

Synthesis and Characterization of Heterobimetallic Carbonyl Clusters with Direct Au-Fe and Au…Au Interactions supported by *N*-Heterocyclic Carbene and Phosphine Ligands

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Abstract: The reaction of Collman's reagent Na₂[Fe(CO)₄]·2thf with one equivalent of Au(NHC)Cl (NHC = IMes, IPr; IMes = $C_3N_2H_2(C_6H_2Me_3)_2$; IPr = $C_3N_2H_2(C_6H_3^{1}Pr_2)_2$) in dmso resulted in the $[Fe(CO)_4(AuNHC)]^-$ (NHC = IMes, 1; IPr, 2) mono-anions. 1-2 further reacted with Au(NHC)Cl or Au(PPh₃)Cl affording the neutral complexes $Fe(CO)_4(AuNHC)_2$ (NHC = IMes, 3; IPr, 4), $Fe(CO)_4(AuIMes)(AuIPr)$ (5) and $Fe(CO)_4(AuNHC)(AuPPh_3)$ (NHC = IMes, 6; IPr, 7). 1-7 have been spectroscopically characterized by IR, 1 H, 13 C{ 1 H} and 31 P{ 1 H} NMR techniques. Moreover, the molecular structures of 1, 2, 4, 6 and 7 have been determined through single crystal X-ray diffraction [NMe₄][Fe(CO)₄(AuIMes)], [NEt₄][Fe(CO)₄(AuIMes)], as their [NEt₄][Fe(CO)₄(AuIPr)], Fe(CO)₄(AuIPr)₂·1.5toluene, Fe(CO)₄(AuIPr)(AuPPh₃), Fe(CO)₄(AuIMes)(AuPPh₃)·0.5CH₂Cl₂ salts and solvates. The nature of the bonds in 1 and 2 was elucidated on the basis of atoms-in molecules (AIM) analyses on the DFT-optimized structures and compared with the corresponding compounds 3 and 4. 1-7 contained strong Fe-CO, Fe-Au, Au-P and Au-NHC bonds as well as weak Au…Au interactions. The different stability and reactivity of IMes-derivatives vs. IPr-ones was rationalized on the basis of steric effects.

Keywords: Heterometallic clusters / Carbonyl / Gold / Iron / N-Heterocyclic carbene

Introduction

Several heterobimetallic Au-Fe carbonyl clusters have been reported and these may be grouped into five main categories:^[1]

1) Iron carbonyl clusters surface-decorated by [AuL]⁺ fragments. This represents the largest class of heterobimetallic Au-Fe carbonyl clusters, that comprises species such as Fe(CO)₄(AuPPh₃)₂,^[2] $Fe(CO)_4(AuNHC)_2$ (NHC = IMes, IPr, IBu; IMes = $C_3N_2H_2(C_6H_2Me_3)_2$; IPr = $C_3N_2H_2(C_6H_3^{i}Pr_2)_2$; $IBu = C_3N_2H_2(CMe_3)_2),^{[3]} [Fe_2(CO)_8(AuPPh_3)]^{-,[4]} [Fe_3(CO)_{11}(AuPPh_3)]^{-,[5]} [Fe_3E(CO)_9(AuPPh_3)]^{-,[6]} [Fe_3E(CO)_9(AuPPh_3)]^{-,$ (E = O, S, Te), [6,7] $Fe_3E(CO)_9(AuPPh_3)_2$ (E = O, S), [8,9] $[HFe_4(CO)_{12}(AuPPh_3)_{3-n}]^{n-}$ (n = 0, 1), [10] $Fe_4C(CO)_{12}(AuPEt_3)_2$,^[11] $Fe_5C(CO)_{14}(AuPEt_3)_2$,^[12] $[Fe_6C(CO)_{16}(AuPPh_3)]^-$ [13] and $[Fe_6C(CO)_{15}(AuPPh_3)_2]^{2-.[14]}$ These may be viewed as the result of the addition of $[AuL]^+$ (L = phosphine, N-heterocyclic carbene) fragments to the surface of an iron carbonyl cluster anion, i.e., $[Fe(CO)_4]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$, $[Fe_2(CO)_8]^{2-}$, $[Fe_3E(CO)_9]^{2-}$ (E= O, S, Te), $[HFe_4(CO)_{12}]^{3-}$, $[Fe_4C(CO)_{12}]^{2-}$, $[Fe_5C(CO)_{14}]^{2-}$, $[Fe_6C(CO)_{16}]^{2-}$ and $[Fe_6C(CO)_{15}]^{4-}$. These reactions have been widely employed in order to selectively increase of a few units the nuclearity of the clusters.^[1,15-17] Moreover, based on the isolobal analogy between $[AuL]^+$ and H^+ , the former fragments have been used in order to have information on the protonation sites of anionic clusters.^[18-20] When two or more [AuL]⁺ fragments are present on the surface of the same cluster, because of aurophilicity, often gold atoms prefer to gather together in order to form weak d¹⁰-d¹⁰ Au(I)…Au(I) interactions.^[21-24]

2) Iron carbonyl clusters with naked Au connecting atoms. At the moment, the only species belonging to this category is $[Fe_4Au(CO)_{16}]^-$, which may be viewed as composed of a central Au(III) ion bonded to two $[Fe_2(CO)_8]^{2-}$ iron cluster anions.^[25]

3) 1-D (chain) gold clusters stabilised by iron carbonyls, such as $[Au_3Fe_2(CO)_8(IMes)_2]^{-,[3]}$ and $[AuFe{Si(OMe)_3}(CO)_3(\mu$ -dppm)].^[26] These clusters contain linear 1-D $[Au_n]^{n+}$ chains protected by $[Fe(CO)_4]^{2-}$ carbonyl anions and miscellaneous ligands. They allow investigations about single, direct bonds between metals.^[26]

4) 2-D gold clusters stabilised by iron carbonyls. Representative examples are: $[Au_3Fe(CO)_4(dppm)_2]^+$,^[27] $[Au_3Fe_2(CO)_8(dppm)]^-$,^[28] $[Au_3Fe_3(CO)_{12}]^{3-}$,^[29] $[Au_4Fe_4(CO)_{16}]^{4-}$,^[30] $[Au_5Fe_4(CO)_{16}]^{3-}$,^[31] $[Au_5Fe_2(CO)_8(dppm)_2]^+$ ^[28] and $Au_8Fe_4(CO)_{16}(dppe)_4$.^[32] These clusters are composed of planar 2-D $[Au_n]^{n+}$ cores decorated on the surface by $[Fe(CO)_4]^{2-}$ carbonyl anions and, in some cases, by additional phosphine or NHC ligands.

10.1002/ejic.201900537

5) 3-D gold clusters embedded in iron carbonyls. This category includes Au-Fe-CO nanoclusters such as $[Au_{21}Fe_{10}(CO)_{40}]^{5-}$, $[Au_{22}Fe_{12}(CO)_{48}]^{6-}$, $[Au_{28}Fe_{14}(CO)_{52}]^{8-}$ and $[Au_{34}Fe_{14}(CO)_{50}]^{8-}$.^[31] These are metalloid nanoclusters where a Au_n core is stabilised by Fe(CO)₄ and Fe(CO)₃ groups present on their surface. Linear Fe-Au-Fe staple motives, reminiscent of the very well known S-Au-S staple motives found in Au-thiolate nanoclusters, are present on the surface of these organometallic Au-Fe carbonyl clusters.

