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Chelation enforcing a dual gold configuration in the catalytic hydroxyphenoxylation of alkynes

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Abstract

The functionalization of alkynes by Au (N-heterocyclic carbene, NHC) complexes via the hydrophenoxylation reaction is a paradigm for the discussion between mono and dual metal catalysis. With the aim of mimicking the framework containing two gold units, achieved with molecular boxes, two NHC ligands were joined here with a chelated chain and this motif was examined in the hydrophenoxylation/hydroalkoxylation reactions through DFT calculations. This synthetic motif transforms the standard hydrophenoxylation intermolecular reaction from an inter- into an intra-molecular nucleophilic attack, when forming the C–O bond. Various chain lengths were tested with regard to the coordination of the alkyne to the cationic NHC-gold(I) center.

KEYWORDS

hydrophenoxylation, DFT, energy decomposition analysis, gold, C-O coupling

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1 | INTRODUCTION

In the search for an efficient synthetic route to obtain vinyl ethers via the hydrophenoxylation of alkynes, progress has been made in achieving more sustainable and greener synthetic methods,^[1,2] moving from the use of mercury (II) salts, with their associated undesirable toxicity,^[3] to the use of catalysts of Group 11, centering on gold, but later extended to silver and copper.^[4] In an attempt to better understand how alkyne and alcohol interact, Toste et al. conducted a pioneering study on a cycloisomerization mediated by digold catalysts.^[5] The following year, Gagosz highlighted the dual character of this type of catalyst with alkynes and described both the nucleophilic C-H activation and the electrophilic C-C activation.^[6] Thus, both gold centers work in a synergistic manner to facilitate the formation of C-O bonds necessary for this reaction.^[7] To broaden the spectrum of substrates containing a C-C triple bond, allenyne and dyines molecules were considered.^[8,9] In 2013, the chemistry was extended from phosphinegold(I) to (NHC)-Aubased (NHC = N-heterocyclic carbene) catalysts by Nolan et al.^[10–13] The unique NHC systems have assisted in better understanding the dual role of the metal in the reaction mechanism of the hydrophenoxylation of alkynes by gold catalysts.^[14] Through density functional theory (DFT) calculations, Houk et al. in parallel to Cavallo et al.,^[15] have found that not only a gold(I) catalyst is needed to activate the alkyne but also the alcohol should be activated, especially when dealing with phenols.^[16-19]

When two metal moieties are either joined or placed in close proximity, the corresponding dimer catalysts where both metals are linked by a hydroxide or phenoxide ligand led to impressive catalytic results.^[20,21] Note that these gem-diaurated species were synthesized some years ago^[22] but were more recently coined as off-cycle catalytic species,^[23] far from the current definition of the cationic gold fragment as a Lewis acid^[24] and the gold hydroxide as a Brønsted base, with capacity to deprotonate the alcohols to the corresponding alkoxides.^[13,25,26] Furthermore, the gem-diaurated species show dynamic character since they are available for reactivity once cleaved and interact with alkyne and alcohol/ phenol, in an initial reagent activation step.^[27] On the other hand, mass spectrometric (MS) experiments by Roithová et al. have shown that these catalysts were not simple catalyst reservoirs.^[28,29] These MS experiments have shed light on the role of these diaurated species in organometallic catalysis,^[30–32] particularly in the synthesis of (Z)-vinyl ethers.^[33,34] The unclear results obtained with low catalyst loading, and the still ambiguous explanations of kinetic experiments,^[15,35,36] have reinforced the controversy over the dual nature of the catalysis of the hydroalkoxylation/hydrophenoxylation of alkynes and especially in the case of non-phenol substrates.^[37–39] The latter are often omitted in DFT calculations, in favor of the potential role of the counteranion.^[40–46] Nonetheless, Reek et al. confirmed that the hydrophenoxylation of alkynes improved when encapsulating the *gem*diaurated gold catalysts.^[47,48] Another dogma that has fallen recently is that two gold atoms were indispensable.^[49] Indeed, the heterobimetallic system Au/C^[50–52] has been found to be optimal in the hydrophenoxylation of alkynes as well, by Cazin et al.^[15,53]

In the present study, the effects of linking the two metal fragments by joining them through two-tethered NHC ligands and evolving the system from an intermolecular to intramolecular process are examined via DFT.

