $\text{cm}^{-1}$ ).

Figure 1 shows the DFT-optimized structures (PBEh-3c method) of the IMes derivatives **1**, **3** and **5**. The  $\nu_{\text{CO}}$  shifts related to the change of the coinage metal were confirmed by the IR simulations on the DFT-optimized geometries, as observable in Figures S46-S48 and Table S1 in the Supporting Information. For what concerns the simulated IR spectra of **1**, **3** and **5**, the four computed  $\nu_{\text{CO}}$  bands corresponded, from the highest to the lowest wavenumber, to: (1) the in-phase stretching of the four CO; (2) the in-phase stretching of the three equatorial CO, combined with the out-of-phase stretching of the axial CO; (3) the in-phase stretching of two equatorial CO and the out-of-phase stretching of the third equatorial CO, with minimal contribution from the axial CO; (4) the out-of-phase stretching of two equatorial CO. It is likely that in the experimental spectra, the sharp band at higher wavenumbers corresponded to (1), whereas the broader band at lower wavenumbers was actually the result of the unresolved overlap (convolution) of (2), (3) and (4).

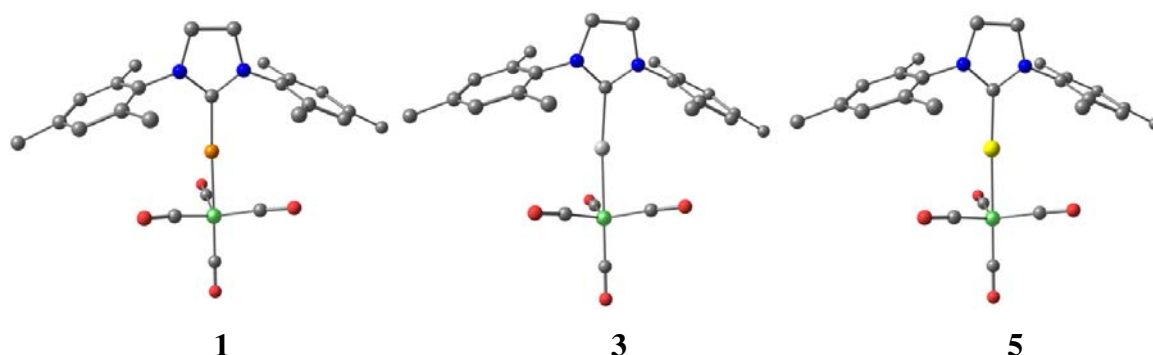


Figure 1. DFT-optimized geometries of **1**, **3** and **5** (PBEh-3c method). Hydrogen atoms were omitted for clarity. Colour map: green Fe; orange Cu; light grey Ag; yellow Au; blue N; red O; grey C. Selected computed bond lengths ( $\text{\AA}$ ) for **1**: Fe-Cu 2.295, Fe-CO(axial) 1.720, Fe-CO(equatorial, average) 1.726, Cu-C(IMes) 1.929. Selected computed bond lengths ( $\text{\AA}$ ) for **3**: Fe-Ag 2.477, Fe-CO(axial) 1.718, Fe-CO(equatorial, average) 1.733, Ag-C(IMes) 2.135. Selected computed bond lengths ( $\text{\AA}$ ) for **5**: Fe-Au 2.401, Fe-CO(axial) 1.723, Fe-CO(equatorial, average) 1.735, Au-C(IMes) 2.047.

The AIM analyses of the Fe-C bonds in **1**, **3** and **5** highlighted the slight reduction of electron density ( $\rho$ ) and the less negative values of potential energy density ( $V$ ) at Fe-C bond critical points (b.c.p.) in the case of the Au derivative **5** (Table S2 in the Supporting Information). This may be explained on the basis of the greater electronegativity of Au (2.4) compared to Ag (1.9) and Cu (1.9),<sup>[25]</sup> which resulted in a decrease of the electron density on Fe bonded to Au greater than in the case of Cu and Ag. This, in turn, reduced the  $\pi$ -Fe-CO back-donation in the Fe-Au complexes compared to Fe-Cu and Fe-Ag, in agreement with the experimental and computed IR frequencies of the  $\nu_{\text{CO}}$  stretchings.

The role of the electronegativity of the coinage metal is evidenced by the relative position of the Fe-M b.c.p. with respect to the Fe centre in **1**, **3**, and **5**. The computed Fe-(b.c.p.<sub>Fe-M</sub>) distances are 1.178 Å for **1** and 1.167 Å for **3**, while a meaningfully shorter distance was found for the Au derivative **5** (1.136 Å).<sup>[26]</sup> On the same basis, it might also be concluded that Fe-Au bonds are stronger than Fe-Cu and Fe-Ag bonds, in agreement with the greater stability of **5** and **6** compared to **1-4**. Therefore, it might be concluded that the fact that Au complexes are more easily isolated than Cu and Ag ones was based mainly on thermodynamic effects, that is the strength on the Fe-M bonds. Indeed, the computed values for the dissociation of  $[\text{Fe}(\text{CO})_4\{\text{M}(\text{IMes})\}]^-$  into  $[\text{Fe}(\text{CO})_4]^{2-}$  and  $[\text{M}(\text{IMes})]^+$  (C-PCM/ $\omega$ B97X-v calculations, dmso as continuous medium) are 72.9 kcal mol<sup>-1</sup> for **1**, 65.7 kcal mol<sup>-1</sup> for **3** and 77.8 kcal mol<sup>-1</sup> for **5**; therefore the calculated stability order for the Fe-M bonds is Au > Cu > Ag. The three bonds are however comparable considering the properties at b.c.p., with negative values of energy density ( $E$ ) and positive values for the Laplacian of electron density ( $\nabla^2\rho$ ), in agreement with Bianchi's definition of M-M bonds.<sup>[27]</sup> It is worth noting that the  $\rho$  values at b.c.p. follow the previously described Fe-M stability order. Selected data concerning the properties at Fe-M b.c.p. are summarized in Table S3 in the Supporting Information.

The nature of complexes **1-4** was further corroborated by the crystallographic determination of the molecular structure of **2** as its  $[\text{NEt}_4]^+$  salt (Figure 2). Crystals of  $[\text{NEt}_4][\textbf{2}]$  were obtained by addition of a saturated solution of  $[\text{NEt}_4]\text{Br}$  in water to the dmso reaction mixture, the solid recovered by filtration and extracted in toluene (see Experimental Section for further details). Eventually, crystals of  $[\text{NEt}_4][\textbf{2}]$  suitable for X-ray analyses were obtained by slow diffusion of n-pentane on the toluene solution.

**2** adopted a trigonal bipyramidal structure, with the CuIPr fragment in an axial position. Similar structures were found for the gold related species **5** and **6**,<sup>[23]</sup> and in the cobalt complexes

$\text{Co}(\text{CO})_4(\text{AuPPh}_3)$  <sup>[28]</sup> and  $\text{Co}(\text{CO})_4(\text{CuIPr})$ . <sup>[29]</sup> The root mean square deviation (RMSD) between the experimental data for **2** and the computed geometry for **1**, once removed the N-bonded substituents, was quite low (0.229 Å), supporting the quality of the geometries predicted by the PBEh-3c method.

**2** contained strong Cu-Fe, Fe-C(O) and Cu-C<sub>carbene</sub> interactions as well as some weak Cu $\cdots$ C(O) contacts. In general, it was rather debated if such M $\cdots$ C(O) (M = Cu, Ag, Au) contacts were merely due to the steric arrangement of the CO ligands, or they were the consequence of any attraction (even van der Waals) between the carbonyls and M(I). <sup>[30]</sup> The AIM analyses on **1**, **3** and **5** were unable to find any (3,-1) b.c.p. for the M $\cdots$ CO contacts. The gradient of electron density is higher than zero along the M $\cdots$ C directions, the minimum average values are 0.019 a.u. (M = Cu), 0.016 a.u. (M = Ag) and 0.018 a.u. (M = Au). The computed data do not support the presence of any meaningful localized interaction. The distortions of the equatorial Fe-C bonds with respect to the ideal positions for a trigonal bipyramid do not appear directly related to the Fe-M bond lengths or to the Fe-M stability order previously described, being the computed C<sub>axial</sub>-Fe-C<sub>equatorial</sub> average angles 101.8 ° for M = Cu (**1**), 100.0 ° for M = Ag (**3**) and 99.4 ° for M = Au (**5**). A linear relationship was instead found between the angles and the computed Hirshfeld charges <sup>[31]</sup> on the coinage metals, the values being 0.111 a.u. for Cu, 0.050 a.u. for Ag and 0.013 a.u. for Au, this suggesting a dominant electrostatic origin for the distortion.

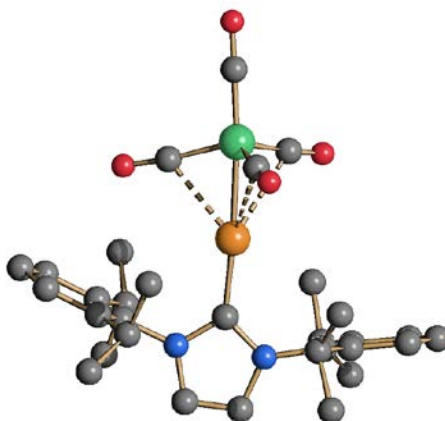


Figure 2. Molecular structures of  $[\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}]^-$  (**2**). Cu $\cdots$ C(O) contacts [2.462(5)-2.670(5) Å] are represented as fragmented lines. Hydrogen atoms have been omitted for clarity (green Fe; orange Cu; blue N; red O; grey C). Main bond distances (Å) and angles (°): Fe-Cu 2.3216(7), Cu-C<sub>carbene</sub> 1.903(3), Fe-C(O) 1.749(6)-1.773(5), Fe-Cu-C<sub>carbene</sub> 176.80(11).



Isolation of **2** was possible because of the enhanced steric stability of IPr-derivatives compared to IMes-derivatives,<sup>[23]</sup> as well as the (slightly) greater stability of Fe-Cu species compared to Fe-Ag, as pointed out by DFT calculations. Indeed, all attempts to isolate **1**, **3** and **4** following a similar procedure failed, leading to the formation of complex mixtures of decomposition products.

In particular, attempting the isolation of **3**, crystals of  $[\text{NEt}_4]_2[\text{Ag}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}] \cdot \text{solv}$ ,<sup>[18]</sup>  $[\text{NEt}_4]_2[\text{HIMes}]_2[\text{Ag}_4\text{Fe}_4(\text{CO})_{16}]$ ,  $[\text{NEt}_4]_4[\text{Ag}_4\text{Fe}_4(\text{CO})_{16}] \cdot 2\text{CH}_3\text{CN}$  and  $[\text{NEt}_4]_3[\text{Ag}_5\text{Fe}_4(\text{CO})_{16}]$  were obtained. Crystal data of the new salts were included as Supporting Information and deposited within the Cambridge Crystallographic Datacenter for sake of completeness. All these salts contained the  $[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  (**7**),<sup>[18]</sup>  $[\text{Ag}_4\text{Fe}_4(\text{CO})_{16}]^{4-}$  (**8**), and  $[\text{Ag}_5\text{Fe}_4(\text{CO})_{16}]^{3-}$  (**9**) cluster anions,<sup>[20]</sup> that were already described in the literature (Figures S33-S35 in Supporting Information). Their formation suggested that the Ag-IMes bond was mainly broken during work-up, leading to homoleptic Ag-Fe-CO clusters. The presence among the decomposition products of the imidazolium  $[\text{HIMes}]^+$  cation indicated that, once liberated in solution, the IMes carbene may be readily protonated.

Furthermore, during the attempts of isolating **4**, crystals of  $[\text{Ag}(\text{IPr})_2][\text{Fe}_2(\text{CO})_8\{\text{Ag}(\text{IPr})\}] \cdot \text{CH}_2\text{Cl}_2$ ,  $[\text{NEt}_4]_2[\text{HIPr}][\text{Fe}_2(\text{CO})_8\{\text{Ag}(\text{IPr})\}]_2[\text{Cl}] \cdot 2\text{CH}_2\text{Cl}_2$  and  $[\text{NEt}_4]_4[\text{Ag}_4\text{Fe}_4(\text{CO})_{16}]$  were obtained. A part  $[\text{Ag}_4\text{Fe}_4(\text{CO})_{16}]^{4-}$  (**8**) which did not contain the IPr ligand, all the other products retained the AgIPr fragment. This was a further indication of the different reactivity of the IPr-containing species compared to IMes-ones, mainly imputable to their different steric properties. Formation of the  $[\text{Fe}_2(\text{CO})_8]^{2-}$  moiety (as found in  $[\text{Ag}(\text{IPr})_2][\text{Fe}_2(\text{CO})_8\{\text{Ag}(\text{IPr})\}] \cdot \text{CH}_2\text{Cl}_2$  and  $[\text{NEt}_4]_2[\text{HIPr}][\text{Fe}_2(\text{CO})_8\{\text{Ag}(\text{IPr})\}]_2[\text{Cl}] \cdot 2\text{CH}_2\text{Cl}_2$ ) was due to oxidation of the  $[\text{Fe}(\text{CO})_4]^{2-}$  unit present in **4**. Overall, because of the different NHC ligands present, **3** and **4** followed different decomposition routes.