Within category (1), most of the species reported to date contained phosphines as ancillary ligands. More recently, we reported the Fe(CO)₄(AuNHC)₂ clusters, which displayed Nheterocyclic carbenes bonded to gold.^[3] Interestingly, heating a solution of Fe(CO)₄(AuIMes)₂ in dmf at 100 °C resulted in [Au₃Fe₂(CO)₈(IMes)₂]⁻, whereas by performing its thermal decomposition in dmso at 130 °C, [Au₃Fe₃(CO)₁₂]³⁻ was obtained.^[29] This suggested that lower nuclearity Au-Fe carbonyl clusters containing NHC ligands might be suitable precursors for the preparation of larger clusters. In order to widen the scope of this study, we have started a systematic investigation on heterobimetallic Au-Fe carbonyl clusters containing NHC as well as phosphine ligands. Herein, we report the synthesis of the mono-anionic complexes $[Fe(CO)_4(AuNHC)]^-$ (NHC = IMes, 1; IPr, 2) well as the heteroleptic neutral clusters Fe(CO)₄(AuIMes)(AuIPr) (5)and as $Fe(CO)_4(AuNHC)(AuPPh_3)$ (NHC = IMes, 6; IPr, 7). All the new species have been spectroscopically characterized by IR and multinuclear NMR techniques, and their structures determined by single crystal X-ray diffraction. The nature of the bonds in 1 and 2 was elucidated on the basis of atoms-in molecules (AIM) analyses on the DFT-optimized structures and compared with the corresponding compounds 3 and 4.

Results and Discussion

Synthesis and characterization of [Fe(CO)₄(AuNHC)]⁻ (NHC = IMes, 1; IPr, 2)

The reaction of Collman's reagent Na₂[Fe(CO)₄]·2thf with one equivalent of Au(NHC)Cl (NHC = IMes, IPr) in dmso resulted in the [Fe(CO)₄(AuNHC)]⁻ (NHC = IMes, **1**; IPr, **2**) mono-anions in accord to Scheme 1. It is noteworthy that, as previously reported,^[3] by performing the same reactions in thf, a mixture of the neutral clusters $Fe(CO)_4(AuNHC)_2$ (NHC = IMes, **3**; IPr, **4**) and the starting Collman's reagent were formed. As expected, the reaction of Na₂[Fe(CO)₄]·2thf with two equivalents of Au(NHC)Cl in dmso, as well as thf, resulted in **3**, **4**. Thus, it seemed that the polarity of the solvent played a fundamental role in the reaction, when a 1:1 stoichiometry is employed, whereas it was less relevant for a 1:2 stoichiometry. This might be related to the fact that in polar solvents all ions are well solvated and, thus, [Fe(CO)₄(AuNHC)]⁻ was formed at first with a

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1 : 1 stoichiometric ratio. Then, after the addition of the second equivalent of Au(NHC)Cl, $Fe(CO)_4(AuNHC)_2$ was obtained. Conversely, in less polar solvents, the formation of neutral products seemed to be favoured over anionc ones. This result was supported by the computed Gibbs energy variations associated to the reaction $[Fe(CO)_4(AuNHC)]^- + [AuNHC]^+ \rightarrow$ $Fe(CO_4)(AuNHC)_2$, obtained using continuous models for the two solvents. The $\Delta G_{dmso}-\Delta G_{thf}$ differences were 12.1 and 14.4 kcal mol⁻¹ for NHC = IMes and NHC = IPr, respectively, in agreement with the less favourable formation of the neutral trinuclear products in the presence of solvents possessing quite high dielectric constants.



Scheme 1. Syntheses of 1-7

1 and **2** were characterized by means of IR, ¹H and ¹³C{¹H} NMR spectroscopy (Figures S.1-S.4 in Supporting Information) and their structures determined by X-ray crystallography (Figure 1 and Table 1). Compounds **1** and **2** displayed v_{CO} bands in acetone solution at ca. 1924(s) and 1820(vs) cm⁻¹, considerably shifted towards lower wavenumbers compared to **3** and **4** (v_{CO} 1974(s) and 1884(vs) cm⁻¹) in view of their anionic charges. The Au-coordinated carbene resonated in the ¹³C{¹H} NMR spectra at δ_C 196.3 and 198.3 ppm for **1** and **2**, respectively. For comparison, the neutral complexes **3** and **4** displayed carbene resonances at very similar chemical shifts, that is

194.5 and 194.3 ppm. A singlet was present at all temperatures in the CO region of the ${}^{13}C{}^{1}H$ NMR spectra of **1** and **2**, suggesting a fluxional behaviour for the carbonyl ligands. This rapid exchange process made the equatorial and apical CO ligands equivalent also at low temperature.



Figure 1. Molecular structures of (a) $[Fe(CO)_4(AuIMes)]^-$ (1) and (b) $[Fe(CO)_4(AuIPr)]^-$ (2). Au-C(O) contacts [2.630(4)-2.900(4) Å for 1; 2.688(4)-2.805(3) Å for 2] are represented as fragmented lines. Hydrogen atoms have been omitted for clarity (green Fe; yellow Au; blue N; red O; grey C)

Table 1. Main bond distances (Å) and angles (°) of $[Fe(CO)_4(AuIMes)]^-$ (1) and [Fe(CO)_4(AuIMes)]^- (1) and [Fe(CO)_4(AuIPr)] [_]
(2)	

	[Fe(CO) ₄ (AuIMes)] ^{- a}	[Fe(CO) ₄ (AuIMes)] ^{-b}	[Fe(CO) ₄ (AuIPr)] ⁻
Fe-Au	2.5168(5)	2.5244(6)	2.5015(4)
Au-C _{carbene}	2.031(4)	2.029(4)	2.019(2)
Fe-C(O)	1.749(4)-1.780(4)	1.755(5)-1.780(4)	1.757(3)-1.778(3)
Au…C(O)	2.630(4)-2.900(4)	2.565(5)-2.931(4)	2.688(4)-2.805(3)
Fe-Au-C _{carbene}	173.66(10)	174.96(11)	175.21(7)

^a As found in [NMe₄][Fe(CO)₄Au(IMes)].

^b As found in [NEt₄][Fe(CO)₄Au(IMes)].

The monoanions **1** and **2** adopted a trigonal bipyramidal structure, with the AuNHC fragment in an axial position. Similar structures were found in the cobalt complexes $Co(CO)_4(AuPPh_3)^{[33]}$ and $Co(CO)_4(CuIPr).^{[34]}$

1 and 2 contained strong Au-Fe, Fe-C(O) and Au-C_{carbene} interactions as well as some weak Au····C(O) contacts (see Table 1). Regarding the latter contacts, their detection in the solid state structures could merely be the consequence of the preferred arrangement of the CO ligands about the Fe centre, which brings the CO ligands in closer proximity to the Au centre, rather than any

attraction (even van der Waals) between the carbonyls and Au. Indeed, their theoretical study (see below) did not support bonding interactions between Au and CO (which could at best be a kind of back-bonding from the d^{10} shell). The nature of such Au····C(O) contacts was already discussed in the literature,^[35] concluding that relatively short non-bonding contacts between Au(I) and C(carbonyl) atoms must be analyzed with caution.