2 | RESULTS AND DISCUSSION

To study the effect of the intramolecular reactivity, we considered a system with two identical gold catalysts bearing IPr (IPr = N,N'-bis[2,6-(di-isopropyl)phenyl] imidazol-2-ylidene) NHC ligands. The IPr groups are modified by linking the two IPr fragments with two methylenic units at the aromatic sites so as not to change the overall electronic properties of the NHC significantly. The number of methylenic units (CH₂) between IPr ligands is increased from 2 to 11.

Initially, the chelated complexes are homobimetallic linked by a bridging hydroxide or phenoxide ligand and linked through the bidentate bis NHC ligand. Because we know that those dual gold catalysts can easily exchange the hydroxide by the phenoxide bridge, here we start our calculations directly with the phenoxide bridge (**A** in Figure 1) to facilitate the next C–O bond formation (Step **B** - **C**). First, the interaction with diphenylacetylene leads to the binding of one of the gold centers to the phenoxide ligand, whereas the other is attached to the entering alkyne (Step **A** - **B** in Figure 1). Then, the cationic gold center undergoes the hydrophenoxylation reaction



FIGURE 1 C-O bond formation from the interaction of the diphenylacetylene with the phenoxide chelated complex linked by repeating methylenic units (n = 2-11)

interacting with the phenoxide moiety.^[54] It is convenient to remark that with an odd number of methylenic units the structure is nearly symmetric.

From the results in Table 1, it is clear that going from **A** to **B** is easier when the methylenic chain is relatively long (around 7 to 9 units), but then it becomes again more difficult when increasing this number to 11 methylene units. This is reasonable as when the chain that links both NHC ligands elongates the Au–O–Au angle tends to approach linearity, and it becomes a bit more constrained. Note that this chain can bend when increasing the number of methylene units. Then, there is no benefit to increase the chelate chain to more than 11 methylene units, as this would decrease the possibility of bimetallic synergy sought out here.

The dimer can then be cleaved by either PhOH or the alkyne substrate (here, Ph-CC-Ph). For the A-B transition state, lower energy barriers are found in the case of systems with odd number of methylenic units, and the thermodynamics improve, that is, the reaction energy is more negative and thus the reaction more exoergonic, by increasing the length of the chelating chain to 7 or 9 because there is more space to allow both metal moieties to separate after the attack of $Ph-C \equiv C-Ph$. Considering alkyne as the dimer cleaving agent, the thermodynamics is not favored for the formation of intermediate **B**. When the number of methylene units is 9, the thermodynamics is favored because there is sufficient space available between the two metal moieties. Even though the results for the chelated systems show that the barrier for the C-O bond formation is not lower with respect to the two separated gold species, the resulting catalytic performance should be improved because the two gold moieties are pre-organized to carry out such a step; thus, the constructive collision between two gold centers in an intermolecular sense would not be necessary, and this could result in operations at lower catalysts loadings. The transition state for the C-O bond formation, for instance, with seven CH₂ units, clearly confirms that the structure is not overly strained, and the linking chain between both NHC ligands is completely linear

(see Figure 2). The Au…Au distance in the transition state for the C–O bond formation differs with the length of the alkyl chain that links both NHC ligands, ranging from 4.637 Å (n = 2) to 6.666 Å (n = 9) to be compared with 6.336 Å for the non-chelated system. Actually, the distance is quite stable from n = 5, ranging closely from 6.088 to 6.666 Å. Nevertheless, the flexibility of the alkyl chain does not facilitate a clear trend,^[55,56] between the Au…Au distances and the energy barrier for the C–O bond formation.