The molecular structure of the new  $[\text{Fe}_2(\text{CO})_8\{\text{Ag}(\text{IPr})\}]^-$  (**10**) anion, as found in both  $[\text{Ag}(\text{IPr})_2][\text{Fe}_2(\text{CO})_8\{\text{Ag}(\text{IPr})\}] \cdot \text{CH}_2\text{Cl}_2$  and  $[\text{NEt}_4]_2[\text{HIPr}][\text{Fe}_2(\text{CO})_8\{\text{Ag}(\text{IPr})\}]_2[\text{Cl}] \cdot 2\text{CH}_2\text{Cl}_2$ , is reported for sake of completeness in Figure 3. It may be viewed as the result of the addition of a  $[\text{Ag}(\text{IPr})]^+$  fragment to  $[\text{Fe}_2(\text{CO})_8]^{2-}$ . It displayed six terminal and two edge bridging carbonyl ligands, as previously found in the AuIPr and AuPPh<sub>3</sub>-congeners  $[\text{Fe}_2(\text{CO})_8\{\text{Au}(\text{IPr})\}]^-$ <sup>[24]</sup> and  $[\text{Fe}_2(\text{CO})_8\{\text{Au}(\text{PPh}_3)\}]^-$ .<sup>[32]</sup> In contrast, the related copper species  $[\text{Fe}_2(\text{CO})_8\{\text{Cu}(\text{PCy}_3)\}]^-$  displayed

only terminal carbonyls.<sup>[33]</sup> The Fe-Fe distance in compounds with the  $\text{Fe}_2(\text{CO})_6(\mu\text{-CO})_2$  unit spanned a rather large range [2.39-2.62 Å].<sup>[34,35]</sup> The Fe-Fe distance found in **10** [2.5927(9) Å] was in keeping with those of  $[\text{Fe}_2(\text{CO})_8\{\text{Au}(\text{IPr})\}]^-$  [2.573(4) Å] and  $[\text{Fe}_2(\text{CO})_8\{\text{Au}(\text{PPh}_3)\}]^-$  [2.605 Å].

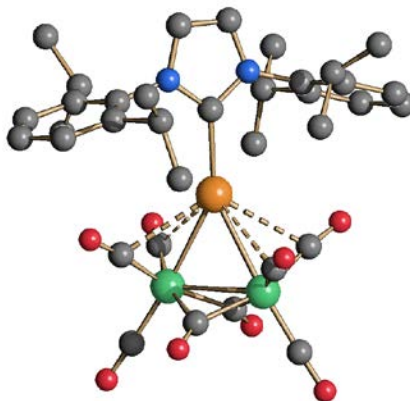


Figure 3. Molecular structure of  $[\text{Fe}_2(\text{CO})_8\{\text{Ag}(\text{IPr})\}]^-$  (**10**).  $\text{Ag}\cdots\text{C}(\text{O})$  contacts [2.775(5)-3.012(7) Å] are represented as fragmented lines. Hydrogen atoms have been omitted for clarity (green Fe; orange Ag; blue N; red O; grey C). Selected bond lengths (Å): Fe-Fe 2.5927(9); Fe-Ag 2.7159(7) and 2.7201(7); Ag- $\text{C}_{\text{carbene}}$  2.142(4); Fe- $\text{C}(\text{O})_{\text{bridge}}$  1.927(5)-1.993(5); Fe- $\text{C}(\text{O})_{\text{terminal}}$  1.750(5)-1.807(5).

### Synthesis and characterization of neutral bimetallic $\text{Fe}(\text{CO})_4\{\text{M}(\text{NHC})\}_2$ complexes ( $\text{M} = \text{Cu}$ , $\text{Ag}$ , $\text{NHC} = \text{IMes}$ , $\text{IPr}$ )

The neutral bimetallic  $\text{Fe}(\text{CO})_4\{\text{M}(\text{NHC})\}_2$  ( $\text{M} = \text{Cu}$ ,  $\text{NHC} = \text{IMes}$ , **11**;  $\text{M} = \text{Cu}$ ,  $\text{NHC} = \text{IPr}$ , **12**;  $\text{M} = \text{Ag}$ ,  $\text{NHC} = \text{IMes}$ , **13**;  $\text{M} = \text{Ag}$ ,  $\text{NHC} = \text{IPr}$ , **14**) complexes were obtained from the reaction of  $\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot 2\text{thf}$  with two equivalents of  $\text{M}(\text{NHC})\text{Cl}$  in thf. Compounds **11-14** were spectroscopically characterized by means of IR,  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR techniques after work-up of the reaction mixtures (see Experimental Section and Figures S13-S20 and S41-S42 in the Supporting Information). The molecular structures of **11** and **13** were previously included in a communication but not discussed in details (see Figures S36 and S37 in Supporting Information).<sup>[18]</sup> Moreover, the molecular structure of the new species **12** was crystallographically determined as its **12**·2thf solvate (Figure 4 and Table 1).

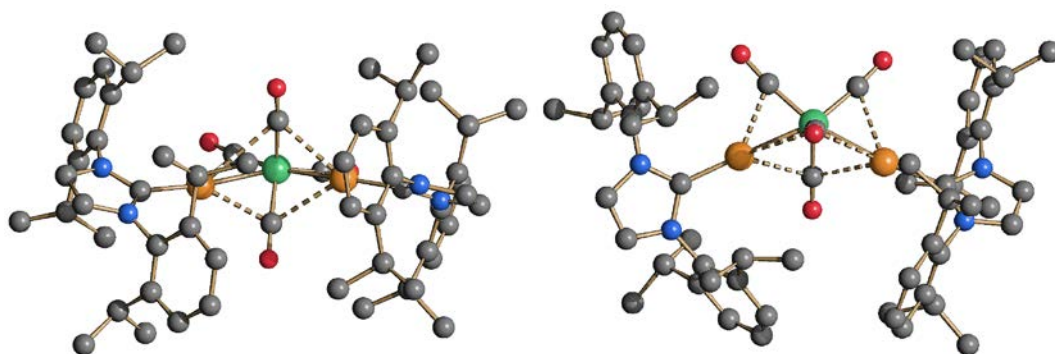


Figure 4. Molecular structure of  $\text{Fe(CO)}_4\{\text{Cu(IPr)}\}_2$  (**12**). Two different views of the molecule are reported.  $\text{Cu}\cdots\text{C(O)}$  contacts [2.345(5)-2.9742(6) Å] are represented as fragmented lines. Hydrogen atoms have been omitted for clarity (green Fe; orange Cu; blue N; red O; grey C).

Table 1. Main bond distances (Å) and angles (deg) of  $\text{Fe(CO)}_4\{\text{Cu(IPr)}\}_2$  (**12**) compared to  $\text{Fe(CO)}_4\{\text{Au(IPr)}\}_2$  (**16**),<sup>[22]</sup>  $\text{Fe(CO)}_4\{\text{Au(IMes)}\}_2$  (**15**),<sup>[22]</sup>  $\text{Fe(CO)}_4\{\text{Cu(IMes)}\}_2$  (**11**) and  $\text{Fe(CO)}_4\{\text{Ag(IMes)}\}_2$  (**13**).<sup>[18]</sup>

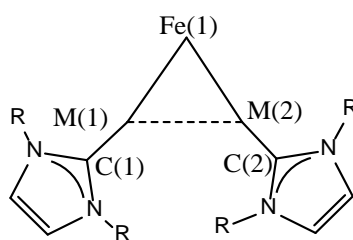
	<b>12</b>	<b>16</b> *	<b>11</b> **	<b>13</b> **	<b>15</b> *
M(1)-Fe(1)	2.3603(8)	2.512(2)	2.3586(4)	2.5292(4)	2.5158(15)
M(2)-Fe(1)	2.3438(8)	2.524(2)	2.3582(4)	2.5423(4)	2.5312(15)
M(1)-M(2)	4.223(2)	4.082(1)	3.1990(9)	3.1185(3)	3.2015(8)
M(1)-C(1)	1.911(4)	2.012(11)	1.903(2)	2.105(2)	2.008(10)
M(2)-C(2)	1.889(4)	1.949(14)	1.908(2)	2.104(2)	2.020(10)
Fe(1)-CO	1.775(5) - 1.785(5)	1.737(15)- 1.781(15)	1.770(2)-1.776(2)	1.770(2)-1.781(2)	1.756(13)- 1.783(13)
Fe(1)-M(1)- C(1)	170.67(12)	168.3(3)	168.64(7)	178.02(6)	177.8(3)
Fe(1)-M(2)- C(2)	171.36(13)	168.4(5)	178.04(7)	165.05(6)	165.9(3)
M(1)-Fe(1)- M(2)	127.75(3)	107.90(9)	73.53(7)	75.890(12)	78.74(4)
Fe(1)-M(1)- M(2)	26.03(2)	36.15(5)	47.30(2)	52.245(9)	50.84(4)
Fe(1)-M(2)- M(1)	26.23(2)	35.95(5)	47.31(2)	51.865(9)	50.42(3)

\* From ref. [22]

\*\* From ref [18].

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**11-13** were composed of a  $C_{2v}$ -Fe(CO)<sub>4</sub> sawhorse/seesaw unit coordinated to two M(NHC) fragments in relative *cis* position, as previously found in the Au-species Fe(CO)<sub>4</sub>{Au(NHC)}<sub>2</sub> (NHC = IMes, **15**; IPr, **16**).<sup>[22]</sup> All these compounds displayed short Fe-M, Fe-CO and M-C<sub>carbene</sub> contacts, as well as sub-van der Waals M...C(O) contacts (Table 1). Regarding the M...M distances, they were shorter in the IMes-derivatives and rather longer in the IPr-derivatives. Thus, the former contacts may be viewed as weak metallophilic interactions, whereas they were completely non-bonding in the latter compounds. These differences were explained on the basis of the greater steric demand of IPr compared to IMes, which caused the complete loss of any M...M interaction. As a consequence, the M-Fe-M angles were considerably smaller in the IMes-derivatives [73.53(7)-78.74(4)°] than in the IPr-congeners [107.90(9)-127.75(3)°]. The results herein described and summarized in Table 1 further pointed out that metallophilic M...M interactions were rather deformable and adapted themselves to the steric properties of the ancillary ligands employed in such complexes.

In agreement with the results previously reported for the Au compound **15**,<sup>[22,23]</sup> no M...M b.c.p. was found by carrying out AIM analyses on the DFT-optimized structures of the Cu and Ag derivatives **11** and **13**. The gradient of electron density is higher than zero along the M...M directions, and the minimum average values are 0.012 a.u. (M = Cu), 0.007 a.u. (M = Ag) and 0.007 a.u. (M = Au). Delocalized dispersion-driven nature for the M---M interactions is therefore suggested.

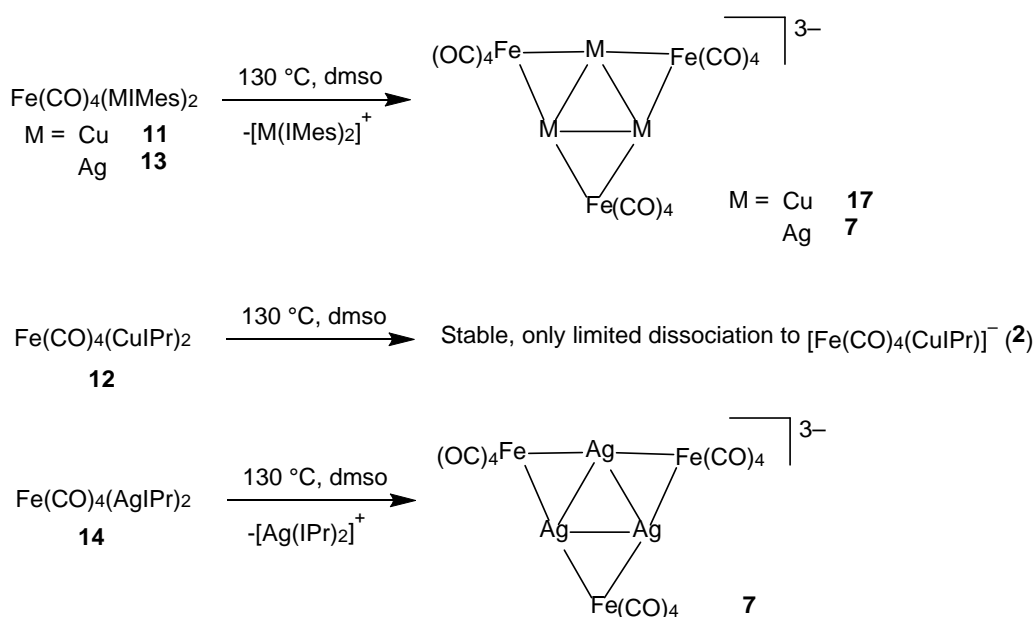
The data concerning the Fe-M b.c.p. obtained from the DFT-optimized geometries of **11**, **13** and **15** indicate that the bonds are qualitatively comparable with those previously described for the anionic species **1**, **3**, and **5** (see Table S4, Supporting Information). The coordination of a second [M(IMes)]<sup>+</sup> fragment caused the expected reduction of electron density at Fe-M b.c.p., and less negative values of V at b.c.p. were found. The ρ values follow the order Au > Cu > Ag and the Fe-

(b.c.p.<sub>Fe-M</sub>) distance is shorter for the Au derivative (1.211 Å for **11**, 1.201 Å for **13** and 1.167 Å for **15**). No M...CO (3,-1) b.c.p. was found for the Fe(CO)<sub>4</sub>{M(IMes)}<sub>2</sub> derivatives.