The Au-Fe distances [2.50-2.52 Å] found in these monoanionic complexes were very similar to those previously reported for the neutral complexes $Fe(CO)_4(AuNHC)_2$ [2.51-2.53 Å] (Table 2).^[3] Conversely, a slight elongation of the Au-Fe contact [2.56-2.57 Å] was observed in the cationic complexes $[Fe(CO)_5(AuNHC)]^+$ and $[Fe(CO)_5(AuPR_3)]^+$ that contained a $Fe(CO)_5$ rather than a $Fe(CO)_4$ fragment.^[36]

Synthesis and characterization of Fe(CO)₄(AuIMes)(AuIPr) (5) and Fe(CO)₄(AuNHC)(AuPPh₃) (NHC = IMes, 6; IPr, 7)

The mono-anions 1-2 further reacted with Au(NHC)Cl or Au(PPh₃)Cl affording the neutral complexes $Fe(CO)_4(AuNHC)_2$ (NHC = IMes, 3; IPr, 4), $Fe(CO)_4(AuIMes)(AuIPr)$ (5) and $Fe(CO)_4(AuNHC)(AuPPh_3)$ (NHC = IMes, 6; IPr, 7). Compounds 3-4 were identified by comparison of their IR and NMR spectroscopic data with those previously reported in the literature (Figures S.5-S.8 in Supporting Information).^[3] Moreover, the nature of 4 was further corroborated by single crystal X-ray diffractometry on its new solvate $Fe(CO)_4(AuIPr)_2 \cdot 1.5$ toluene. The molecular structure was comparable to that previously reported, and the crystallographic data were included as supplementary material for sake of completeness (Figure S.17 in the Supporting Information).

The mixed complex **5** was spectroscopically characterized (Figures S.9 and S.10 in the Supporting Information), and it displayed an IR spectrum in the v_{CO} region very similar to that of **3** and **4**. An unique resonance was observed in the ${}^{13}C{}^{1}H$ NMR spectrum at δ_{C} 217.8 ppm for the CO ligands, whereas two distinct resonances were observed in the Au-C_{carbene} region (δ_{C} 195.1 and 193.7 ppm) in view of the presence of both AuIMes and AuIPr fragments.

Compounds 6 and 7, containing both an AuNHC and AuPPh₃ fragments, displayed very similar spectroscopic features (see experimental and Figures S.11-S.16 in Supporting Information). Moreover, their molecular structures were determined by single crystal X-ray diffraction (Figures 2 and 3, and Table 2). They are composed of a $C_{2\nu}$ -Fe(CO)₄ sawhorse/seesaw unit coordinated to one AuNHC and one AuPPh₃ fragment in relative *cis* position. The structures of 6 and 7 were similar to those previously reported for the homoleptic complexes 3, 4 and Fe(CO)₄(AuPPh₃)₂ (8).^[2,3] The Au····Au contacts [3.0471(4) Å for 6, 3.0479(2) Å for 7] were indicative of weak aurophilic

interactions, which were intermediate between those found in 8 [2.8750(3)-3.0698(2) Å, depending of the polymorph] and 3 [3.2015(8) Å]. Conversely, the Au···Au distance of 4 [3.984(1) and 4.082(1) Å, depending of the polymorph] was completely non-bonding. The fact that the Au···Au distance was strongly affected by the steric properties of the Au-bonded ligands as well as packing effects pointed out that such aurophilic interactions were rather deformable. In particular, the Au···Au distance increased with the increasing bulkiness of the ligands when passing from PPh₃ to IMes and eventually IPr. All complexes 3, 4 and 6-8 displayed also some sub-van der Waals Au···C(O) contacts.



Figure 2. Molecular structure of Fe(CO)₄(AuIMes)(AuPPh₃) (**6**). Two different views as well as its core are reported. Au-C(O) contacts [2.621(8)-2.885(7) Å] are represented as fragmented lines. Hydrogen atoms have been omitted for clarity (green Fe; yellow Au; purple P; blue N; red O; grey C)



Figure 3. Molecular structure of Fe(CO)₄(AuIPr)(AuPPh₃) (7). Two different views as well as its core are reported. Au-C(O) contacts [2.573(3)-2.955(3) Å] are represented as fragmented lines. Hydrogen atoms have been omitted for clarity (green Fe; yellow Au; purple P; blue N; red O; grey C)

8 ^d

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8 ^c

3 ^a

							1
Au(1)-Fe(1)	2.5158(15)	2.512(2)	2.5203(9)	2.5471(9)	2.5371(4)	2.5344(6)	2.5329(4)
Au(2)-Fe(1)	2.5312(15)	2.524(2)	2.5326(9)	2.5089(9)	2.5107(4)	2.5555(6)	2.5181(4)
Au(1)-Au(2)	3.2015(8)	4.082(1)	3.984(1)	3.0471(4)	3.0479(2)	2.8750(3)	3.0698(2)
Au(1)-X(1)	2.008(10)	2.012(11)	2.018(6)	2.020(6)	2.011(3)	2.2696(10)	2.2756(7)
Au(2)-X(2)	2.020(10)	1.949(14)	2.023(6)	2.2661(16)	2.2621(8)	2.2707(10)	2.2646(7)
Fe(1)-CO	1.756(13)-	1.737(15)-	1.727(8)-	1.768(8)-	1.772(3)-	1.787(4)-	1.772(3)-
	1.783(13)	1.781(15)	1.769(8)	1.777(8)	1.786(3)	1.800(4)	1.790(3)
Au…C(O)	2.609(12)-	2.572(14)-	2.629(7)-	2.621(8)-	2.573(3)-	2.604(6)-	2.638(3)-
	2.764(13)	2.873(18)	2.827(8)	2.885(7)	2.955(3)	3.069(5)	3.050(3)
Fe(1)-Au(1)-	177.8(3)	168.3(3)	172.75(18)	175.77(17)	174.65(8)	172.02(3)	177.55(2)
X(1)							
Fe(1)-Au(2)-	165.9(3)	168.4(5)	168.16(17)	170.15(5)	171.12(2)	173.45(3)	173.71(2)
X(2)							
Au(1)-Fe(1)-	78.74(4)	107.90(9)	104.08(3)	74.12(3)	74.284(12)	68.781(14)	74.855(12)
Au(2)							
Fe(1)-Au(1)-	50.84(4)	36.15(5)	38.07(2)	52.37(2)	52.462(10)	55.956(13)	52.354(10)
Au(2)							
Fe(1)-Au(2)-	50.42(3)	35.95(5)	37.85(2)	53.51(2)	53.254(10)	55.263(13)	52.791(9)
Au(1)							
	Fe(1)		Fe(1)			Fe(1)	
						\square	
Au(1	Au(2) Au(1	I)/\	Au(2)	Au(1)	A	u(2)
	C(1) $C(2)$		Č(1)	P (2)	P(1)		P (2)
Ń, N	Ń,				• (•)		(-)

Table 2. Main bond distances (Å) and angles (deg) of Fe(CO)₄(AuIMes)₂ (**3**), Fe(CO)₄(AuIPr)₂ (**4**), Fe(CO)₄(AuIMes)(AuPPh₃) (**6**), Fe(CO)₄(AuIPr)(AuPPh₃) (**7**) and Fe(CO)₄(AuPPh₃)₂ (**8**).

4 ^b

6

7

4 ^a

^a See ref. [3]. ^b As found in Fe(CO)₄(AuIPr)₂·1.5toluene. ^c As found in Fe(CO)₄(AuPPh₃)₂ ($P\overline{\mathbf{1}}$). ^d As found in Fe(CO)₄(AuPPh₃)₂ ($P\overline{\mathbf{1}}$).

Despite the structural analogies between 6 and 7, their chemical behaviour was rather different. 7 was very stable and could be easily obtained in a very pure form, as indicated by the presence of a single resonance at δ_P 40.8 ppm in the ${}^{31}P{}^{1}H$ NMR spectrum (Figure S.16 in Supporting Information). Conversely, 6 was less stable and its synthesis was not so straightforward. Thus, it was often obtained in mixtures with minor amounts of 8 and a, yet, unknown species 9, as evidenced by the presence of three distinct resonances in the ${}^{31}P{}^{1}H$ NMR spectrum (Figure S.13 in Supporting Information) at δ_P 40.8 ppm (6), 40.1 ppm (8) and 38.5 ppm (9).