On the other hand, even though Cazin et al. have reported that for the hydrophenoxylation reaction the combination of [Cu (OPh)(IPr)] and [Au(η^2 -alkyne) (IPr)]⁺ led to an improvement,^[4,53] here we keep gold on both metal moieties for the sake of simplicity and comparison with the non-linked system.^[57,58] For the system with seven methylene units, we also tested here this Au-Cu combination. The energy barrier for the C–O bond formation has identical energy, that is, 17.3 kcal/mol, whereas if copper is substituted by silver, the Gibbs energy barrier increases to 19.5 kcal/mol.

The C–O bond formation cannot be studied directly by an energy decomposition analysis (EDA) because it is not feasible to examine a situation where two separated fragments are operating since both metal moieties are linked.^[59,60] However, it is possible to study how the entering alkyne coordinates to contribute to the opening of the digold species with the phenoxide linking both gold centers (Step **A** - **B** in Figure 1). Table 2 contains the contributions that are part of the interaction energy associated with the formation of the Au–C bond between the phenoxide bridge among both gold atoms and diphenylacetylene, taking into account that the two IPr ligands are bridged by an alkyl chain,^[61] of 2–11 methylene units.

Amsterdam Density Functional (ADF) is used here at the ZORA-BP86(D3BJ)/TZ2P level of theory to show the affinity for the chelated gold complex to attach diphenylacetylene as to activate the complex for the nucleophilic attack made by the alcohol, which is already coordinated by one of the gold atoms. Comparing the

TABLE 1Reaction pathway thatleads to the C-O bond formation fromthe phenoxide bridge dimer with theinsertion of diphenylacetylene, with thelinked or not NHC ligands (relativeGibbs energies in kilocalories per mole)

		Number of methylenic units bridging both NHC ligands									
Species	Free	2	3	4	5	6	7	8	9	10	11
Α	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
A-B	4.7	10.1	14.4	10.6	14.8	14.7	11.0	12.7	9.3	15.9	15.1
В	9.9	10.0	18.7	9.1	16.9	9.7	12.4	15.6	4.5	11.3	7.5
В-С	10.5	17.2	21.1	14.0	17.5	17.1	17.3	19.9	18.4	19.1	16.3
С	-3.1	7.1	6.3	1.2	4.7	0.7	3.9	4.6	0.0	3.6	6.9

Abbreviation: NHC, N-heterocyclic carbene.

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FIGURE 2 Transition state responsible of the C–O bond formation, with seven methylene units linking the two NHC moieties (distance in Å)

TABLE 2	EDA of the Au-C bond between	diphenylacetylene and	l the digold chelated	complex (in kilocal	lories per mole)
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Species	State	ΔE_{Pauli}	ΔE_{elst}	ΔE_{oi}	ΔE_{disp}	ΔE_{int}	$\%\Delta E_{elst}$	$\%\Delta E_{oi}$
Non-chelated	А-В	49.5	-31.1	-31.3	-23.5	-36.5	36	36
	В	320.0	-166.4	-213.6	-27.5	-87.6	41	52
2 units	А-В	149.4	-105.9	-96.8	-32.3	-85.6	45	41
	В	447.8	-256.7	-279.1	-41.4	-129.3	44	48
3 units	А-В	152.8	-114.8	-82.7	-30.2	-74.9	50	36
	В	468.6	-262.1	-295.4	-41.9	-130.7	44	49
4 units	А-В	163.6	-111.7	-96.6	-38.5	-83.1	45	39
	В	462.3	-258.0	-291.3	-42.8	-129.9	44	49
5 units	А-В	156.6	-108.2	-94.6	-37.4	-83.7	45	39
	В	453.6	-256.0	-285.7	-42.8	-131.0	44	49
6 units	А-В	155.6	-106.9	-92.9	-39.5	-83.6	45	39
	В	460.4	-253.7	-294.0	-44.9	-132.1	43	50
7 units	А-В	163.1	-111.3	-99.9	-39.7	-87.7	44	40
	В	444.3	-251.7	-281.0	-43.3	-131.7	44	49
8 units	А-В	162.5	-105.6	-100.9	-42.3	-86.3	42	41
	В	434.0	-244.4	-275.8	-44.0	-130.2	43	49
9 units	А-В	162.3	-103.1	-103.7	-41.1	-85.6	42	42
	В	418.2	-236.1	-264.6	-46.9	-129.5	43	48
10 units	А-В	160.0	-103.4	-100.0	-43.4	-86.7	42	41
	В	444.4	-252.4	-279.8	-47.3	-135.1	44	48
11 units	А-В	162.1	-105.0	-101.6	-42.0	-86.5	42	41
	В	418.8	-236.4	-264.4	-47.9	-129.9	43	48