Compounds **11-14** displayed  $\nu_{\text{CO}}$  bands in CH<sub>2</sub>Cl<sub>2</sub> at 1943-1950 and 1849-1878 cm<sup>-1</sup>, significantly downshifted compared to **15-16** [*ca.* 1974(m), 1884(s) cm<sup>-1</sup>]. As explained in the previous section, this was related to the greater electronegativity of Au compared to Cu and Ag. The IR simulations on the DFT-optimized structures of **11**, **13** and **15** confirmed the variations to the  $\nu_{\text{CO}}$  stretchings on changing the coinage metal (see Figures S49-S51 and Table S5 in the Supporting Information), in agreement with the lower  $\rho$  and less negative  $V$  values at Fe-C b.c.p. for the Au compound **15** (Supporting Information, Table S6).

The two NHC ligands were equivalent in the <sup>1</sup>H and <sup>13</sup>C NMR spectra at all temperatures, in agreement with the solid state structures. The M-coordinated carbene resonated at  $\delta_{\text{C}}$  177.3, 181.5, 182.6 and 189.2 ppm for **11**, **12**, **13** and **14**, respectively. The expected coupling to <sup>107</sup>Ag and <sup>109</sup>Ag was detected in the Ag-complexes **13** and **14**. A singlet was present at all temperatures in the CO region of the <sup>13</sup>C NMR spectra of **11-14**, suggesting a fluxional behavior for the carbonyl ligands. This rapid exchange process made the equatorial and apical CO ligands equivalent also at low temperature and hampered the spectroscopic detection in solution of possible M...C(O) interactions.

As previously reported, the IMes-complexes **11** and **13** rapidly decomposed after heating in dmso at 130 °C affording the triangular clusters [M<sub>3</sub>Fe<sub>3</sub>(CO)<sub>12</sub>]<sup>3-</sup> (M = Cu, **17**; Ag, **7**) (Scheme 2).<sup>[18]</sup> Under similar experimental conditions, complex **14**, that contained two Ag(IPr) moieties, was rapidly transformed into **7**, as for the IMes-derivative **13**. In contrast, the Cu-complex **12** was thermally stable, and displayed only limited dissociation of one [Cu(IPr)]<sup>+</sup> group and resulted in a mixture of unreacted **12** (major) and **2** (minor). These results were in keeping with our previous observations, that indicated that IPr-containing species were more stable than IMes-ones (based on steric effects) and Cu complexes were more stable than Ag ones (based on the greater strength of Fe-Cu bonds compared to Fe-Ag, as deduced by DFT calculations). From this point of view, Cu-containing complexes resembled more to Au-complexes than Ag-complexes.



Scheme 2. Thermal decomposition of **11-14**

### Synthesis and characterization of neutral trimetallic $\text{Fe(CO)}_4\{\text{M(NHC)}\}\{\text{M' (NHC)}\}$ complexes (M = Cu, Ag, M' = Cu, Ag, NHC = IMes, IPr)

The mono-anions **1-6** (containing the M(NHC) fragment) were reacted with one equivalent of M'(NHC)Cl in the attempt to prepare neutral trimetallic clusters of the general type  $\text{Fe(CO)}_4\{\text{M(NHC)}\}\{\text{M' (NHC)}\}$  (NHC = IMes, IPr; M, M' = Cu, Ag, Au, M ≠ M'). Different results were obtained depending on the nature of the NHC carbene ligand employed.

When NHC = IPr, it was possible to isolate in satisfactory yields (see Experimental Section for details) all the three species  $\text{Fe(CO)}_4\{\text{Cu(IPr)}\}\{\text{Ag(IPr)}\}$  (**18**),  $\text{Fe(CO)}_4\{\text{Cu(IPr)}\}\{\text{Au(IPr)}\}$  (**19**), and  $\text{Fe(CO)}_4\{\text{Ag(IPr)}\}\{\text{Au(IPr)}\}$  (**20**). **18-20** were quite stable both in the solid state and in solution, and they were fully characterized through IR,  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopies (Figures S21-S26 and S43 in Supporting Information). Moreover, the molecular structures of **18-20** were determined by means of single crystal X-ray diffraction as their isomorphous  $\text{Fe(CO)}_4\{\text{Cu(IPr)}\}_{1.27}\{\text{Ag(IPr)}\}_{0.73} \cdot 1.5\text{toluene}$  (**I**),  $\text{Fe(CO)}_4\{\text{Cu(IPr)}\}_{0.71}\{\text{Au(IPr)}\}_{1.29} \cdot 1.5\text{toluene}$  (**II**) and  $\text{Fe(CO)}_4\{\text{Ag(IPr)}\}_{0.95}\{\text{Au(IPr)}\}_{1.05} \cdot 1.5\text{toluene}$  (**III**) solvates (Figures 5-7, Table 2). The same complexes **18-20** could not be obtained by mixing of the neutral bimetallic complexes **2**, **4** and **6**.



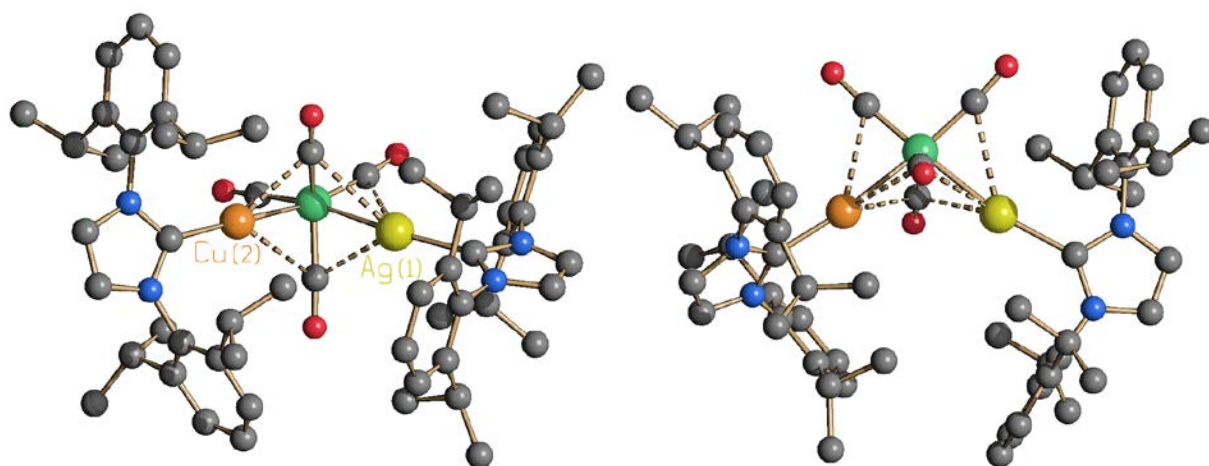


Figure 5. Molecular structure of  $\text{Fe(CO)}_4\{\text{Cu(IPr)}\}\{\text{Ag(IPr)}\}$  (**18**). Two different views of the molecule are reported.  $\text{M}\cdots\text{C(O)}$  contacts [2.414(5)-2.787(5) Å] are represented as fragmented lines. Hydrogen atoms have been omitted for clarity (green Fe; orange Cu; yellow, Ag; blue N; red O; grey C).

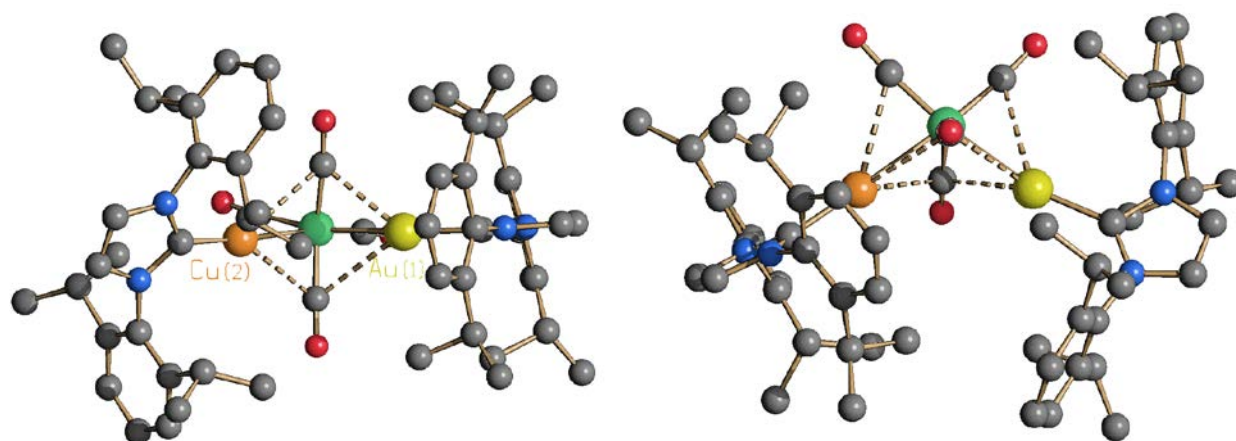


Figure 6. Molecular structure of  $\text{Fe(CO)}_4\{\text{Cu(IPr)}\}\{\text{Au(IPr)}\}$  (**19**). Two different views of the molecule are reported.  $\text{M}\cdots\text{C(O)}$  contacts [2.556(5)-2.842(5) Å] are represented as fragmented lines. Hydrogen atoms have been omitted for clarity (green Fe; orange Cu; yellow, Au; blue N; red O; grey C).

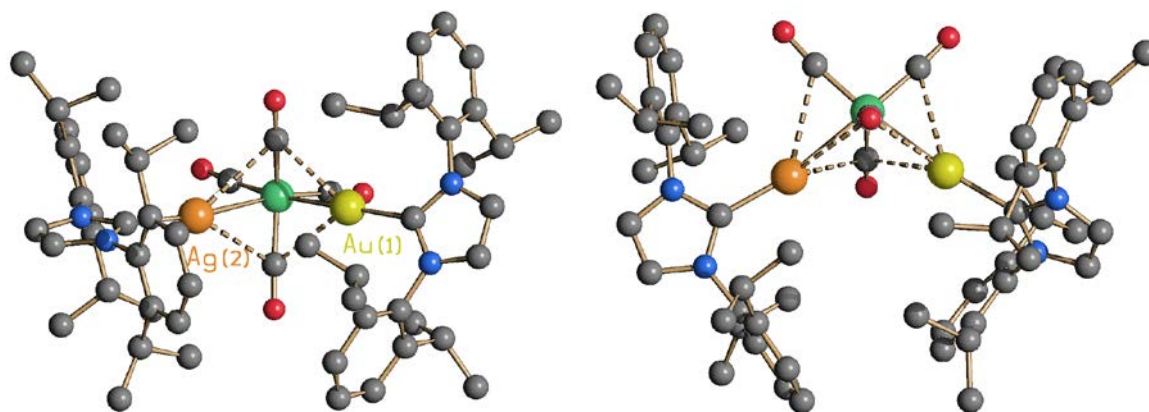
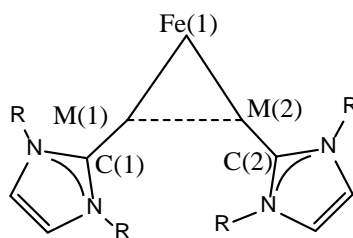


Figure 7. Molecular structure of  $\text{Fe(CO)}_4\{\text{Ag(IPr)}\}\{\text{Au(IPr)}\}$  (**20**). Two different views of the molecule are reported.  $\text{M}\cdots\text{C(O)}$  contacts [2.588(4)–2.912(4) Å] are represented as fragmented lines. Hydrogen atoms have been omitted for clarity (green Fe; orange Ag; yellow, Au; blue N; red O; grey C).

Table 2. Main bond distances (Å) and angles (deg) of  $\text{Fe(CO)}_4\{\text{Cu(IPr)}\}\{\text{Ag(IPr)}\}$  (**18**),  $\text{Fe(CO)}_4\{\text{Cu(IPr)}\}\{\text{Au(IPr)}\}$  (**19**) and  $\text{Fe(CO)}_4\{\text{Ag(IPr)}\}\{\text{Au(IPr)}\}$  (**20**) as found in **I–III**.