More in details, the addition of increasing amounts of Au(PPh₃)Cl to an acetone solution of 1 resulted in the partial substitution of the AuIMes fragment with AuPPh₃ (Scheme 2). Thus, after the addition of one equivalent of Au(PPh₃)Cl a mixture of $[Fe(CO)_4(AuPPh_3)]^-$ (10) (major) and 1 (minor) was present in solution. Further addition of Au(PPh₃)Cl resulted in the formation of 8 as the major product. Compound 8 was spectroscopically detected and, moreover, its molecular structure was corroborated by X-ray crystallography on two new polymorphs (Figure S.18 and S.19 in Supporting Information), that is Fe(CO)₄(AuPPh₃)₂ ($P\overline{1}$) and Fe(CO)₄(AuPPh₃)₂ ($P2_1/n$). The new crystal data have been included as Supporting Information, for sake of completeness.

Concerning the ability of the AuPPh₃ fragment to replace AuIMes in the coordination sphere of Fe(CO)₄, this suggested that the AuPPh₃ fragment was more electrophilic than AuIMes. To demonstrate this point, 3 was reacted with increasing amounts of Au(PPh₃)Cl. As a result, 6 and, formed of then. 8 sequence. During this study, few crystals were in а [Au(IMes)₂][Fe₂(CO)₈(AuPPh₃)]·CH₂Cl₂ were obtained and characterized by single crystal X-ray crystallography (Figure S.20 in Supporting Information). It is likely that some $[Fe_2(CO)_8]^{2-}$ was formed by oxidation of $[Fe(CO)_4]^{2-}$ at some stage of the reaction that, eventually, reacted with Au(PPh₃)Cl. The structure of the $[Fe_2(CO)_8(AuPPh_3)]^-$ mono-anion was previously reported as [NEt₄]⁺ salt,⁴ displaying almost identical geometry and bonding parameters. It must be remarked that 8 did not react with Au(IMes)Cl even when used in large excess.



Scheme 2. Reactivity of 1 and 3 with Au(PPh₃)Cl.

Therefore, the best way in order to obtain **6** was to mix **1** and Au(PPh₃)Cl in a 1:1 ratio in acetone, remove the solvent in vacuum and let the reaction to continue in CH_2Cl_2 . This allowed to obtain **6** in a pure crystalline form, after slow diffusion of n-pentane. Conversely, the reaction of **2**

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with Au(PPh₃)Cl directly afforded 7, without any evidence of the formation of **10**. Only after the addition of a slight excess of Au(PPh₃)Cl, 7 was eventually transformed into **8** (Scheme 3).



Scheme 3. Reactivity of 2 with Au(PPh₃)Cl.

From a mechanistic point of view, the substitution reaction, which transformed 1 into 10 (Scheme 2), was likely to proceed via an associative mechanism involving 6 as an intermediate. Since 6 was not very stable in polar solvents such as acetone, it rapidly dissociated a $[Au(IMes)]^+$ fragment, affording 10 as the major product. Therefore, in order to favour the formation of 6, a less polar solvent such as CH_2Cl_2 must be employed in order to hamper dissociation. Conversely, because of the greater stability of 7 compared to 6, addition was observed rather than substitution, regardless of the solvent employed.

To address the point of whether in some cases the whole AuL (L = NHC, PPh₃) fragment migrates or only the ligand L, **3** and **4** were reacted with increasing amounts of PPh₃ and the reaction monitored *via* IR and ³¹P NMR spectroscopies. No reaction was observed, suggesting that substitution of the whole Au(NHC) fragment by AuPPh₃ occurred.

The different behaviour of the IMes-derivatives compared to the IPr-derivatives was also evidenced by investigating the reactions of **6** and **7** with Au(Et₂S)Cl. Thus, **6** readily reacted with Au(Et₂S)Cl affording Au-Fe-CO nanoclusters of the type $[Au_{22}Fe_{12}(CO)_{48}]^{6-}$, $[Au_{21}Fe_{10}(CO)_{40}]^{5-}$, $[Au_{28}Fe_{14}(CO)_{52}]^{8-}$ and $[Au_{34}Fe_{14}(CO)_{50}]^{10-}$, as evidenced by comparison of their IR spectra with those reported in the literature.^[31] Conversely, **7** did not react with Au(Et₂S)Cl. Overall, it seemed that the IPr-derivatives were always far more stable than the analogous IMes-derivatives.

IMes and IPr ligands possessed very similar Tolman Electronic Parameter (TEP) values,^[37] as also evidenced by the almost identical v_{CO} frequencies displayed by their complexes. Thus, the different behaviour of IMes and IPr-containing species should be attributed mainly to steric effects. This prompted a computational investigation, whose results are described in the next section.

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Computational studies

AIM analyses were performed of the DFT-optimized ground-state structures of the compounds 1, 2, 3 and 4. (3,-1) bond critical points (b.c.p) were localized for the metal-carbon interactions and the Fe-Au bonds. Selected data are collected in Tables 3-6. The comparison of the data indicated negligible changes on the properties at b.c.p. on changing the solvent from dmso to thf. More important, quantities related to the strength of the bonds such as the electron density p and the potential energy density V remained almost constant on changing the carbene ligand from IMes to IPr. The negative values of energy densities E and the positive values for the Laplacian of electron density $\nabla^2 \rho$ agreed with Bianchi's definitions of dative M-M bonds.^[38,39]

Table 3. Selected electron densities ρ (a.u.) at b.c.p. for compounds 1-4; dmso as continuous medium, data for thf in parenthesis.

[Fe(CO)4(AuNHC)] ⁻				Fe(CO) ₄ (AuNHC) ₂				
	ρ_{C-Au}	ρ_{Au-Fe}	ρ_{Fe-C}	ρ_{Fe-C}	ρ_{C-Au}	ρ_{Au-Fe}	ρ_{Fe-C}	$\rho_{Fe\text{-}C}$
			trans-Au	cis-Au, aver.			trans-Au, aver.	cis-Au, aver.
IMes	0.127	$0.605 \cdot 10^{-1}$	0.162	0.161	0.129	$0.573 \cdot 10^{-1}$	0.157	0.155
	(0.126)	$(0.617 \cdot 10^{-1})$	(0.162)	(0.162)	(0.128)	$(0.577 \cdot 10^{-1})$	(0.157)	(0.155)
IPr	0.128	0.606.10-1	0.162	0.161	0.128	0.578.10-1	0.157	0.157
	(0.128)	$(0.613 \cdot 10^{-1})$	(0.162)	(0.161)	(0.127)	$(0.580 \cdot 10^{-1})$	(0.156)	(0.156)

Table 4. Selected potential energy densities V (a.u.) at b.c.p. for compounds 1-4; dmso as continuous medium, data for thf in parenthesis.

[Fe(CO)4(AuNHC)] ⁻				Fe(CO) ₄ (AuNHC) ₂				
	V _{C-Au}	V _{Au-Fe}	V _{Fe-C}	V _{Fe-C}	V _{C-Au}	V _{Au-Fe}	V _{Fe-C}	$V_{\text{Fe-C}}$
			trans-Au	cis-Au, aver.			trans-Au, aver.	cis-Au, aver.
IMes	-0.179	-0.532·10 ⁻¹	-0.301	-0.289	-0.180	-0.497·10 ⁻¹	-0.284	-0.270
	(-0.183)	(-0.540·10 ⁻¹)	(-0.301)	(-0.289)	(-0.181)	(-0.502·10 ⁻¹)	(-0.284)	(-0.269)
IPr	-0.181	-0.533·10 ⁻¹	-0.300	-0.289	-0.179	-0.502·10 ⁻¹	-0.283	-0.272
	(-0.182)	(-0.542.10-1)	(-0.299)	(-0.289)	(-0.179)	(-0.505·10 ⁻¹)	(-0.283)	(-0.271)

Table 5. Selected energy densities E (a.u.) at b.c.p. for compounds 1-4; dmso as continuous medium, data for thf in parenthesis.