Abbreviation: EDA, energy decomposition analysis.

resulting energies, we conclude that the most favored system among all the chelated linkers is the one having seven methylene units. However, from 7 to 11 methylene units the formation of the bond is also highly favored, which suggests that the flexibility of the chelated dimer is important for the reaction. The system without the chelating chain, that is, with the two separated gold moieties, was used for comparison.

To analyze the transformation of **B** to **C**, we had to cut the chain of methylene units to generate two different fragments. In those systems with an even number of units, we have cut the C–C bond just in the middle, so each fragment has the same number of methylene units. Then, we converted each CH_2 connected to the cut bond into a H atom, and the two new C–H bonds have been fixed to 1.11 Å without reoptimizing the geometries. In those systems with an odd number of methylene units, the fragment with Au connected to OPh has one more methylene unit than the other (geometries enclosed in the supporting information). Following this procedure, the EDA can only be performed for systems with more than three methylene units.

Equivalent to Table 2, from the ΔE_{int} in Table 3 corresponding to the transition state of formation of the C–O bond (see Scheme 1 for the EDA fragments considered and their conformation), it is corroborated that the system with seven methylene units presents the most favored interaction. By decomposing ΔE_{int} , we observe more favorable ΔE_{elstat} and ΔE_{oi} , despite also more unfavorable repulsive ΔE_{Pauli} term, although it cannot compensate the former two attractive terms. Finally, despite the EDA data obtained in gas phase, the trends in toluene would be the same, but with smaller absolute value ΔE_{int}

TABLE 3 EDA of the C–O bond between the two units of the digold chelated complex, once cleaved the chelating chain (in kilocalories per mole)

Species	State	ΔE_{Pauli}	ΔE_{elst}	ΔE_{oi}	ΔE_{disp}	ΔE_{int}	ΔE_{elst}	$\%\Delta E_{oi}$
Non-chelated	В	9.3	-12.3	-5.9	-7.8	-16.7	47	23
	В-С	50.5	-31.9	-32.2	-23.0	-36.5	37	37
	С	318.1	-165.3	-213.1	-26.3	-86.6	41	53
4 units	В	13.2	-13.1	-7.3	-12.0	-19.2	40	23
	В-С	53.2	-32.1	-31.4	-23.1	-33.3	37	36
	С	325.4	-166.8	-216.9	-26.6	-84.9	41	53
5 units	В	7.9	-9.4	-4.7	-12.1	-18.3	36	18
	В-С	46.4	-29.7	-29.1	-22.5	-34.8	37	36
	С	314.5	-164.8	-211.9	-27.7	-90.0	41	52
6 units	В	9.4	-11.0	-5.3	-12.3	-19.3	38	19
	В-С	44.7	-29.3	-27.0	-21.0	-32.7	38	35
	С	314.5	-163.1	-211.3	-25.7	-85.6	41	53
7 units	В	10.1	-12.5	-5.6	-11.7	-19.6	42	19
	В-С	54.7	-34.9	-34.9	-22.2	-37.2	38	38
	С	314.1	-164.5	-211.2	-26.6	-88.2	41	53
8 units	В	5.7	-10.3	-3.8	-6.3	-14.5	51	19
	В-С	45.7	-30.3	-27.1	-21.1	-32.8	39	34
	С	297.6	-153.5	204.9	-25.7	-86.6	40	53
9 units	В	9.1	-12.7	-5.8	-8.3	-17.7	47	22
	В-С	51.1	-31.8	-31.4	-22.2	-34.2	37	37
	С	291.7	-149.0	-198.7	-26.5	-82.4	40	53
10 units	В	9.2	-12.4	-5.5	-11.0	-19.7	43	19
	В-С	44.4	-28.9	-26.1	-23.1	-33.8	37	33
	С	318.5	-164.8	-213.4	-27.2	-86.9	41	53
11 units	В	6.3	-10.4	-4.0	-6.1	-14.2	51	20
	В-С	46.7	-29.9	-28.2	-23.0	-34.4	37	35
	С	292.8	-149.9	-198.5	-26.4	-82.0	40	53