	<b>18</b>	<b>19</b> (crystal 1)	<b>19</b> (crystal 2)	<b>20</b>
M(1)–Fe(1)	2.404(7)	2.4848(13)	2.4962(11)	2.500(4)
M(2)–Fe(1)	2.411(13)	2.488(10)	2.485(9)	2.536(3)
M(1)–M(2)	3.763(6)	3.948(8)	3.958(8)	3.911(7)
M(1)–C(1)	2.079(9)	2.001(4)	2.001(4)	2.067(6)
M(2)–C(2)	1.953(13)	1.933(11)	1.950(10)	2.027(7)
Fe(1)–CO	1.751(6)–1.774(5)	1.763(5)–1.779(5)	1.766(4)–1.780(4)	1.765(4)–1.786(4)
Fe(1)–M(1)–C(1)	168.9(5)	167.37(13)	167.34(11)	171.7(2)
Fe(1)–M(2)–C(2)	172.2(8)	175.9(6)	177.8(5)	169.6(3)
M(1)–Fe(1)–M(2)	101.5(6)	101.71(5)	101.51(4)	101.5(2)
Fe(1)–M(1)–M(2)	38.65(5)	37.47(7)	37.30(8)	39.94(8)
Fe(1)–M(2)–M(1)	38.52(5)	37.41(4)	37.49(8)	38.82(8)





The molecular structures of **18-20** were very similar to those reported for the related bimetallic clusters  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IPr})\}_2$ , both concerning the overall geometries and bonding parameters. In particular, the  $\text{M}\cdots\text{M}$  distances were essentially non-bonding, as previously found in all the bimetallic IPr-derivatives. The most interesting point was that, within the solid state structures of **I-III**, the positions occupied by M(1) and M(2) were disordered Cu/Ag for **I**, Cu/Au for **II**, and Ag/Au for **III**. The occupancy factors refined as follows: 0.476(6) Ag(1), 0.255(6) Ag(2) for **I**; 0.710(2) Au(1), 0.577(2) Au(2) for **II**; and 0.522(3) Au(1), 0.530(2) Au(2) for **III** [the occupancy factors of the second metal are the complement at one of these values]. The resulting composition were Ag 0.731(6) and Cu 1.269(6) for **I**, Au 1.287(2) and Cu 0.713(2) for **II**, and Au 1.052(3) and Ag 0.948(3) for **III**. A second crystal was collected in the case of **II**, and the free variables refined as follows: 0.734(2) Au(1), 0.628(2) Au(2). The resulting composition was Au 1.362(2) and Cu 0.638(2), quite similar to that found in the first crystal.

This disorder model may be explained assuming the presence of a mixture of  $\text{Fe}(\text{CO})_4\{\text{Ag}(\text{IPr})\}_2$  (**14**),  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}\{\text{Ag}(\text{IPr})\}$  (**18**) and  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}_2$  (**12**) for **I**,  $\text{Fe}(\text{CO})_4\{\text{Au}(\text{IPr})\}_2$  (**16**),  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}\{\text{Au}(\text{IPr})\}$  (**19**) and  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}_2$  (**12**) for **II**, and  $\text{Fe}(\text{CO})_4\{\text{Au}(\text{IPr})\}_2$  (**16**),  $\text{Fe}(\text{CO})_4\{\text{Ag}(\text{IPr})\}\{\text{Au}(\text{IPr})\}$  (**20**) and  $\text{Fe}(\text{CO})_4\{\text{Ag}(\text{IPr})\}_2$  (**14**) for **III**, as also indicated by NMR analyses. Indeed, after dissolving the crystals in  $\text{CD}_2\text{Cl}_2$ , three resonances were present in the CO region of the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **I** ( $\delta_{\text{CO}}$  217.6, 216.5 and 215.6 attributable to **14**, **18** and **12**, respectively), **II** ( $\delta_{\text{CO}}$  216.8, 216.1 and 215.6 attributable to **16**, **19** and **12**, respectively) and **III** ( $\delta_{\text{CO}}$  220.1, 217.6 and 217.1 attributable to **14**, **20** and **16**, respectively).

In the case of  $\text{NHC} = \text{IMes}$ , all the attempts to prepare the trimetallic clusters  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IMes})\}\{\text{M}'(\text{IMes})\}$  failed. As in the case of  $\text{NHC} = \text{IPr}$ , the reactions were carried out by mixing the mono-anions **1**, **3** and **5** with one equivalent of  $\text{M}'(\text{IMes})\text{Cl}$  in dmsO or thf. In some cases, by performing the IR analyses of the crude reaction mixtures, there was the *in-situ* spectroscopic evidence of  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IMes})\}\{\text{M}'(\text{IMes})\}$  (by comparison with the IR spectra of **18-20**). Nonetheless, after work-up of the reaction mixtures,  $[\text{M}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  ( $\text{M} = \text{Cu}$ , **17**;  $\text{Ag}$ , **7**)

clusters, or their oxidized products  $[\text{M}_5\text{Fe}_4(\text{CO})_{16}]^{3-}$ , were always isolated. Indeed, **7** and **17** clusters were often detected (by IR) as the major species in solution in the crude reaction mixtures prior to work-up.

In particular, the reaction of **3** with one equivalent of  $\text{Au}(\text{IMes})\text{Cl}$  in dmsO, followed by precipitation with water, extraction of the residue in acetone and slow diffusion of n-hexane, afforded crystals of  $[\text{Au}(\text{IMes})_2]_3[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot\text{solv}$  suitable for X-ray analyses. Following the same procedure but using a saturated solution of  $[\text{NEt}_4]\text{Br}$  in water for precipitation, crystals of  $[\text{NEt}_2]_2[\text{Au}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot\text{dmf}$  were obtained. The molecular structures of the  $[\text{Au}(\text{IMes})_2]^+$  cations and **7** anions were already reported in the literature as miscellaneous salts (Figure 8).

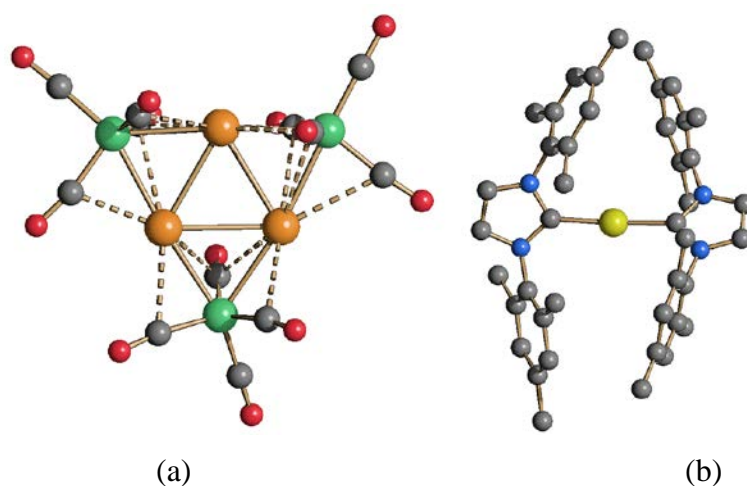


Figure 8. Molecular structures of (a)  $[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  (**7**) and (b)  $[\text{Au}(\text{IMes})_2]^+$  as found in  $[\text{Au}(\text{IMes})_2]_3[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot\text{solv}$  and  $[\text{NEt}_2]_2[\text{Au}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot\text{dmf}$ .  $\text{Ag}\cdots\text{C}(\text{O})$  contacts [2.453(4)-2.993 (4) Å] are represented as fragmented lines. Hydrogen atoms have been omitted for clarity (green Fe; orange Ag; yellow, Au; blue N; red O; grey C).

Similarly, the reaction of **3** with one equivalent of  $\text{Cu}(\text{IMes})\text{Cl}$  under analogous experimental conditions, resulted in crystals of  $[\text{NEt}_2]_2[\text{Cu}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot\text{CH}_3\text{COCH}_3$  and  $[\text{NEt}_2]_2[\text{Cu}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot\text{solv}$ , suitable for X-ray crystallography (Figure S38 in Supporting Information).

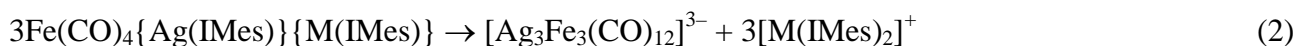
It must be remarked that **7** was easily oxidized to  $[\text{Ag}_5\text{Fe}_4(\text{CO})_{12}]^{3-}$  (**9**) by adventitious air and, therefore, particular attention must be used during work-up. As a proof of this point, crystals of

$[\text{NEt}_4][\text{M}(\text{IMes})_2]_2[\text{Ag}_5\text{Fe}_4(\text{CO})_{16}] \cdot 4\text{thf}$  ( $\text{M} = 0.94 \text{ Au}, 1.06 \text{ Ag}$ ) were once obtained due to problems during work-up.

Formation of  $[\text{M}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  species during the attempts to isolate  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IMes})\}\{\text{M}'(\text{IMes})\}$  was not surprising. Indeed, as previously reported,<sup>[18]</sup> thermal treatment, even under gentle conditions, of  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IMes})\}_2$  ( $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$ ) species resulted in  $[\text{M}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  in accord to equation (1):



It was already pointed out that thermal treatment of  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IMes})\}_2$  was the only way to prepare  $[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  and  $[\text{Au}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$ , since the reaction of  $[\text{Fe}(\text{CO})_4]^{2-}$  with  $\text{M}(\text{I})$  ( $\text{M} = \text{Ag}, \text{Au}$ ) salts afforded  $[\text{Ag}_4\text{Fe}_4(\text{CO})_{16}]^{4-}$  and  $[\text{Au}_4\text{Fe}_4(\text{CO})_{16}]^{4-}$ . In contrast,  $[\text{Cu}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  was obtained by thermal decomposition of  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IMes})\}_2$  as well as reaction of  $[\text{Fe}(\text{CO})_4]^{2-}$  with  $\text{Cu}(\text{I})$  salts. In the case of the purported trimetallic species  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IMes})\}\{\text{M}'(\text{IMes})\}$ , it was interesting to notice that complete segregation of the two group 11 metals was observed during the decomposition, at least in the case of  $\text{Cu}/\text{Ag}$  and  $\text{Ag}/\text{Au}$ . Unfortunately, crystals were not obtained for the  $\text{Cu}/\text{Au}$ -IMes system. As summarized in equation (2), these reactions selectively afforded  $[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  anions and  $[\text{M}(\text{IMes})_2]^+$  ( $\text{M} = \text{Cu}, \text{Au}$ ) cations.



In order to shed light on the decomposition products of  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IMes})\}\{\text{M}'(\text{IMes})\}$  clusters, the Gibbs energy variations of the reactions were computationally estimated by means of PBEh-3c calculations. The reactions are summarized in Table 3. As observable, in the case of  $\text{M} = \text{Ag}$  and  $\text{M}' = \text{Cu}$  or  $\text{Au}$ , the formation of  $[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  is thermodynamically favored with respect to  $[\text{Cu}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  or  $[\text{Au}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$ . Despite the fact that there is no experimental evidence, DFT calculations suggest the formation of  $[\text{Cu}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  instead of  $[\text{Au}_3\text{Fe}_3(\text{CO})_{12}]^{3-}$  for the decomposition of  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IMes})\}\{\text{Au}(\text{IMes})\}$ . The data in Table 3 can be rationalized on the basis of the different stability of the  $\text{M}$ -IMes bonds on changing the coinage metal. The computed dissociation energy for the reaction  $[\text{Au}(\text{IMes})_2]^+ \rightarrow [\text{Au}(\text{IMes})]^+ + \text{IMes}$  is  $6.5 \text{ kcal mol}^{-1}$  higher than that for the corresponding reaction with  $\text{M} = \text{Cu}$  and  $19.5 \text{ kcal mol}^{-1}$  higher on

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comparing  $M = \text{Au}$  with  $M = \text{Ag}$ . The stability of the  $M\text{-IMes}$  bonds therefore follows the order  $\text{Au} > \text{Cu} > \text{Ag}$ , and the decompositions of the  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IMes})\}\{\text{M}'(\text{IMes})\}$  clusters afford the most stable  $[\text{M}(\text{IMes})_2]^+$  complex as product. The computed data here reported are in line with the previously stated experimental observation that Cu-containing complexes resembled more to Au-complexes than Ag-complexes.

Table 3. Relative Gibbs energy variations ( $\text{kcal mol}^{-1}$ ) between the possible products of the decomposition reactions of  $\text{Fe}(\text{CO})_4\{\text{M}(\text{IMes})\}\{\text{M}'(\text{IMes})\}$  clusters.