[Fe(CO) ₄ (AuNHC)] ⁻				Fe(CO) ₄ (AuNHC) ₂				
	E _{C-Au}	E_{Au-Fe}	E _{Fe-C}	E _{Fe-C}	E _{C-Au}	E _{Au-Fe}	E _{Fe-C}	E _{Fe-C}
			trans-Au	cis-Au, aver.			trans-Au	cis-Au, aver.
IMes	-0.569·10 ⁻¹	-0.180·10 ⁻¹	-0.786·10 ⁻¹	-0.780·10 ⁻¹	-0.581·10 ⁻¹	-0.169·10 ⁻¹	-0.735·10 ⁻¹	-0.727·10 ⁻¹
	$(-0.554 \cdot 10^{-1})$	(-0.179·10 ⁻¹)	$(-0.783 \cdot 10^{-1})$	$(-0.782 \cdot 10^{-1})$	$(-0.580 \cdot 10^{-1})$	(-0.170·10 ⁻¹)	$(-0.734 \cdot 10^{-1})$	$(-0.721 \cdot 10^{-1})$
IPr	-0.572·10 ⁻¹	-0.181·10 ⁻¹	-0.783·10 ⁻¹	-0.780·10 ⁻¹	-0.575·10 ⁻¹	-0.172·10 ⁻¹	-0.732·10 ⁻¹	-0.738·10 ⁻¹
	(-0.572·10 ⁻¹)	(-0.183·10 ⁻¹)	(-0.781.10-1)	(-0.780.10-1)	(-0.571.10-1)	(-0.172·10 ⁻¹)	(-0.730.10-1)	(-0.733·10 ⁻¹)

Table 6. Selected Laplacian of electron densities $\nabla^2 \rho$ (a.u.) at b.c.p. for compounds 1-4; dmso as continuous medium, data for thf in parenthesis.

[Fe(CO)4(AuNHC)] ⁻					Fe(CO)4(AuNHC)2	
Γ ² ρ _{C-Au}	² ρ _{Au-Fe}	P ² ρ _{Fe-C}	V ² ρ _{Fe-C}	$\nabla^2 \rho_{C-Au}$	^{γ2} ρ _{Au-Fe}	V ² ρ _{Fe-C}	$\nabla^2 \rho_{Fe-C}$
		trans-Au	cis-Au, aver.			trans-Au, aver.	cis-Au, aver.

IMes	0.259	$0.688 \cdot 10^{-1}$	0.575	0.533	0.254	$0.637 \cdot 10^{-1}$	0.549	0.499
	(0.290)	$(0.730 \cdot 10^{-1})$	(0.578)	(0.531)	(0.259)	$(0.650 \cdot 10^{-1})$	(0.548)	(0.498)
IPr	0.264	$0.685 \cdot 10^{-1}$	0.573	0.532	0.256	$0.632 \cdot 10^{-1}$	0.548	0.498
	(0.270)	$(0.702 \cdot 10^{-1})$	(0.573)	(0.532)	(0.258)	$(0.629 \cdot 10^{-1})$	(0.547)	(0.499)

The most noticeable difference, that was detected from the AIM analysis of the bonds, was the lowering of ρ and V at Fe-Au b.c.p. moving from anionic dinuclear species to trinuclear neutral compounds. The coordination of a second [AuNHC]⁺ fragment caused, also, the expected lowering of electron densities at Fe-C b.c.p. The Au-NHC interactions appeared instead roughly comparable among all the complexes here considered. The lowering of Fe-Au and Fe-C bond strengths in Fe(CO₄)₄(AuNHC)₂ complexes was confirmed by the computed Wiberg bond orders, collected in Table 7. The electronic structure of the gold centres was comparable among [Fe(CO₄)₄(AuNHC)]⁻ and Fe(CO₄)₄(AuNHC)₂ compounds, as suggested by the Hirshfeld charges, ranging between 0.032 and 0.096 a.u. The coordination of a second [Au(NHC)]⁺ ligand slightly reduced the partial negative charge on iron, the average Hirshfeld charge being -0.304 a.u. in [Fe(CO₄)₄(AuNHC)]⁻ and -0.246 a.u. in Fe(CO₄)₄(AuNHC)₂.

Table 7. Selected Wiberg bond orders for compounds 1-4; dmso as continuous medium, data for thf in parenthesis.

[Fe(CO)4(AuNHC)] ⁻				Fe(CO)4(AuNHC)2				
	Au-C	Au-Fe	Fe-C	Fe-C	Au-C	Au-Fe	Fe-C	Fe-C
			trans-Au	cis-Au, aver.			trans-Au, aver.	cis-Au, aver.
IMes	0.921	0.487	1.405	1.416	0.903	0.444	1.318	1.297
	(0.954)	(0.512)	(1.387)	(1.406)	(0.905)	(0.449)	(1.305)	(1.296)
IPr	0.916	0.481	1.403	1.415	0.889	0.439	1.306	1.306
	(0.923)	(0.489)	(1.398)	(1.414)	(0.890)	(0.444)	(1.301)	(1.302)

No b.c.p was found between the gold centres in **3** and **4**, in agreement with the lack of any localized interaction. Moreover, no (3,+1) ring critical point (r.c.p) was found in the [Au₂Fe] triangles. Finally, no b.c.p. was found also for the Au···CO contacts, suggesting a dispersion-driven nature or no interaction at all. The electron density map of compound **3**, reported as an example in the Supporting Information, showed relatively poor electron density between the gold centres and between Au and CO. The ρ values at the middle of the Au---Au distances in the Fe(CO)₄(AuNHC)₂ complexes here considered were around $0.25 \cdot 10^{-1}$ a.u. for NHC = IMes and $0.19 \cdot 10^{-1}$ a.u. for the bulkier IPr carbene derivative. For what concerns Au···CO, the electron density minima between gold and carbon are comprised between $0.35 \cdot 10^{-1}$ and $0.39 \cdot 10^{-1}$ a.u. in **1** and **2**, with no meaningful difference between the two compounds. The highest density values for the Au···CO contacts in **3** and **4** fall in the same range.

The population analyses on the ground-state structures did not highlight any appreciable electronic difference able to explain the different reactivity of the compounds on changing the substituents on the carbene ligands, in agreement with the similar TEP values reported for IMes and IPr.^[35] Steric effects were therefore tentatively invoked. The space occupied by the NHC ligands in the first coordination sphere of gold can be described by the buried volume, $%V_{Bur}$. The calculated $%V_{Bur}$ values for IMes and IPr in the DFT-optimized structures of **1** and **2** were respectively 36.0% and 42.9%, and the different reactivity of the IPr derivatives was probably related to the higher $%V_{Bur}$. Figure 4 showed plots of the electron density surfaces for the [Fe(CO)₄(AuNHC)]⁻ complexes. The LUMO of the complexes were localized on the carbene donor atom and on gold, and in the case of NHC = IPr the substituents seemed to better protect the unoccupied orbital from incoming nucleophiles. We might therefore conclude that the different reactivity experimentally observed could be ascribed to the different reactivity of the Au-NHC groups on changing the bulkiness of the carbene substituents.