Note: \mathbf{B} = reactant complex intermediate, \mathbf{B} - \mathbf{C} = transition state of the C-O bond formation, and \mathbf{C} = resulting intermediate after the C-O bond formation Abbreviation: EDA, energy decomposition analysis.



SCHEME 1 Fragments and geometries considered in the energy decomposition analysis (EDA) for the C-O bond between the two units of digold non-chelated complex



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FIGURE 3 Schematic representation of the selected rings to study the aromaticity. The number of repeating methylenic units (n) goes from 2 to 10

the solvent. For instance, the ΔE_{int} values in toluene for the non-chelated system are -11.5, -29.8, and -79.6 kcal/mol for **B**, **B**-**C**, and **C**, respectively; or those for the system with 5 units are -13.1, -28.4, and -82.7 kcal/mol, respectively.

From data in Table 3, it is not unequivalent which of the covalent or ionic component is prevalent, but the numbers show both are equally important. This guided the next step of our analysis in exploring the possible change in aromaticity in the rings (see Figure 3). We wished to evaluate if there is a change in the aromaticity of the phenoxide and the phenyl rings of the phenylacetylene reactants,^[56,62] as well as the imidazole ring, that is, the five member rings (MRs) of the NHC ligands, produced by the progressive elongation of the bridging chain composed of methylene units. Consequently, an exhaustive study of the aromaticity has been performed employing geometrical, electronic, and magnetic criteria of aromaticity.

The effect of the methylene chain length and subsequent changes produced in the species involved in the C-O bond formation step (intermediates **B** and **C**, and the transition state in between **B** and **C**) have been analyzed by means of the aromaticity of five MRs of the NHC ligand (Rings I and II) and six MRs of the former reactants (Rings III, IV and V), shown in Figure 3.

Without cleaving the chelating chain that joints NHC ligands, if we first examine the molecular geometries of **B**, **B**–**C**, and **C**, we observe that the relative orientation of the phenyl rings of the phenoxide and diphenylacetylene is not the same in all systems. First, in the case of the **B** intermediate, there are several arrangements: for n = 2-6 and 10, one of the rings of the diphenylacetylene is placed in a T-shape (or edge-to-face) conformation; for n = 7, they are in a parallel-displaced (or offset) situation; and for n = 8 and 9, the rings are in a T-shape-displaced conformation. Second, in the B-C transition state, the two rings in n = 2, 3, 9, and 10 systems are in a sandwich (or face-to-face) conformation, all the others (n = 4-8) are in a parallel-displaced (or offset) conformation.

The aromaticity results can be found in Tables S1 and S2, whereas Figure 3 presents the nomenclature used for the rings (in those cases with more than one nonequivalent ring). According to magnetic, geometric, and electronic indices, the phenyl units present in phenol and

diphenylacetylene display a similar aromaticity to benzene. It can be seen that once the reactants are coordinated forming the monometallic species, the aromaticity is slightly reduced, especially in the case of the phenoxy, and it is recovered after forming the bimetallic intermediate and transition state.