Reactants	First set of products (R1)	Second set of products (R2)	$\Delta G(\text{R2}) - \Delta G(\text{R1})$
$3 \text{Fe}(\text{CO})_4\{\text{Cu}(\text{IMes})\}\{\text{Ag}(\text{IMes})\}$	$[\text{Cu}_3\text{Fe}_3(\text{CO})_{12}]^{3-} + 3 [\text{Ag}(\text{IMes})_2]^+$	$[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]^{3-} + 3 [\text{Cu}(\text{IMes})_2]^+$	-28.1
$3 \text{Fe}(\text{CO})_4\{\text{Ag}(\text{IMes})\}\{\text{Au}(\text{IMes})\}$	$[\text{Au}_3\text{Fe}_3(\text{CO})_{12}]^{3-} + 3 [\text{Ag}(\text{IMes})_2]^+$	$[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]^{3-} + 3 [\text{Au}(\text{IMes})_2]^+$	-46.7
$3 \text{Fe}(\text{CO})_4\{\text{Cu}(\text{IMes})\}\{\text{Au}(\text{IMes})\}$	$[\text{Au}_3\text{Fe}_3(\text{CO})_{12}]^{3-} + 3 [\text{Cu}(\text{IMes})_2]^+$	$[\text{Cu}_3\text{Fe}_3(\text{CO})_{12}]^{3-} + 3 [\text{Au}(\text{IMes})_2]^+$	-18.7

Finally, whilst attempting to isolate the purported  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IMes})\}\{\text{Ag}(\text{IMes})\}$  by reaction of  $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 2\text{thf}$  with  $\text{Cu}(\text{IMes})\text{Cl}$  and  $\text{Ag}(\text{IMes})\text{Cl}$  in  $\text{thf}$ , followed by extraction with  $\text{CH}_2\text{Cl}_2$  and slow diffusion of  $n\text{-pentane}$ , a few crystals of  $\text{Fe}(\text{CO})_4(\text{CH}_2\text{IMes})$  (**21**) were obtained (Figure 9). These were likely to arise from decomposition of  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IMes})\}\{\text{Ag}(\text{IMes})\}$  and activation of  $\text{CH}_2\text{Cl}_2$ , as previously reported for related Fe-Au-NHC complexes.<sup>[24]</sup> **21** contained the zwitterionic (1,3-di-mesitylimidazolium-2-yl)methyl ligand (formally a two-electron donor) bonded to  $\text{Fe}(\text{CO})_4$ . Some examples of related zwitterionic ligands derived by NHC carbene bonded to miscellaneous metals have been previously reported in the literature.<sup>[36,37]</sup>

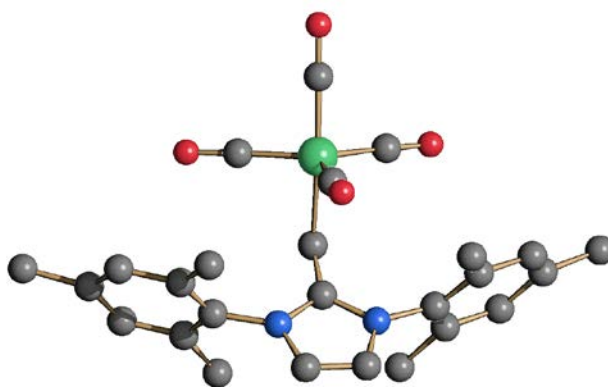


Figure 9. Molecular structure of  $\text{Fe}(\text{CO})_4(\text{CH}_2\text{IMes})$  (**21**). Hydrogen atoms have been omitted for clarity (green Fe; blue N; red O; grey C). Main bond distances (Å) and angles (°): Fe-C<sub>CH<sub>2</sub></sub> 2.158(2), Fe-CO 1.771(3)-1.796(3), C<sub>CH<sub>2</sub></sub>-C<sub>IMes</sub> 1.448(5), Fe-C<sub>CH<sub>2</sub></sub>-C<sub>IMes</sub> 111.24(16).

## Conclusions

Anionic bimetallic Fe-Ag and Fe-Cu (**1-4**), neutral bimetallic Fe-Ag and Fe-Cu (**11-14**) and neutral trimetallic Fe-Cu-Ag, Fe-Cu-Au and Fe-Ag-Au (**18-20**) carbonyl clusters containing NHC ligands have been obtained and compared to related Fe-Au-containing species (**5**, **6**, **15** and **16**) on the basis of chemical, structural, spectroscopic and computational methods. Stability of the Fe-M (M = Cu, Ag, Au) species decreases in the order Au > Cu > Ag, as corroborated by DFT calculations. Moreover, IPr-containing species are usually more stable than IMes-ones, mainly due to steric effects as previously reported.<sup>[23]</sup> Therefore, the IPr ligand appears to be the most effective one in order to isolate also elusive Ag-species. The stability order herein found is in keeping with usual trend for transition metals, where third row metals usually form the strongest bonds.<sup>[25]</sup> Indeed, the stabilities of the compounds herein reported mainly rely on the strength of the M-Fe and M-NHC bonds, that are very strong for Au and considerably weaker for Ag, whereas Cu displays an intermediate behavior. Metallophilic M...M interactions are present in the case of IMes complexes or in homoleptic carbonyl clusters containing two or more coinage metals. In contrast, in the presence of the bulkier IPr ligand, M...M contacts are essentially non-bonding. This gives further support to the conclusion that metallophilic interactions are rather soft and strongly depends on the steric properties of the ancillary ligands employed in such complexes.<sup>[1-17]</sup>

## Experimental Section

### General experimental procedures

All reactions and sample manipulations were carried out using standard Schlenk techniques under nitrogen and in dried solvents. All the reagents were commercial products (Aldrich) of the highest purity available and used as received, except  $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 2\text{thf}$ <sup>[38]</sup> and  $\text{M}(\text{NHC})\text{Cl}$  (M = Cu, Ag, Au; NHC = IMes, IPr)<sup>[39]</sup> which were prepared according to the literature. Analyses of C, H and N were obtained with a Thermo Quest Flash EA 1112NC instrument. IR spectra were recorded on a Perkin Elmer Spectrum One interferometer in  $\text{CaF}_2$  cells.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR measurements were performed on a Varian Mercury Plus 400 MHz instrument.

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The proton and carbon chemical shifts were referenced to the non-deuterated aliquot of the solvent. Structure drawings have been performed with SCHAKAL99.<sup>[40]</sup>

#### Synthesis of Na[Fe(CO)<sub>4</sub>{Cu(IMes)}] (Na[1])

Na<sub>2</sub>[Fe(CO)<sub>4</sub>]·2thf (0.320 g, 0.894 mmol) and Cu(IMes)Cl (0.360 g, 0.892 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and dmso (10 mL) was added. The mixture was stirred for 2 h at room temperature and, then, the crude product was characterized through IR, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies (a few drops of d<sup>6</sup>-dmso were added as reference for the NMR characterization). All attempts to isolate **1** in the solid state as [NEt<sub>4</sub>]<sup>+</sup> salt after addition of a saturated solution of [NEt<sub>4</sub>]Br in H<sub>2</sub>O failed. Thus, yields were not been determined.

IR (dmso, 293 K) ν<sub>CO</sub>: 1909(s), 1800(vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (dmso with 5% d<sup>6</sup>-dmso, 298 K): δ 7.38 (s, 2H, CH<sub>imid</sub>), 6.97 (s, 4H, CH<sub>Ar</sub>), (aliphatic protons were hidden by the dmso resonance). <sup>13</sup>C{<sup>1</sup>H} NMR (dmso with 5% d<sup>6</sup>-dmso, 298 K): δ 225.9 (CO), 179.3 (C-Cu), 137.7, 135.8, 134.5, 128.7, 121.9 (C<sub>Ar</sub> and CH<sub>imid</sub>), 20.7, 17.4 (CH<sub>3</sub>).

#### Synthesis of [NEt<sub>4</sub>][Fe(CO)<sub>4</sub>{Cu(IPr)}] ([NEt<sub>4</sub>][2])

Na<sub>2</sub>[Fe(CO)<sub>4</sub>]·2thf (0.220 g, 0.614 mmol) and Cu(IPr)Cl (0.430 g, 0.882 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and dmso (15 mL) was added. The mixture was stirred for 2 h at room temperature and, then, a saturated solution of [NEt<sub>4</sub>]Br in H<sub>2</sub>O (40 mL) was added up to complete precipitation. The resulting solid was recovered by filtration, washed with H<sub>2</sub>O (3 × 15 mL), and extracted with toluene (20 mL). Crystals of [NEt<sub>4</sub>][Fe(CO)<sub>4</sub>(CuIPr)] suitable for X-ray crystallography were obtained by slow diffusion of n-pentane (40 mL) on the toluene solution at -20°C (yield 0.207 g, 45% based on Fe, 31% based on Cu). **2** resulted to be rather unstable in solution. Therefore, the NMR characterization was carried out on the crude reaction mixture in dmso as Na<sup>+</sup> salt after the addition of a few drops of d<sup>6</sup>-dmso.

C<sub>39</sub>H<sub>54</sub>CuFeN<sub>3</sub>O<sub>4</sub> (748.24): calcd. (%): C 62.63, H 7.29, N 5.62; found: C 62.89, H 6.94, N 5.39. IR (nujol, 293 K) ν<sub>CO</sub>: 1913(s), 1801(vs) cm<sup>-1</sup>. IR (dmso, 293 K) ν<sub>CO</sub>: 1911(ms), 1800(vs) cm<sup>-1</sup>. IR (toluene, 293 K) ν<sub>CO</sub>: 1913(s), 1807(vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (dmso with 5% d<sup>6</sup>-dmso, 298 K): δ 7.51, 7.34, 7.23 (br, 8H, CH<sub>Ar</sub> and CH<sub>imid</sub>), (the resonance due to CH(CH<sub>3</sub>)<sub>2</sub> was hidden by the dmso resonance), 1.17, 1.12 (br, 24H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (dmso with 5% d<sup>6</sup>-dmso, 298 K): δ 226.1 (CO), 181.8 (C-Cu), 145.5, 135.9, 129.7, 123.8, 123.4 (C<sub>Ar</sub> and CH<sub>imid</sub>), 28.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.5, 24.0 (CH(CH<sub>3</sub>)<sub>2</sub>).

#### Synthesis of Na[Fe(CO)<sub>4</sub>{Ag(IMes)}] (Na[3])

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Na<sub>2</sub>[Fe(CO)<sub>4</sub>]·2thf (0.330 g, 0.922 mmol) and Ag(IMes)Cl (0.550 g, 1.23 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and dmsO (10 mL) was added. The mixture was stirred for 2 h at room temperature and, then, the crude product was characterized through IR, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies (a few drops of d<sup>6</sup>-dmsO were added as reference for the NMR characterization). All attempts to isolate **3** in the solid state as [NEt<sub>4</sub>]<sup>+</sup> salt after addition of a saturated solution of [NEt<sub>4</sub>]Br in H<sub>2</sub>O failed. Thus, yields were not been determined. Among the decomposition products formed during the attempts to isolate **3**, crystals suitable for X-ray crystallography of [NEt<sub>4</sub>]<sub>2</sub>[Ag(IMes)<sub>2</sub>][Ag<sub>3</sub>Fe<sub>3</sub>(CO)<sub>12</sub>]·solv,<sup>[18]</sup> [NEt<sub>4</sub>]<sub>2</sub>[HIMes][Ag<sub>4</sub>Fe<sub>4</sub>(CO)<sub>16</sub>], [NEt<sub>4</sub>]<sub>4</sub>[Ag<sub>4</sub>Fe<sub>4</sub>(CO)<sub>16</sub>]·2CH<sub>3</sub>CN and [NEt<sub>4</sub>]<sub>3</sub>[Ag<sub>5</sub>Fe<sub>4</sub>(CO)<sub>16</sub>] were obtained.

IR (dmsO, 293 K) ν<sub>CO</sub>: 1910(s), 1796(vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (dmsO with 5% d<sup>6</sup>-dmsO, 298 K): δ 7.56 (s, 2H, CH<sub>imid</sub>), 7.01 (s, 4H, CH<sub>Ar</sub>), (aliphatic protons were hidden by the dmsO resonance). <sup>13</sup>C{<sup>1</sup>H} NMR (dmsO with 5% d<sup>6</sup>-dmsO, 298 K): δ 227.0 (CO), (C-Ag too weak to be detected), 138.3, 136.3, 134.8, 129.3, 123.0 (C<sub>Ar</sub> and CH<sub>imid</sub>), 21.1, 17.8 (CH<sub>3</sub>).

#### Synthesis of Na[Fe(CO)<sub>4</sub>{Ag(IPr)}] (Na[4])

Na<sub>2</sub>[Fe(CO)<sub>4</sub>]·2thf (0.336 g, 0.934 mmol) and Ag(IPr)Cl (0.645 g, 1.21 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and dmsO (10 mL) was added. The mixture was stirred for 2 h at room temperature and, then, the crude product was characterized through IR, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies (a few drops of d<sup>6</sup>-dmsO were added as reference for the NMR characterization). All attempts to isolate **4** in the solid state as [NEt<sub>4</sub>]<sup>+</sup> salt after addition of a saturated solution of [NEt<sub>4</sub>]Br in H<sub>2</sub>O failed. Thus, yields were not been determined. Among the decomposition products formed during the attempts to isolate **4**, crystals suitable for X-ray crystallography of [Ag(IPr)<sub>2</sub>][Fe<sub>2</sub>(CO)<sub>8</sub>{Ag(IPr)}]·CH<sub>2</sub>Cl<sub>2</sub>,\* [NEt<sub>4</sub>]<sub>2</sub>[HIPr][Fe<sub>2</sub>(CO)<sub>8</sub>{Ag(IPr)}]<sub>2</sub>[Cl]·2CH<sub>2</sub>Cl<sub>2</sub> and [NEt<sub>4</sub>]<sub>4</sub>[Ag<sub>4</sub>Fe<sub>4</sub>(CO)<sub>16</sub>] were obtained.

IR (dmsO, 293 K) ν<sub>CO</sub>: 1910(s), 1797(vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (dmsO with 5% d<sup>6</sup>-dmsO, 298 K): δ 7.69, 7.42, 7.28 (br, 8H, CH<sub>Ar</sub> and CH<sub>imid</sub>), (the resonance due to CH(CH<sub>3</sub>)<sub>2</sub> was hidden by the dmsO resonance), 1.22, 1.16 (br, 24H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (dmsO with 5% d<sup>6</sup>-dmsO, 298 K): δ 226.8 (CO), 190.0 (br, C-Ag), 145.6, 142.4, 135.8, 129.9, 124.0 (C<sub>Ar</sub> and CH<sub>imid</sub>), 28.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.3, 24.2 (CH(CH<sub>3</sub>)<sub>2</sub>).