Figure 4. Electron density surfaces (light blue, isovalue = 0.1 a.u.) and LUMOs (yellow tones, isovalue = 0.03 a.u.) for compounds 1 and 2. The high isovalue for electron density surfaces was chosen to make the plot clear.

Conclusions

The synthesis, spectroscopic and structural characterization as well as theoretical investigation of new heterobimetallic carbonyl clusters supported by NHC and phosphine ligands were reported. Despite the fact that N-heterocyclic carbenes were widely employed as ligands in coordination and organometallic chemistry,^[40-43] molecular clusters containing NHC ligands were more scarce.^[3,29,44-49] The compounds herein reported demonstrated the ability of obtaining heteroleptic clusters containing CO, NHC and PR₃ ligands by the stepwise addition of [AuNHC]⁺ and [AuPPh₃]⁺ fragments to anionic carbonyl clusters. This might be a general strategy in order to obtain molecular clusters supported by NHC ligands.

1-7 contained strong Fe-CO, Fe-Au, Au-P and Au-NHC bonds as well as weak Au····Au interactions. AIM analyses and DFT studies pointed out that the Au····Au interactions in such heterobimetallic clusters were not covalent bonds but mainly dispersion-driven.^[21] In addition, the different behaviour of IMes and IPr derivatives was essentially due to steric effects, since no appreciable electronic difference was evidenced by population analyses performed at DFT level. This was also in keeping with the very similar TEP values reported for IMes and IPr.^[37] In particular, it seemed that the bulkier IPr ligand provided a better steric protection to the LUMO localized on the AuNHC fragment than IMes. Overall, molecular carbonyl clusters might be considered as valuable platforms for the study of M-M and M-ligand interaction as well as their related reactivities.^[1,15,20-22]

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 Na₂[Fe(CO)₄]·2thf,^[50] Au(NHC)Cl (NHC = IMes, IPr) ^[51] and Fe(CO)₄(AuNHC)₂ ^[3] 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 CaF₂ cells. Structure drawings have been performed with SCHAKAL99.^[52]

Synthesis of [NEt₄][Fe(CO)₄(AuIMes)] ([NEt₄][1])

 $Na_2[Fe(CO)_4]$ ·2thf (0.180 g, 0.500 mmol) and Au(IMes)Cl (0.270 g, 0.500 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 [NEt₄]Br in H₂O (40 mL) was added up to complete precipitation. The resulting yellow solid was recovered by filtration, washed with H₂O (3 × 15 mL), toluene (3 × 15 mL), and extracted with acetone (15 mL). Crystals of [NEt₄][Fe(CO)₄(AuIMes)] suitable for X-ray crystallography were obtained by slow diffusion of n-hexane (35 mL) on the acetone solution (yield 0.232 g, 58 % based on Fe, 58 % based on Au).

[NMe₄][Fe(CO)₄(AuIMes)] was obtained following a similar procedure and employing [NMe₄]Cl instead of [NEt₄]Br.

 $C_{33}H_{44}AuFeN_{3}O_{4}$ (799.53): calcd. (%): C 49.55, H 5.55, N 5.26; found: C 50.04, H 5.34, N 5.07. IR (nujol, 293 K) v_{CO} : 1975(w), 1927(s), 1830(vs), 1790(vs) cm⁻¹. IR (dmso, 293 K) v_{CO} : 1923(s),

1814(vs) cm⁻¹. IR (CH₃CN, 293 K) v_{CO}: 1927(s), 1821(vs) cm⁻¹. IR (acetone, 293 K) v_{CO}: 1924(s), 1820(vs) cm⁻¹. ¹H NMR (CD₃CN, 298 K): δ 7.20 (s, 2H, CH_{imid}), 7.05 (s, 4H, CH_{Ar}), 3.19 (q, ²J_{HH} = 7.2 Hz, 8H, NCH₂CH₃), 2.35 (s, 6H, CH₃), 2.18 (s, 12H, CH₃), 1.22 (t, ²J_{HH} = 7.2 Hz, 12H, NCH₂CH₃). ¹³C{¹H} NMR (CD₃CN, 298 K): δ 226.5 (CO), 196.3 (C-Au), 138.7, 135.9, 135.1, 128.9, 121.4 (C_{Ar} and CH_{imid}), 52.2 (NCH₂CH₃), 20.3, 17.2 (CH₃), 6.8 (NCH₂CH₃).

Synthesis of [NEt₄][Fe(CO)₄(AuIPr)] ([NEt₄][2])

 $Na_2[Fe(CO)_4]$ ·2thf (0.210 g, 0.580 mmol) and Au(IPr)Cl (0.360 g, 0.580 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 [NEt₄]Br in H₂O (40 mL) was added up to complete precipitation. The resulting yellow solid was recovered by filtration, washed with H₂O (3 × 15 mL), toluene (3 × 15 mL), and extracted with acetone (15 mL). Crystals of [NEt₄][Fe(CO)₄(AuIPr)] suitable for X-ray crystallography were obtained by slow diffusion of n-hexane (35 mL) on the acetone solution (yield 0.287 g, 56 % based on Fe, 56 % based on Au).

C₃₉H₅₆AuFeN₃O₄ (883.68): calcd. (%): C 52.98, H 6.39, N 4.76; found: C 53.12, H 6.21, N 4.54. IR (nujol, 293 K) v_{CO} : 1972(w), 1924(s), 1810(vs) cm⁻¹. IR (dmso, 293 K) v_{CO} : 1923(s), 1815(vs) cm⁻¹. IR (CH₃CN, 293 K) v_{CO} : 1926(s), 1820(vs) cm⁻¹. IR (acetone, 293 K) v_{CO} : 1924(s), 1821(vs) cm⁻¹. IR (CD₃CN, 298 K): δ 7.49 (t, ²J_{HH} = 7.4 Hz, 2H, CH_{Ar}), 7.34 (d, ²J_{HH} = 7.4 Hz, 4H, CH_{Ar}), 7.32 (s, 2H, CH_{imid}), 3.19 (q, ²J_{HH} = 7.2 Hz, 8H, NCH₂CH₃), 2.75 (sept, ²J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 1.39 (d, ²J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.22 (t, ²J_{HH} = 7.2 Hz, 12H, NCH₂CH₃), 1.21 (d, ²J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (CD₃CN, 298 K): δ 226.4 (CO), 198.3 (C-Au), 145.9, 135.5, 129.6, 123.7, 122.4 (C_{Ar} and CH_{imid}), 52.1 (NCH₂CH₃), 28.5 (CH(CH₃)₂), 23.4, 23.0 (CH(CH₃)₂), 6.8 (NCH₂CH₃).

Synthesis of Fe(CO)₄(AuIMes)₂ (3)

Au(IMes)Cl (0.176 g, 0.328 mmol) was added as a solid in small portions to a solution of $[NEt_4][Fe(CO)_4(AuIMes)]$ (0.260 g, 0.325 mmol) in acetone (15 mL) and the reaction monitored by IR spectroscopy. The resulting mixture was stirred for 2 h at room temperature and, then, the solvent removed under reduced pressure. The residue was washed with H₂O (3 × 20 mL), isopropanol (3 × 20 mL), and extracted with acetone (15 mL). A microcrystalline powder of Fe(CO)₄(AuIMes)₂ was obtained after removal of the solvent under reduced pressure (yield 0.213 g, 56 % based on Fe, 56 % based on Au).