In the systems with sandwich conformation (Tables S3 and S4), nucleus-independent chemical shift (NICS) $(-1)_{zz}$ values are higher in absolute value than the NICS(1)_{zz} ones (-1 and 1 correspond to ghost atoms)placed at the internal and external face of the sandwich, respectively) for Rings III and V (the ones that form the sandwich). For instance, in the system with n = 9, the NICS $(-1)_{zz}$ and NICS $(1)_{zz}$ of Ring III are -34.19 and -29.09 ppm, respectively. This increase of the NICS, in terms of absolute value, in the internal position, is an artifact as a result of the overlap of the shielding regions of each of the two phenyl groups, as can be seen in Figure 4, and should not be associated to a real increase of the aromaticity of the rings as it was demonstrated by Solà et al. in 2006.^[63] Finally, in the case of **C**, where the C-O bond is already formed, the phenoxy moiety is displaced almost perpendicularly to the rings of the diphenylacetylene moiety. To facilitate the comparison of the NICS(1 and $-1)_{zz}$, we have computed the absolute value of the difference between these two measures and compiled them in Table 4. For further insight, all the NICS and NICS_{zz} are available in Tables S3 and S4, whereas the other aromaticity indexes including harmonic oscillator model of aromaticity (HOMA), fluctuation index (FLU), Iring, multicenter index (MCI), and para-delocalization index (PDI) are found in Table S5. Regarding these latter geometric and electronic aromaticity measures in Table S5, we can observe that the differences in aromaticity due to the variation in the chain length are really small.^[64] Therefore, from this analysis, we can conclude that the aromaticity of the ring is not affected by the change in the chain length. As it has been mentioned above, the larger differences are found in those cases with sandwich conformations between phenyl rings. In the case of Ring IV in B, the difference of 3.36 ppm is due to the π - π stacking interaction of this ring with one of the rings of the NHC ligand.

TABLE 4 Absolute value of the difference between NICS_{zz} 1 and -1 (in parts per million) of the studied Rings I to V for the three intermediates; the metal complex with the alkyne coordinated (**B**), the transition state of the C–O bond formation (**B–C**) and the intermediate with the product coordinated to the metal complex (**C**)

n	Ring I	Ring II	Ring III	Ring IV	Ring V
В					
2	0.44	1.35	1.78	3.36	0.44
3	1.03	0.88	2.13	2.32	1.59
4	0.40	0.77	0.46	0.10	2.25
5	0.37	0.21	1.62	0.29	2.43
6	0.52	0.13	0.79	1.88	0.56
7	0.06	0.48	1.00	1.08	4.42
8	0.41	0.26	0.12	0.81	0.45
9	0.47	0.00	0.29	1.79	1.46
10	0.35	0.06	0.16	0.92	0.01
B-C					
2	0.09	1.66	1.51	0.14	3.74
3	0.69	0.94	1.21	0.44	4.11
4	0.55	0.95	0.18	2.30	0.42
5	0.31	1.06	1.85	0.83	0.87
6	0.82	0.47	0.06	0.54	0.44
7	0.21	0.51	1.94	0.74	0.88
8	0.67	0.47	1.03	1.55	1.43
9	0.47	0.05	5.10	0.46	5.08
10	0.47	0.35	2.12	0.41	4.38
С					
2	0.19	0.63	0.51	0.73	0.19
3	0.72	0.37	2.12	1.60	0.91
4	0.50	1.19	0.88	1.19	1.14
5	0.18	0.14	1.81	0.68	1.59
6	0.66	0.71	0.08	0.39	0.30
7	0.34	0.28	0.62	1.60	1.62
8	0.66	0.28	0.12	0.60	0.64
9	0.10	0.28	3.46	1.14	2.32
10	0.63	0.61	2.01	2.24	3.67

Note: Systems present n from 2 to 10 units.

FIGURE 4 Schematic representation of (a) the induced magnetic field in benzene in the presence of B_0 , indicating the shielded regions, and (b) the shielded regions in the Au (N-heterocyclic carbene, NHC) dimer complexes with the reactants in a sandwich conformation





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3 | CONCLUSIONS

Predictive catalysis by design has provided here diaurated chelated systems, to improve the possibility to carry out the hydrophenoxylation of alkynes. We here study the Au–C bond formation, that is, alkyne coordination step, which leads to the reacting compound that would form, now, the intramolecular C–O bond. By means of an EDA, we have observed remarkable orbital attractive interaction particularly favored for the chain of seven methylene units. Next, an aromaticity analysis provides insight into how the aryl rings are placed in the right orientation to provide π - π stacking interactions, between aryl rings.