\* [Ag(IPr)<sub>2</sub>][Fe<sub>2</sub>(CO)<sub>8</sub>{Ag(IPr)}]·CH<sub>2</sub>Cl<sub>2</sub>: IR (nujol, 293 K) ν<sub>CO</sub>: 1944(s), 1901(ms), 1884(s), 1725(ms) cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>, 293 K) ν<sub>CO</sub>: 1952(s), 1869(s), 1851(ms), 1833(ms) cm<sup>-1</sup>.

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### Synthesis of $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IMes})\}_2$ (**11**)

$\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 2\text{thf}$  (0.210 g, 0.587 mmol) and  $\text{Cu}(\text{IMes})\text{Cl}$  (0.469 g, 1.180 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and thf (20 mL) was added. The mixture was stirred for 5 h at room temperature and then filtered off. The solution was layered with n-hexane to give yellow crystals of **11** (yield 0.22 g, 42% based on Fe, 41% based on Cu).<sup>[18]</sup>

$\text{C}_{46}\text{H}_{48}\text{Cu}_2\text{FeN}_4\text{O}_4$  (903.81): calcd. (%): C 61.19, H 5.36, N 6.21; found: C 60.98, H 5.49, N 6.42. IR (nujol, 293 K)  $\nu_{\text{CO}}$ : 1958(s), 1873(m), 1856(s), 1833(m)  $\text{cm}^{-1}$ . IR (thf, 293 K)  $\nu_{\text{CO}}$ : 1950(m), 1872(s), 1850(m)  $\text{cm}^{-1}$ . IR (acetone, 293 K)  $\nu_{\text{CO}}$ : 1950(m), 1859(vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 298 K):  $\delta$  7.44 (s, 4H,  $\text{CH}_{\text{imid}}$ ), 7.04 (s, 8H,  $\text{CH}_{\text{Ar}}$ ), 2.45 (s, 12H,  $\text{CH}_3$ ), 1.74 (s, 24H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 298 K):  $\delta$  217.8 (CO), 177.3 (C-Cu), 139.2, 134.8, 134.5, 129.0, 123.1 ( $\text{C}_{\text{Ar}}$  and  $\text{CH}_{\text{imid}}$ ), 20.3, 16.3 ( $\text{CH}_3$ ).

### Synthesis of $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}_2 \cdot 2\text{thf}$ (**12**·2thf)

$\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 2\text{thf}$  (0.270 g, 0.754 mmol) and  $\text{Cu}(\text{IPr})\text{Cl}$  (0.920 g, 1.89 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and thf (20 mL) was added. The mixture was stirred for 5 h at room temperature and then filtered off. The solution was layered with n-hexane to give yellow crystals of **12**·2thf (yield 0.52 g, 56% based on Fe, 45% based on Cu).

$\text{C}_{66}\text{H}_{88}\text{Cu}_2\text{FeN}_4\text{O}_6$  (1216.33): calcd. (%): C 65.21, H 7.30, N 4.61; found: C 64.89, H 7.03, N 4.93. IR (nujol, 293 K)  $\nu_{\text{CO}}$ : 1953(s), 1875(m), 1838(s), 1821(vs)  $\text{cm}^{-1}$ . IR (thf, 293 K)  $\nu_{\text{CO}}$ : 1951(s), 1872(s), 1851(vs)  $\text{cm}^{-1}$ . IR (acetone, 293 K)  $\nu_{\text{CO}}$ : 1950(m), 1849(vs)  $\text{cm}^{-1}$ . IR ( $\text{CH}_2\text{Cl}_2$ , 293 K)  $\nu_{\text{CO}}$ : 1951(s), 1848(vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  7.49 (t,  $^2J_{\text{HH}} = 7.6$  Hz, 4H,  $\text{CH}_{\text{Ar}}$ ), 7.30 (d,  $^2J_{\text{HH}} = 7.4$  Hz, 8H,  $\text{CH}_{\text{Ar}}$ ), 7.12 (s, 4H,  $\text{CH}_{\text{imid}}$ ), 2.67 (br, 8H,  $\text{CH}(\text{CH}_3)_2$ ), 1.24 (br, 48H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  215.7 (CO), 181.5 (C-Cu), 145.6, 135.1, 129.8, 123.7, 122.6 ( $\text{C}_{\text{Ar}}$  and  $\text{CH}_{\text{imid}}$ ), 28.6 ( $\text{CH}(\text{CH}_3)_2$ ), 24.1, 23.9 ( $\text{CH}(\text{CH}_3)_2$ ).

### Synthesis of $\text{Fe}(\text{CO})_4\{\text{Ag}(\text{IMes})\}_2$ (**13**)

$\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 2\text{thf}$  (0.210 g, 0.587 mmol) and  $\text{Ag}(\text{IMes})\text{Cl}$  (0.522 g, 1.180 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and thf (20 mL) was added. The mixture was stirred for 5 h at room temperature and then filtered off. The solution was layered with n-hexane to give colorless crystals of **13** (yield 0.21 g, 36% based on Fe, 36% based on Ag).

$\text{C}_{46}\text{H}_{48}\text{Ag}_2\text{FeN}_4\text{O}_4$  (992.47): calcd. (%): C 55.75, H 4.89, N 5.66; found: C 55.92, H 4.74, N 5.48. IR (nujol, 293 K)  $\nu_{\text{CO}}$ : 1958(s), 1874(m), 1860(s), 1841(m)  $\text{cm}^{-1}$ . IR ( $\text{CH}_2\text{Cl}_2$ , 293 K)  $\nu_{\text{CO}}$ : 1948(m), 1878(s)  $\text{cm}^{-1}$ . IR (acetone, 293 K)  $\nu_{\text{CO}}$ : 1943(m), 1878(s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  7.70 (s, 4H,  $\text{CH}_{\text{imid}}$ ), 7.10 (s, 8H,  $\text{CH}_{\text{Ar}}$ ), 2.38 (s,

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12H, CH<sub>3</sub>), 2.15 (s, 24H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 219.3 (CO), 182.6 (C-Ag, <sup>1</sup>J<sub>C-Ag</sub> = 209 and 180 Hz), 141.7, 134.5, 134.2, 129.8, 129.1 (C<sub>Ar</sub> and CH<sub>imid</sub>), 20.9, 17.2 (CH<sub>3</sub>).

#### Synthesis of Fe(CO)<sub>4</sub>{Ag(IPr)}<sub>2</sub> (**14**)

Na<sub>2</sub>[Fe(CO)<sub>4</sub>]·2thf (0.380 g, 1.06 mmol) and Ag(IPr)Cl (1.45 g, 2.73 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and thf (15 mL) was added. The mixture was stirred for 5 h at room temperature and then the solvent was removed under reduced pressure. The residue was washed with H<sub>2</sub>O (3 × 20 mL), and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). A microcrystalline powder of **14** was obtained by addition of n-pentane (40 mL) to the CH<sub>2</sub>Cl<sub>2</sub> solution (yield 0.503 g, 41% based on Fe, 32% based on Ag).

C<sub>58</sub>H<sub>72</sub>Ag<sub>2</sub>FeN<sub>4</sub>O<sub>4</sub> (1158.30): calcd. (%): C 60.09, H 6.26, N 4.84; found: C 59.86, H 6.42, N 5.01. IR (CH<sub>2</sub>Cl<sub>2</sub>, 293 K) ν<sub>CO</sub>: 1951(s), 1870(vs), 1952(sh), 1832(sh) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 7.44 (br, 4H, CH<sub>Ar</sub>), 7.25 (br, 8H, CH<sub>Ar</sub>), 7.14 (s, CH<sub>imid</sub>), 2.53 (br, 8H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17 (br, 48H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 217.6 (CO), 189.2 (C-Ag, <sup>1</sup>J<sub>C-Ag</sub> = 204 and 182 Hz), 145.6, 135.0, 129.9, 123.8, 122.8 (C<sub>Ar</sub> and CH<sub>imid</sub>), 28.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.2, 23.7 (CH(CH<sub>3</sub>)<sub>2</sub>).

#### Synthesis of Fe(CO)<sub>4</sub>{Cu(IPr)}<sub>1.27</sub>{Ag(IPr)}<sub>0.73</sub>·1.5toluene

Na<sub>2</sub>[Fe(CO)<sub>4</sub>]·2thf (0.336 g, 0.938 mmol) and Ag(IPr)Cl (0.645 g, 1.21 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and dmso (10 mL) was added. The mixture was stirred for 2 h at room temperature up to the disappearance of the ν<sub>CO</sub> peak at 1740 cm<sup>-1</sup> in the IR spectrum due to Na<sub>2</sub>[Fe(CO)<sub>4</sub>]·2thf. Then, Cu(IPr)Cl (0.500 g, 1.03 mmol) was added as a solid in small portions. The crude product was precipitated by the slow addition of H<sub>2</sub>O (40 mL) to the dmso solution. The solid was recovered after filtration, washed with H<sub>2</sub>O (3 × 20 mL), and extracted with toluene (10 mL). Crystals of Fe(CO)<sub>4</sub>{Cu(IPr)}<sub>1.27</sub>{Ag(IPr)}<sub>0.73</sub>·1.5toluene suitable for X-ray crystallography were obtained by slow diffusion of n-pentane (40 mL) on the toluene solution at -20°C (yield 0.560 g, 48% based on Fe, 27% based on Ag, 56% based on Cu).

C<sub>68.5</sub>H<sub>84</sub>Ag<sub>0.73</sub>Cu<sub>1.27</sub>FeN<sub>4</sub>O<sub>4</sub>(1242.79): calcd. (%): C 66.26, H 6.82, N 4.52; found: C 66.48, H 7.01, N 4.22. IR (nujol, 293 K) ν<sub>CO</sub>: 1953(s), 1867(s), 1852(s), 1835(s) cm<sup>-1</sup>. IR (thf, 293 K) ν<sub>CO</sub>: 1954(s), 1871(m), 1858(vs), 1834(s) cm<sup>-1</sup>. IR (acetone, 293 K) ν<sub>CO</sub>: 1952(s), 1853(vs) cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>, 293 K) ν<sub>CO</sub>: 1953(s), 1851(vs), 1833(sh) cm<sup>-1</sup>. IR (toluene, 293 K) ν<sub>CO</sub>: 1957(s), 1876(s), 1853(vs), 1832(s) cm<sup>-1</sup>. IR (CH<sub>3</sub>CN, 293 K) ν<sub>CO</sub>: 1952(s), 1852(vs) cm<sup>-1</sup>. IR (dmso, 293 K) ν<sub>CO</sub>: 1947(s), 1848(vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 7.34 (br, 4H, CH<sub>Ar</sub>), 7.16 (br, 8H, CH<sub>Ar</sub>), 7.04 (s, 4H, CH<sub>imid</sub>), 2.47 (br, 8H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.08 (br, 48H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR

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(CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  217.6, 216.5, 215.6 (CO)\*, 189.2 (C-Ag,  $^1J_{C-Ag}$  = 194 and 167 Hz)\*\*, 181.6, 181.5 (C-Cu)\*\*, 145.6, 135.0, 129.9, 123.8, 122.8 (C<sub>Ar</sub> and CH<sub>imid</sub>), 28.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.2, 23.7 (CH(CH<sub>3</sub>)<sub>2</sub>).

\* The three resonances in the CO region may be assigned to Fe(CO)<sub>4</sub>{Ag(IPr)}<sub>2</sub> (**14**), Fe(CO)<sub>4</sub>{Cu(IPr)}{Ag(IPr)} (**18**) and Fe(CO)<sub>4</sub>{Cu(IPr)}<sub>2</sub> (**12**), respectively.

\*\* The carbene C-M resonances of the three compounds are very close and can be assigned as follow: C-Cu of Fe(CO)<sub>4</sub>{Cu(IPr)}<sub>2</sub> (**12**) at  $\delta$  181.5 ppm; C-Cu of Fe(CO)<sub>4</sub>{Cu(IPr)}{Ag(IPr)} (**18**) at  $\delta$  181.6 ppm; the resonance at  $\delta$  189.2 ppm showing coupling to Ag is somehow broad and seems to result from the overlapping of the C-Ag resonances of Fe(CO)<sub>4</sub>{Ag(IPr)}<sub>2</sub> (**14**) and Fe(CO)<sub>4</sub>{Cu(IPr)}{Ag(IPr)} (**18**).

### Synthesis of Fe(CO)<sub>4</sub>{Cu(IPr)}<sub>0.64</sub>{Au(IPr)}<sub>1.36</sub>·1.5toluene

Na<sub>2</sub>[Fe(CO)<sub>4</sub>]·2thf (0.310 g, 0.866 mmol) and Cu(IPr)Cl (0.470 g, 0.964 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and dmsO (10 mL) was added. The mixture was stirred for 2 h at room temperature up to the disappearance of the  $\nu_{CO}$  peak at 1740 cm<sup>-1</sup> in the IR spectrum due to Na<sub>2</sub>[Fe(CO)<sub>4</sub>]·2thf. Then, Au(IPr)Cl (0.620 g, 1.00 mmol) was added as a solid in small portions. The crude product was precipitated by the slow addition of H<sub>2</sub>O (40 mL) to the dmsO solution. The solid was recovered after filtration, washed with H<sub>2</sub>O (3 × 20 mL), and extracted with toluene (10 mL). Crystals of Fe(CO)<sub>4</sub>{Cu(IPr)}<sub>0.64</sub>{Au(IPr)}<sub>1.36</sub>·1.5toluene suitable for X-ray crystallography were obtained by slow diffusion of n-pentane (40 mL) on the toluene solution at -20°C (yield 0.639 g, 53% based on Fe, 62% based on Au, 30% based on Cu).