Alternatively, 3 may be obtained from the reaction of Na₂[Fe(CO)₄]·2thf with two equivalents

Au(IMes)Cl in thf, as described previously.^[3]

C₄₆H₄₈Au₂FeN₄O₄ (1170.67): calcd. (%): C 47.17, H 4.13, N 4.79, Fe 4.78, Au 33.66; found: C 46.89, H 4.34, N 4.98, Fe 5.02, Au 33.35. IR (nujol, 293 K) v(CO): 1980(vs), 1898(sh), 1875(s) cm⁻¹. IR (CH₂Cl₂, 293 K) v(CO): 1979(m), 1894(s) cm⁻¹. IR (acetone, 293 K) v(CO): 1977(m), 1895(s) cm⁻¹. IR (DMF, 293 K) v(CO): 1975(m), 1890(s) cm⁻¹. ¹H NMR (CD₂Cl₂, 298 K): δ 7.04 (s, 4H, CH_{imid}), 6.96 (s, 8H, CH_{Ar}), 2.35 (s, 12H, CH₃), 2.07 (s, 24H, CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 298 K): δ 7.04 (s, 4H, CH_{imid}), 6.96 (cond), 194.5 (C-Au), 138.7, 135.2, 134.7, 128.9 (C_{Ar}), 121.0 (CH_{imid}), 20.8, 17.7 (CH₃).

Synthesis of Fe(CO)₄(AuIPr)₂ (4)

Au(IPr)Cl (0.204 g, 0.328 mmol) was added as a solid in small portions to a solution of $[NEt_4][Fe(CO)_4(AuIPr)]$ (0.287 g, 0.325 mmol) in acetone (15 mL) and the reaction monitored by IR spectroscopy. The resulting mixture was stirred for 2 h at room temperature and, then, the solvent removed under reduced pressure. The residue was washed with H₂O (3 × 20 mL), isopropanol (3 × 20 mL), and extracted with toluene (15 mL). Crystals of Fe(CO)₄(AuIPr)₂·1.5toluene, suitable for X-ray crystallography were obtained by slow diffusion of n-pentane (35 mL) on the toluene solution (yield 0.265 g, 61 % based on Fe, 61 % based on Au). Alternatively, **4** may be obtained from the reaction of Na₂[Fe(CO)₄]·2thf with two equivalents Au(IPr)Cl in thf, as described previously.^[3]

C₅₈H₇₂Au₂FeN₄O₄ (1338.99): calcd. (%): C 52.03, H 5.42, N 4.18, Fe 4.17, Au 29.42; found: C 51.89, H 5.64, N 4.03, Fe 4.38, Au 29.19. IR (nujol, 293 K) v(CO): 1974(vs), 1901(sh), 1890(s) cm⁻¹. IR (CH₂Cl₂, 293 K) v(CO): 1974(m), 1884(s) cm⁻¹. ¹H NMR (CD₂Cl₂, 298 K): δ 7.51, 7.33 (br, 12H, CH_{Ar}), 7.16 (s, 4H, CH_{imid}), 2.69 (br, 8H, CH(CH₃)₂), 1.30 (br, 48H, CH(CH₃)₂). ¹³C{¹H} NMR (CD₂Cl₂, 298 K): δ 216.9 (CO), 194.3 (C-Au), 145.7, 134.8, 129.9, 123.8 (C_{Ar}), 122.3 (CH_{imid}), 28.7 (CH(CH₃)₂), 24.0 (CH(CH₃)₂).

Synthesis of Fe(CO)₄(AuIPr)(AuIMes) (5)

Au(IMes)Cl (0.176 g, 0.328 mmol) was added as a solid in small portions to a solution of $[NEt_4][Fe(CO)_4(AuIPr)]$ (0.287 g, 0.325 mmol) in acetone (15 mL) and the reaction monitored by IR spectroscopy. The resulting mixture was stirred for 2 h at room temperature and, then, the solvent removed under reduced pressure. The residue was washed with H₂O (3 × 20 mL), isopropanol (3 × 20 mL), and extracted with acetone (15 mL). A microcrystalline powder of Fe(CO)₄(AuIPr)(AuIMes) was obtained after removal of the solvent under reduced pressure (yield 0.208 g, 51 % based on Fe, 51 % based on Au).

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C₅₂H₆₀Au₂FeN₄O₄ (1254.33): calcd. (%): C 49.75, H 4.82, N 4.47; found: C 49.97, H 5.02, N 4.11. IR (acetone, 293 K) v_{CO}: 1971(s), 1885(vs), 1864(sh) cm⁻¹. ¹H NMR (CD₃COCD₃, 298 K): δ 7.53, 7.38 (s, 4H, CH_{imid}), 7.41 (t, ²J_{HH} = 7.4 Hz, 2H, CH_{Ar}), 7.23 (d, ²J_{HH} = 7.4 Hz, 4H, CH_{Ar}), 6.96 (s, 4H, CH_{Ar}), 2.70 (m, 4H, CH(CH₃)₂), 2.31 (s, 6H, CH₃), 2.09 (s, 12H, CH₃), 1.25 (d, ²J_{HH} = 6.5 Hz, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (CD₃COCD₃, 298 K): δ 217.8 (CO), 195.1, 193.7 (C-Au), 145.5, 138.2, 135.5, 135.0, 134.6, 129.7, 128.9, 123.6, 122.7, 121.6 (CH_{Ar}+CH_{imid}), 28.5 (CH(CH₃)₂), 23.6, 23.4 (CH(CH₃)₂), 20.4, 17.4 (CH₃).

Synthesis of Fe(CO)₄(AuIMes)(AuPPh₃)·0.5CH₂Cl₂ (6·0.5CH₂Cl₂)

Au(PPh₃)Cl (0.161 g, 0.326 mmol) was added as a solid in small portions to a solution of $[NEt_4][Fe(CO)_4(AuIMes)]$ (0.260 g, 0.325 mmol) in acetone (15 mL) and the reaction monitored by IR spectroscopy. The resulting mixture was stirred for 5 min at room temperature and, then, the solvent removed under reduced pressure. The residue was dissolved with CH₂Cl₂ (15 mL), filtered and crystals of Fe(CO)₄(AuIMes)(AuPPh₃)·0.5CH₂Cl₂ suitable for X-ray crystallography were obtained by slow diffusion of n-pentane (35 mL) on the CH₂Cl₂ solution (yield 0.171 g, 45 % based on Fe, 45 % based on Au).

 $Fe(CO)_4(AuIMes)(AuPPh_3)$ is less stable than $Fe(CO)_4(AuIPr)(AuPPh_3)$, and rapidly decomposes in acetone solution even at room temperature.

C_{43.5}H₄₀Au₂ClFeN₂O₄P (1170.98): calcd. (%): C 44.61, H 3.45, N 2.39; found: C 44.87, H 3.12, N 2.16. IR (nujol, 293 K) v_{CO} : 1982(s), 1906(sh), 1896(s), 1873(ms) cm⁻¹. IR (acetone, 293 K) v_{CO} : 1988(ms), 1912(ms), 1886(s) cm⁻¹. IR (CH₂Cl₂, 293 K) v_{CO} : 1989(ms), 1893(s) cm⁻¹. ¹H NMR (CD₃COCD₃, 298 K): δ 7.77-7.35 (m, 21H, CH_{Ar}+CH_{imid}+Ph), 2.24 (s, 6H, CH₃), 2.04 (s, 12H, CH₃). ¹³C{¹H} NMR (CD₃COCD₃, 298 K): δ 218.4 (CO), 193.3 (C-Au), 138.6-121.8 (CH_{Ar}+CH_{imid}+Ph), 20.3, 17.0 (CH₃). ¹³C{¹H} NMR (CD₃COCD₃, 298 K): δ 218.4 (CO), 121.8 (CH_{Ar}+CH_{imid}+Ph), 20.3, 17.0 (CH₃). ³¹P{¹H} NMR (CD₃COCD₃, 298 K): δ 40.8.