The concatenation of gold units and the encapsulation or fixation in supports must be an objective in the field of improvement of the catalytic activity of the hydrophenoxylation of alkynes.^[48,65,66]

4 | COMPUTATIONAL DETAILS

Geometry optimizations have been carried out by means of DFT calculations with Gaussian09.^[67] The GGA BP86 functional of Becke and Perdew was used.^[68–70] The electronic configurations of the molecular systems were described with the standard split-valence basis set including the polarization function of Ahlrichs et al. for hydrogen, carbon, nitrogen, and oxygen (SVP keyword in Gaussian09),^[71] whereas for gold we used the quasirelativistic Stuttgart/Dresden effective core potential with the associated valence basis set (standard sdd keyword in Gaussian09).^[72–74] The stationary points were characterized by analytical frequency calculations.

On the BP86/SVP~sdd optimized geometries, singlepoint calculations were performed using the M06 functional^[75] with the triple- ζ basis set of Weigend and Ahlrichs for main-group atoms (TZVP keyword in Gaussian),^[76] and for gold the sdd pseudopotential and basis set. In those latter calculations, the polarizable conductor calculation model (CPCM) was also used to model the solvent effects (toluene).^[77–79] The reported Gibbs energies in this work include energies obtained at the M06/TZVP~sdd level of theory corrected with zero-point energies, thermal corrections, and entropy effects evaluated at 298 K with the BP86/SVP~sdd method in the gas phase.

Morokuma's EDA^[80,81] for the analysis of the interaction between both metal moieties was carried out by $ADF^{[82]}$ on the Gaussian09 optimized geometries. Further insight on the bond nature is obtained by performing EDA analysis on these species, which decomposes the interaction energy into Pauli repulsion (ΔE_{Pauli}), electrostatic (ΔE_{elst}), orbital (ΔE_{oi}), and dispersion (ΔE_{disp}) interaction terms, that is,

$$\Delta E_{\text{int}} = \Delta E_{\text{elst}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}}$$
(1)

The EDA were performed at ZORA-BP86-D3(BJ)/ TZ2P level of theory.^[83] The relativistic effects in heavy metals were treated with the ZORA approach.^[84] Finally, it is important to note that ADF software has proven wide performance on EDA calculations on related interactions. For instance, in 2004, Nemcsok et al. and Meyer et al. studied the significance and nature of the interaction between NHC ligands with Group 11 metals.^[85,86] And more recently, there is a report providing insights into the hydroamination reaction, analyzing the C–N bond formation process between an alkyne and an amine catalyzed by rhodium and gold.^[87] Apart from these investigations, there is little information of gold systems obtained using this useful methodology.

For the aromaticity section, the magnetic index NICS,^[88] the electronic indices FLU,^[89] and I_{ring} ,^[90] MCI,^[91] and PDI^[92] (the PDI is restricted to six MR cases), and the geometrical index HOMA^[93] have been our methods of choice. In the case of magnetic and electronic indices, the calculations were performed at M06/TZVP~sdd//BP86/SVP~sdd level of theory with solvent corrections while in the case of HOMA, BP86/SVP~sdd was used. The computations of NICS have been done with Gaussian 09 rev. e01^[94] package, while for FLU, PDI, MCI, and I_{ring} indices, we used AIMAll^[95] together with ESI-3D^[96,97] packages; and the HOMA index was also computed with the ESI-3D program.

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AUTHOR CONTRIBUTIONS

Sílvia Escayola: Data curation. Jordi Poater: Data curation; formal analysis; investigation; methodology; validation. Miguel Ramos: Data curation; investigation. Jesús Antonio Luque-Urrutia: Data curation; formal analysis; investigation. Josep Duran: Data curation; formal analysis. Sílvia Simon: Data curation; formal analysis. **Miquel Solà:** Conceptualization; formal analysis; methodology. **Luigi Cavallo:** Conceptualization; formal analysis; methodology. **Steven Nolan:** Conceptualization; formal analysis; methodology. **Albert Poater:** Conceptualization; data curation; formal analysis; funding acquisition; methodology; supervision; validation.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supporting information of this article.

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SUPPORTING INFORMATION

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