The same product was also obtained from the 1:1 reaction of [NEt<sub>4</sub>][Fe(CO)<sub>4</sub>{Au(IPr)}] and Cu(IPr)Cl in acetone.

C<sub>68.5</sub>H<sub>84</sub>Au<sub>1.36</sub>Cu<sub>0.64</sub>FeN<sub>4</sub>O<sub>4</sub> (1391.78): calcd. (%): C 59.11, H 6.09, N 4.03; found: C 59.34, H 5.88, N 4.19. IR (nujol, 293 K)  $\nu_{CO}$ : 1974(vs), 1963(s), 1890(vs), 1880(vs), 1865(vs), 1848(vs) cm<sup>-1</sup>. IR (thf, 293 K)  $\nu_{CO}$ : 1975(ms), 1867(vs) cm<sup>-1</sup>. IR (acetone, 293 K)  $\nu_{CO}$ : 1973(ms), 1867(vs) cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>, 293 K)  $\nu_{CO}$ : 1974(ms), 1863(vs)cm<sup>-1</sup>. IR (toluene, 293 K)  $\nu_{CO}$ : 1978(s), 1869(vs)cm<sup>-1</sup>. IR (CH<sub>3</sub>CN, 293 K)  $\nu_{CO}$ : 1971(ms), 1865(vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  7.46 (br, 4H, CH<sub>Ar</sub>), 7.26 (br, 8H, CH<sub>Ar</sub>), 7.09 (s, 4H, CH<sub>imid</sub>), 2.60 (br, 8H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (br, 48H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  216.8, 216.1, 215.6 (CO)\*, 194.5, 194.3 (C-Au)\*\*, 181.6, 181.2 (C-Cu)\*\*, 145.6, 134.7, 129.8, 123.7, 122.1 (C<sub>Ar</sub> and CH<sub>imid</sub>), 28.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.8, 23.7 (CH(CH<sub>3</sub>)<sub>2</sub>).

\* The three resonances in the CO region may be assigned to Fe(CO)<sub>4</sub>{Au(IPr)}<sub>2</sub> (**16**), Fe(CO)<sub>4</sub>{Cu(IPr)}{Au(IPr)} (**19**) and Fe(CO)<sub>4</sub>{Cu(IPr)}<sub>2</sub> (**12**), respectively.

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\*\* The carbene C-M resonances of the three compounds can be assigned as follow: C-Cu of  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}_2$  (**12**) at  $\delta$  181.6 ppm; C-Cu of  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}\{\text{Au}(\text{IPr})\}$  (**19**) at  $\delta$  181.2 ppm; C-Au of  $\text{Fe}(\text{CO})_4\{\text{Au}(\text{IPr})\}_2$  (**16**) at  $\delta$  194.36 ppm; C-Cu of  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}\{\text{Au}(\text{IPr})\}$  (**19**) at  $\delta$  194.5 ppm;

#### Synthesis of $\text{Fe}(\text{CO})_4\{\text{Ag}(\text{IPr})\}_{0.94}\{\text{Au}(\text{IPr})\}_{1.06}$

$\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 2\text{thf}$  (0.336 g, 0.938 mmol) and  $\text{Ag}(\text{IPr})\text{Cl}$  (0.645 g, 1.21 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and  $\text{dmso}$  (10 mL) was added. The mixture was stirred for 2 h at room temperature up to the disappearance of the  $\nu_{\text{CO}}$  peak at  $1740\text{ cm}^{-1}$  in the IR spectrum due to  $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 2\text{thf}$ . Then,  $\text{Au}(\text{IPr})\text{Cl}$  (0.620 g, 1.00 mmol) was added as a solid in small portions. The crude product was precipitated by the slow addition of  $\text{H}_2\text{O}$  (40 mL) to the  $\text{dmso}$  solution. The solid was recovered after filtration, washed with  $\text{H}_2\text{O}$  ( $3 \times 20\text{ mL}$ ), and extracted with toluene (10 mL). Crystals of  $\text{Fe}(\text{CO})_4\{\text{Ag}(\text{IPr})\}_{0.94}\{\text{Au}(\text{IPr})\}_{1.06} \cdot 1.5\text{toluene}$  suitable for X-ray crystallography were obtained by slow diffusion of  $n$ -pentane (40 mL) on the toluene solution at  $-20^\circ\text{C}$  (yield 0.627 g, 48% based on Fe, 37% based on Ag, 45% based on Au).

The same product was also obtained from the 1:1 reaction of  $[\text{NEt}_4][\text{Fe}(\text{CO})_4\{\text{Au}(\text{IPr})\}]$  and  $\text{Ag}(\text{IPr})\text{Cl}$  in acetone.

$\text{C}_{68.5}\text{H}_{84}\text{Ag}_{0.94}\text{Au}_{1.06}\text{FeN}_4\text{O}_4$  (1393.65): calcd. (%): C 59.06, H 6.08, N 4.02; found: C 59.24, H 5.88, N 3.79. IR (acetone, 293 K)  $\nu_{\text{CO}}$ : 1963(s), 1880(sh), 1869(vs), 1853(vs)  $\text{cm}^{-1}$ . IR ( $\text{dmso}$ , 293 K)  $\nu_{\text{CO}}$ : 1960(s), 1863(vs)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 298 K):  $\delta$  7.58-7.25 (br, 16H,  $\text{CH}_{\text{Ar}}$  +  $\text{CH}_{\text{imid}}$ ), 2.63 (br, 8H,  $\text{CH}(\text{CH}_3)_2$ ), 1.20 (br, 48H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 298 K):  $\delta$  220.1, 217.6, 217.1 (CO)\*, 194.7 (C-Au)\*\*\*, 182.3 (C-Ag,  $^1J_{\text{C-Ag}}$  = 213 and 195 Hz)\*\*\*, 145.7-122.2 ( $\text{C}_{\text{Ar}}$  and  $\text{CH}_{\text{imid}}$ ), 28.5 ( $\text{CH}(\text{CH}_3)_2$ ), 24.1-23.3 ( $\text{CH}(\text{CH}_3)_2$ ).

\* The three resonances in the CO region may be assigned to  $\text{Fe}(\text{CO})_4\{\text{Ag}(\text{IPr})\}_2$  (**14**),  $\text{Fe}(\text{CO})_4\{\text{Ag}(\text{IPr})\}\{\text{Au}(\text{IPr})\}$  (**20**) and  $\text{Fe}(\text{CO})_4\{\text{Au}(\text{IPr})\}_2$  (**16**), respectively.

\*\* The carbene C-M resonances are rather weak and, therefore, it has been possible to detect only the two major resonances of C-Au and C-Ag.

#### Synthesis of $[\text{NEt}_4]_2[\text{Cu}(\text{IMes})_2][\text{Cu}_3\text{Fe}_3(\text{CO})_{12}]$

A solution of **11** (0.381 g, 0.384 mmol) in  $\text{dmso}$  (15 mL) was heated at  $130^\circ\text{C}$  for 0.5 h and the reaction monitored by IR spectroscopy. Then, a saturated solution of  $[\text{NEt}_4]\text{Br}$  in  $\text{H}_2\text{O}$  (40 mL) was added up to complete precipitation. The resulting solid was recovered by filtration, washed with  $\text{H}_2\text{O}$  ( $3 \times 15\text{ mL}$ ), toluene ( $3 \times 15\text{ mL}$ ), and extracted with acetone (15 mL). Crystals of  $[\text{NEt}_4]_2[\text{Cu}(\text{IMes})_2][\text{Cu}_3\text{Fe}_3(\text{CO})_{12}]$

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suitable for X-ray crystallography were obtained by slow diffusion of n-hexane (35 mL) on the acetone solution (yield 0.11 g, 54% based on Fe, 35% based on Cu).

$C_{70}H_{88}Cu_4Fe_3N_6O_{12}$  (1627.17): calcd. (%): C 51.72, H 5.46, N 5.17; found: C 51.95, H 5.61, N 4.95. IR (nujol, 293 K)  $\nu_{CO}$ : 1930(s), 1846(s), 1825(m), 1807(w)  $cm^{-1}$ . IR ( $CH_2Cl_2$ , 293 K)  $\nu_{CO}$ : 1927(s), 1845(s)  $cm^{-1}$ . IR ( $CH_3CN$ , 293 K)  $\nu_{CO}$ : 1927(s), 1852(s)  $cm^{-1}$ . IR (acetone, 293 K)  $\nu_{CO}$ : 1924(s), 1853(s)  $cm^{-1}$ .  $^1H$  NMR ( $CD_3COCD_3$ , 298 K):  $\delta$  7.46 (s, 4H,  $CH_{imid}$ ), 7.04 (s, 8H,  $CH_{Ar}$ ), 3.47 (d,  $^2J_{HH} = 5.5$  Hz, 16H,  $NCH_2CH_3$ ), 2.45 (s, 12H,  $CH_3$ ), 1.74 (s, 24H,  $CH_3$ ), 1.37 (t,  $^2J_{HH} = 5.5$  Hz, 24H,  $NCH_2CH_3$ ).  $^{13}C\{^1H\}$  NMR ( $CD_3COCD_3$ , 298 K):  $\delta$  222.8 (CO), 177.4 (C-Cu), 139.3, 134.9, 134.5, 129.0, 123.1 ( $C_{Ar}$  and  $CH_{imid}$ ), 52.2 ( $NCH_2CH_3$ ), 20.3, 16.4 ( $CH_3$ ), 6.9 ( $NCH_2CH_3$ ).

### Synthesis of $[NEt_4]_2[Ag(IMes)_2][Ag_3Fe_3(CO)_{12}] \cdot solv$

A solution of **12** (0.381 g, 0.384 mmol) in dmso (15 mL) was heated at 130 °C for 0.5 h and the reaction monitored by IR spectroscopy. Then, a saturated solution of  $[NEt_4]Br$  in  $H_2O$  (40 mL) was added up to complete precipitation. The resulting solid was recovered by filtration, washed with  $H_2O$  ( $3 \times 15$  mL), toluene ( $3 \times 15$  mL), and extracted with acetone (15 mL). Crystals of  $[NEt_4]_2[Ag(IMes)_2][Ag_3Fe_3(CO)_{12}] \cdot solv$  suitable for X-ray crystallography were obtained by slow diffusion of n-hexane (35 mL) on the acetone solution (yield 0.11 g, 46% based on Fe, 31% based on Ag). Even though the co-crystallized solvent molecule was not refined in the crystal structure (see below), an acetone molecule was included in the calculation of the yields and elemental analyses, in view of the fact that the crystals of  $[NEt_4]_2[Ag(IMes)_2][Ag_3Fe_3(CO)_{12}] \cdot solv$  are isomorphous with  $[NEt_4]_2[Au(IMes)_2][Au_3Fe_3(CO)_{12}] \cdot CH_3COCH_3$ .

$C_{73}H_{94}Ag_4Fe_3N_6O_{13}$  (1858.11): calcd. (%): C 36.32, H 3.54, N 4.10; found: C 36.14, H 3.71, N 3.89. IR (nujol, 293 K)  $\nu_{CO}$ : 1915(s), 1843(sh), 1808(s), 1789(w)  $cm^{-1}$ . IR (dmso, 293 K)  $\nu_{CO}$ : 1917(s), 1832(s)  $cm^{-1}$ . IR ( $CH_2Cl_2$ , 293 K)  $\nu_{CO}$ : 1921(s), 1838(s)  $cm^{-1}$ . IR ( $CH_3CN$ , 293 K)  $\nu_{CO}$ : 1920(s), 1842(s)  $cm^{-1}$ . IR (acetone, 293 K)  $\nu_{CO}$ : 1917(s), 1840(s)  $cm^{-1}$ .  $^1H$  NMR ( $CD_3COCD_3$ , 298 K):  $\delta$  7.54 (s, 4H,  $CH_{imid}$ ), 7.04 (s, 8H,  $CH_{Ar}$ ), 3.46 (q,  $^2J_{HH} = 7.0$  Hz, 16H,  $NCH_2CH_3$ ), 2.46 (s, 12H,  $CH_3$ ), 1.78 (s, 24H,  $CH_3$ ), 1.39 (t,  $^2J_{HH} = 7.2$  Hz, 12H,  $NCH_2CH_3$ ).  $^{13}C\{^1H\}$  NMR ( $CD_3COCD_3$ , 298 K): 223.6 (CO), 183.4 (C-Ag,  $^1J_{C-Ag} = 196$  and 170 Hz), 139.2, 135.2, 134.5, 129.0, 123.3 ( $C_{Ar}$  and  $CH_{imid}$ ), 52.1 ( $NCH_2CH_3$ ), 20.3, 16.4 ( $CH_3$ ), 6.8 ( $NCH_2CH_3$ ).