Synthesis of Fe(CO)₄(AuIPr)(AuPPh₃) (7)

Au(PPh₃)Cl (0.161 g, 0.326 mmol) was added as a solid in small portions to a solution of $[NEt_4][Fe(CO)_4(AuIPr)]$ (0.287 g, 0.325 mmol) in acetone (15 mL) and the reaction monitored by IR spectroscopy. The resulting mixture was stirred for 2 h at room temperature and, then, the solvent removed under reduced pressure. The residue was washed with H₂O (3 × 20 mL), isopropanol (3 × 20 mL), and extracted with CH₂Cl₂ (15 mL). Crystals of Fe(CO)₄(AuIPr)(AuPPh₃) suitable for X-ray crystallography were obtained by slow diffusion of

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n-pentane (35 mL) on the CH₂Cl₂ solution (yield 0.226 g, 57 % based on Fe, 57 % based on Au).

C₄₉H₅₁Au₂FeN₂O₄P (1212.67): calcd. (%): C 48.51, H 4.24, N 2.32; found: C 48.32, H 3.97, N 2.51. IR (nujol, 293 K) v_{CO} : 1984(s), 1911(s), 1892(s), 1867(s) cm⁻¹. IR (acetone, 293 K) v_{CO} : 1989(s), 1914(s), 1882(ms) cm⁻¹. IR (CH₂Cl₂, 293 K) v_{CO} : 1990(s), 1913(s), 1878(ms) cm⁻¹. ¹H NMR (CD₃COCD₃, 298 K): δ 7.74-7.14 (m, 23H, CH_{Ar}+CH_{imid}+Ph), 2.70 (m, 4H, CH(CH₃)₂), 1.28 (d, ${}^{2}J_{HH} = 6.8$ Hz, 12H, CH(CH₃)₂), 1.15 (d, ${}^{2}J_{HH} = 6.8$ Hz, 12H, CH(CH₃)₂). ${}^{13}C{}^{1}H{}$ NMR (CD₃COCD₃, 298 K): δ 217.9 (CO), 194.7 (C-Au), 145.5, 134.2, 134.1, 131.1, 129.9, 129.1, 129.0, 123.7, 123.0 (CH_{Ar}+CH_{imid}+Ph), 28.9 (CH(CH₃)₂), 23.6, 23.5 (CH(CH₃)₂). ${}^{31}P{}^{1}H$ NMR (CD₃COCD₃, 298 K): δ 40.8.

X-ray Crystallographic Study.

Crystal data and collection details for [NMe₄][Fe(CO)₄(AuIMes)], [NEt₄][Fe(CO)₄(AuIMes)], Fe(CO)₄(AuIMes)(AuPPh₃)·0.5CH₂Cl₂, [NEt₄][Fe(CO)₄(AuIPr)], Fe(CO)₄(AuIPr)(AuPPh₃), $Fe(CO)_4(AuPPh_3)_2$ $(P\overline{1}),$ $Fe(CO)_4(AuPPh_3)_2$ $(P2_1/n),$ Fe(CO)₄(AuIPr)₂·1.5toluene, [Au(IMes)₂][Fe₂(CO)₈(AuPPh₃)]·CH₂Cl₂ are reported in Table S.1. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a PHOTON100 detector using Mo-Ka radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).^[53] Structures were solved by direct methods and refined by fullmatrix least-squares based on all data using $F^{2,[54]}$ 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.

 $[NEt_4]^+$ The cation in the structures of [NEt₄][Fe(CO)₄(AuIMes)] and [NEt₄][Fe(CO)₄(AuIPr)] is disordered and, thus, it has been split into two positions and refined using one occupancy factor per disordered group. The atoms of the disordered cations have been restrained to have similar U parameters (SIMU line in SHELXL, s.u. 0.01).

The CH₂Cl₂ molecule in the structure of Fe(CO)₄(AuIMes)(AuPPh₃)·0.5CH₂Cl₂ is disordered over two symmetry related (by a 2-fold axis) positions. The disordered CH₂Cl₂ molecule has been refined isotropically and its atoms have been restrained to have similar U parameters (SIMU line in SHELXL, s.u. 0.01). Restraints to bond distances were applied as follow (s.u. 0.02): 1.75 Å for C–Cl in CH_2Cl_2 .

One toluene molecule in the structure of $Fe(CO)_4(AuIPr)_2 \cdot 1.5$ toluene is disordered over two symmetry related (by an inversion centre) positions. The other toluene molecule (located on a general position) is also disordered and, thus, it has been split into two positions and refined using one occupancy factor per disordered group. All disordered atoms have been refined isotropically. All C, N and O atoms have been restrained to have similar *U* parameters (SIMU line in SHELXL, s.u. 0.01) and to isotropic behaviour (ISOR line in SHELXL, s.u. 0.01). The aromatic C-atoms of the toluene molecules have been constrained to fit regular hexagons (AFIX 66 line in SHELXL).

The CH₂Cl₂ molecule in the structure of $[Au(IMes)_2][Fe_2(CO)_8(AuPPh_3)] \cdot CH_2Cl_2$ is disordered and, thus, it has been split into two positions and refined isotropically using one occupancy factor per disordered group. The atoms of the disordered CH₂Cl₂ molecule have been restrained to have similar *U* parameters (SIMU line in SHELXL, s.u. 0.01). Restraints to bond distances were applied as follow (s.u. 0.02): 1.75 Å for C–Cl in CH₂Cl₂.

CCDC 1911648-1911656 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Computational details

Geometry optimizations of the complexes were carried out using the range-separated hybrid DFT functional $\omega B97X$.^[55] The basis set used was the Ahlrichs' def2 split-valence, with polarization functions and relativistic ECP for Au.^[56] The C-PCM implicit solvation model was added to ωB97X calculations. considering dmso and thf as solvents.^[57] The "restricted" approach was used in all the cases. The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections (T = 298.15 K) were obtained.^[58] Calculations were performed with the Gaussian 09 software.^[59] Single point calculations were then carried out on the optimized geometries with the ORCA 4.0.1.2 software ^[60] with the same method, but including diffusion functions and non-local correlation by the VV10 functional.^[61] The output, converted in .molden format, was used for AIM, Wiberg and Hirshfeld analyses, performed with the software Multiwfn, version 3.5.^[62] Cartesian coordinates of the DFToptimized structures are collected in a separated .xyz file. The buried volumes (%V_{Bur}) of IMes and IPr in compounds 1 and 2 were calculated from the Cartesian coordinates of 1 and 2 with the web application SambVca,^[63] using the calculated Au-C distances (Au-IMes, 2.066 Å; Au-IPr, 2.064 Å). The radius of the sphere built around the metal atom was 3.5 Å. Bondi radii scaled by 1.17 were used for the atoms of the NHC ligands and hydrogen atoms were included in the calculations.

Supporting Information

NMR spectra of 1-7, molecular structures of 4, 8 and 9, electron density map of compound 3, crystal data and experimental details, Cartesian coordinates of the DFT-optimized structures as pdf file.

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NHC ligands protect and tune the properties of heterobimetallic Fe-Au carbonyl clusters.



Organometallic clusters

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Synthesis and Characterization of Heterobimetallic Carbonyl Clusters with Direct Au-Fe and Au···Au Interactions supported by *N*-Heterocyclic Carbene and Phosphine Ligands