### Synthesis of $[NEt_4]_2[Cu(IMes)_2][Ag_3Fe_3(CO)_{12}] \cdot CH_3COCH_3$

$Na_2[Fe(CO)_4] \cdot 2thf$  (0.330 g, 0.920 mmol) and  $Ag(IMes)Cl$  (0.550 g, 1.23 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and dmso (10 mL) was added. The mixture was stirred for 2 h at room temperature up to the disappearance of the  $\nu_{CO}$  peak at  $1740cm^{-1}$  in the IR spectrum due to

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$\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot 2\text{thf}$ . Then,  $\text{Cu}(\text{IMes})\text{Cl}$  (0.370 g, 0.921 mmol) was added as a solid in small portions. The crude product was precipitated by the slow addition of a saturated solution of  $[\text{NEt}_4]\text{Br}$  in  $\text{H}_2\text{O}$  (40 mL) to the dmsO solution. The solid was recovered after filtration, washed with  $\text{H}_2\text{O}$  ( $3 \times 20$  mL), and extracted with acetone (10 mL). Crystals of  $[\text{NEt}_4]_2[\text{Cu}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot \text{CH}_3\text{COCH}_3$  suitable for X-ray crystallography were obtained by slow diffusion of n-hexane (35 mL) on the acetone solution (yield 0.29 g, 52% based on Fe, 39% based on Ag, 17% based on Cu).

Crystals of  $[\text{NEt}_2]_2[\text{Cu}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot \text{solv}$  were obtained following a similar procedure using  $\text{CH}_3\text{CN}/\text{n-hexane}/\text{di-isopropyl-ether}$  for crystallization instead of acetone/n-hexane.

$\text{C}_{73}\text{H}_{94}\text{Ag}_3\text{CuFe}_3\text{N}_6\text{O}_{13}$  (1818.24): calcd. (%): C 48.29, H 5.22, N 4.63; found: C 48.44, H 5.39, N 4.29. IR (nujol, 293 K)  $\nu_{\text{CO}}$ : 1957(w), 1930(s), 1859(m), 1845(m), 1826(s)  $\text{cm}^{-1}$ . IR ( $\text{CH}_2\text{Cl}_2$ , 293 K)  $\nu_{\text{CO}}$ : 1927(s), 1848(vs)  $\text{cm}^{-1}$ . IR ( $\text{CH}_3\text{CN}$ , 293 K)  $\nu_{\text{CO}}$ : 1927(s), 1849(vs)  $\text{cm}^{-1}$ . IR (acetone, 293 K)  $\nu_{\text{CO}}$ : 1923(s), 1849(vs)  $\text{cm}^{-1}$ .

### Synthesis of $[\text{NEt}_4]_2[\text{Au}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot \text{dmf}$

$\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot 2\text{thf}$  (0.390 g, 1.09 mmol) and  $\text{Au}(\text{IMes})\text{Cl}$  (0.790 g, 1.47 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and dmsO (10 mL) was added. The mixture was stirred for 2 h at room temperature up to the disappearance of the  $\nu_{\text{CO}}$  peak at 1740  $\text{cm}^{-1}$  in the IR spectrum due to  $\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot 2\text{thf}$ . Then, a saturated solution of  $[\text{NEt}_4]\text{Br}$  in  $\text{H}_2\text{O}$  was added up to complete precipitation of the reaction mixture. The solid was recovered by filtration and washed with  $\text{H}_2\text{O}$  ( $3 \times 20$  mL) and toluene ( $3 \times 20$  mL), and  $[\text{NEt}_4][\text{Fe}(\text{CO})_4(\text{AuIMes})]$  extracted with acetone (20 mL). Then,  $\text{Ag}(\text{IMes})\text{Cl}$  (0.550 g, 1.23 mmol) was added as a solid in small portions to the acetone solution. A solid was formed, recovered by filtration and dissolved in dmsO (10 mL). The resulting solution was heated at 80 °C for 0.5 h, and the crude reaction mixture was precipitated by addition of a saturated solution of  $[\text{NEt}_4]\text{Br}$  in  $\text{H}_2\text{O}$ . The solid was washed with  $\text{H}_2\text{O}$  ( $3 \times 20$  mL) and toluene ( $3 \times 20$  mL), and extracted with dmf (10 mL). Crystals of  $[\text{NEt}_4]_2[\text{Au}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot \text{dmf}$  suitable for X-ray crystallography were obtained by slow diffusion of isopropanol (35 mL) on the dmf solution (yield 0.32 g, 44% based on Fe, 40% based on Ag, 11% based on Au).

$\text{C}_{73}\text{H}_{94}\text{Ag}_3\text{AuFe}_3\text{N}_7\text{O}_{13}$  (1965.67): calcd. (%): C 44.64, H 4.83, N 5.00; found: C 44.35, H 5.07, N 5.21. IR (acetone, 293 K)  $\nu_{\text{CO}}$ : 1922(s), 1850(s)  $\text{cm}^{-1}$ .

### Synthesis of $[\text{Au}(\text{IMes})_2]_3[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot \text{solv}$

$\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot 2\text{thf}$  (0.390 g, 1.09 mmol) and  $\text{Au}(\text{IMes})\text{Cl}$  (0.850 g, 1.58 mmol) were charged in a Schlenk tube under a nitrogen atmosphere and dmsO (10 mL) was added. The mixture was stirred for 2 h at room

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temperature up to the disappearance of the  $\nu_{\text{CO}}$  peak at  $1740\text{ cm}^{-1}$  in the IR spectrum due to  $\text{Na}_2[\text{Fe}(\text{CO})_4]\cdot 2\text{thf}$ . Then, a saturated solution of  $[\text{NEt}_4]\text{Br}$  in  $\text{H}_2\text{O}$  was added up to complete precipitation of the reaction mixture. The solid was recovered by filtration and washed with  $\text{H}_2\text{O}$  ( $3 \times 20\text{ mL}$ ) and toluene ( $3 \times 20\text{ mL}$ ), and  $[\text{NEt}_4][\text{Fe}(\text{CO})_4(\text{AuIMes})]$  extracted with acetone ( $20\text{ mL}$ ). Then,  $\text{Ag}(\text{IMes})\text{Cl}$  ( $0.550\text{ g}$ ,  $1.23\text{ mmol}$ ) was added as a solid in small portions to the acetone solution. A solid was formed, recovered by filtration and dissolved in  $\text{dmsO}$  ( $10\text{ mL}$ ). The resulting solution was heated at  $80\text{ }^\circ\text{C}$  for  $0.5\text{ h}$ , and the crude reaction mixture was precipitated by addition of  $\text{H}_2\text{O}$ . The solid was washed with  $\text{H}_2\text{O}$  ( $3 \times 20\text{ mL}$ ) and toluene ( $3 \times 20\text{ mL}$ ), and extracted with acetone ( $15\text{ mL}$ ). Crystals of  $[\text{Au}(\text{IMes})_2]_3[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot\text{solv}$  suitable for X-ray crystallography were obtained by slow diffusion of  $n$ -hexane ( $35\text{ mL}$ ) on the acetone solution (yield  $0.61\text{ g}$ ,  $52\%$  based on  $\text{Fe}$ ,  $46\%$  based on  $\text{Ag}$ ,  $36\%$  based on  $\text{Au}$ ).

$\text{C}_{138}\text{H}_{144}\text{Ag}_3\text{Au}_3\text{Fe}_3\text{N}_{12}\text{O}_{12}$  ( $3244.70$ ): calcd. (%): C  $51.10$ , H  $4.48$ , N  $5.19$ ; found: C  $51.38$ , H  $4.16$ , N  $4.91$ . IR (nujol,  $293\text{ K}$ )  $\nu_{\text{CO}}$ :  $1950(\text{sh})$ ,  $1917(\text{s})$ ,  $1843(\text{vs})$ ,  $1793(\text{sh})\text{ cm}^{-1}$ . IR (acetone,  $293\text{ K}$ )  $\nu_{\text{CO}}$ :  $1922(\text{s})$ ,  $1848(\text{s})\text{ cm}^{-1}$ .

### X-ray Crystallographic Study.

Crystal data and collection details for  $[\text{NEt}_4][\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}]$ ,  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}_2\cdot 2\text{thf}$ ,  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}_{1.27}\{\text{Ag}(\text{IPr})\}_{0.73}\cdot 1.5\text{toluene}$ ,  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}_{0.71}\{\text{Au}(\text{IPr})\}_{1.29}\cdot 1.5\text{toluene}$ ,  $\text{Fe}(\text{CO})_4\{\text{Cu}(\text{IPr})\}_{0.64}\{\text{Au}(\text{IPr})\}_{1.36}\cdot 1.5\text{toluene}$ ,  $\text{Fe}(\text{CO})_4\{\text{Ag}(\text{IPr})\}_{0.94}\{\text{Au}(\text{IPr})\}_{1.06}\cdot 1.5\text{toluene}$ ,  $[\text{NEt}_4]_2[\text{HIMes}]_2[\text{Ag}_4\text{Fe}_4(\text{CO})_{16}]$ ,  $[\text{Ag}(\text{IPr})_2][\text{Fe}_2(\text{CO})_8\{\text{Ag}(\text{IPr})\}]\cdot\text{CH}_2\text{Cl}_2$ ,  $[\text{NEt}_4]_2[\text{HIPr}][\text{Fe}_2(\text{CO})_8\{\text{Ag}(\text{IPr})\}]_2[\text{Cl}]\cdot 2\text{CH}_2\text{Cl}_2$ ,  $[\text{NEt}_4]_4[\text{Ag}_4\text{Fe}_4(\text{CO})_{16}]\cdot 2\text{CH}_3\text{CN}$ ,  $[\text{NEt}_4]_3[\text{Ag}_5\text{Fe}_4(\text{CO})_{16}]$ ,  $[\text{NEt}_4]_4[\text{Ag}_4\text{Fe}_4(\text{CO})_{16}]$ ,  $[\text{NEt}_2]_2[\text{Cu}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot\text{CH}_3\text{COCH}_3$ ,  $[\text{NEt}_2]_2[\text{Cu}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot\text{solv}$ ,  $\text{Fe}(\text{CO})_4(\text{CH}_2\text{IMes})$ ,  $[\text{NEt}_2]_2[\text{Au}(\text{IMes})_2][\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot\text{dmf}$ ,  $[\text{Au}(\text{IMes})_2]_3[\text{Ag}_3\text{Fe}_3(\text{CO})_{12}]\cdot\text{solv}$ ,  $[\text{NEt}_4][\text{M}(\text{IMes})_2]_2[\text{Ag}_5\text{Fe}_4(\text{CO})_{16}]\cdot 4\text{thf}$  ( $\text{M} = 0.94\text{ Au}$ ,  $1.06\text{ Ag}$ ) are reported in Table S7. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a PHOTON100 detector using  $\text{Mo-K}\alpha$  radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).<sup>[41]</sup> Structures were solved by direct methods and refined by full-matrix least-squares based on all data using  $F^2$ .<sup>[42]</sup> Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated. Details were included as Supporting Information.

CCDC 1983206-1983214 and 1983295-1983303 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

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## Computational details

Geometry optimizations of the clusters were performed in gas phase using the PBEh-3c method, which is a reparametrized version of PBE0 (with 42% HF exchange) that uses a split-valence double-zeta basis set (def2-mSVP) and adds three corrections that consider dispersion, basis set superposition and other basis set incompleteness effects.<sup>[43]</sup> IR simulations were carried out at the same theoretical level, from which thermodynamic data were obtained. Single point calculations on selected optimized structures and their fragments were performed using the range-separated hybrid DFT functional  $\omega$ B97X,<sup>[44]</sup> including non-local correlation by the VV10 functional (wB97X-v).<sup>[45]</sup> The basis set used was the Ahlrichs' def2 split-valence, with polarization and diffusion functions and relativistic ECP for Ag and Au.<sup>[46]</sup> The C-PCM solvation model was added for some cases,<sup>[47]</sup> considering dmso as continuous medium. The "restricted" approach was used in all the cases. Calculations were performed with the ORCA 4.0.1.2.<sup>[48]</sup> The output, converted in .molden format, was elaborated with the software Multiwfn, version 3.5.<sup>[49]</sup> Cartesian coordinates of the DFT-optimized structures have been included in the Supporting Information..

## Supporting Information

NMR spectra, figures of the experimental molecular structures, simulated IR spectra, computed IR frequencies, crystal data and experimental details, Cartesian coordinates of the DFT-optimized structures as pdf file.

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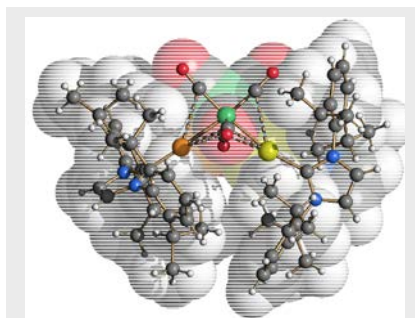


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## Table of contents

The stability of heterometallic carbonyl clusters containing NHC ligands decreases in the order  $\text{Au} > \text{Cu} > \text{Ag}$  as evidenced by experimental and computational studies.



### Organometallic clusters

*Beatrice Berti, Marco Bortoluzzi, Cristiana Cesari, Cristina Femoni, Maria Carmela Iapalucci, Rita Mazzoni, and Stefano Zacchini\**

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**A comparative experimental and computational study of heterometallic Fe-M (M = Cu, Ag, Au) carbonyl clusters containing N-heterocyclic carbene ligands**

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