# Comparing Protonolysis and Transmetalation Reactions: Microcalorimetric studies on C–Au^I bonds in [AuRL] complexes

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ABSTRACT: The protonolysis of C–Au bonds in [AuRL] organometallic complexes has been studied by calorimetry for twelve R groups. The experimental data have been combined with DFT calculations to obtain Bond Dissociation Energy values (BDE). The C–Au BDE values show a good correlation with the corresponding isolobal C–H BDE values. The heat released in the protonolysis of [AuRL] has also been measured for R = Ph and L = P(OPh)$_3$, PPh$_3$, PMe$_3$, PCy$_3$, and IPr, and these values strongly depend on the trans influence of L because of the mutual destabilization of the L–Au and Au–C bonds. The enthalpy of the transmetalation reactions [AuR(PPh$_3$)] + SnIBu$_3$ → [AuI(PPh$_3$)] + SnRBu$_3$ for seven R groups have been measured and compared with the corresponding [AuR(PPh$_3$)] protonolysis.

$$[AuR(PPh_3)] + Ph\cdot \longrightarrow [AuPh(PPh_3)] + R\cdot \qquad \Delta H = \Delta D_R$$
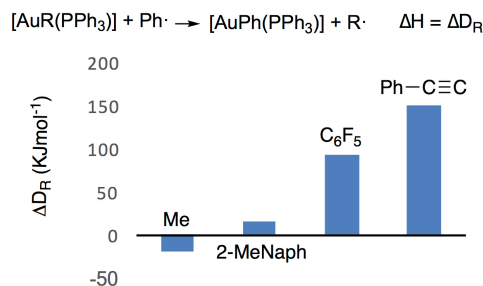
Introduction

Bond energy is a fundamental parameter to understand the chemical behavior. There is much experimental work published for main group elements and these data have been used to validate computational procedures, but for metal complexes of groups 3–12 the opposite situation is found: much computational work has been performed, very often without experimental data available to compare with. This is particularly the case in gold(I) organometallic chemistry. The enormous growth of the use of gold(I) complexes in catalysis over the past fifteen years has run in parallel with a generalization of the application of computational methods. These have been frequently used to understand the chemistry involved in the reactions and to study reaction mechanisms.[1-9] In contrast, very few experimental energy data concerning specifically the C–Au bond have been reported.[10,11]

Data about C–Au^I bonds are relevant because of the prominent involvement of this bond in gold catalysis and in gold-co-catalyzed processes.[1-9,12,13] Other M–C bonds associated to catalytic reactions involving C–H activation have been analyzed in detail,[14-17] including seminal thermodynamic works by Halpern, Bercaw, Bergman and Marks groups,[14,18,21] but gold was not included in them. The initial studies of BDEs (Bond Dissociation Energies) revealed close correlations for different E elements between M–E and H–E BDEs. These correlations, which are particularly relevant for E = C,[22-27] were further confirmed by computational studies of the BDE tendencies in transition elements.[28] These correlation show that plots of M–E BDEs *vs*. M–H BDEs are roughly linear, with a slope larger than 1. In C–H activation processes (E = C) this means that when a R–M bond is to be formed in the reaction there is a thermodynamic preference for activation of stronger R–H bonds (Csp > Csp^2 > Csp^3).

In a work focused to analyze periodic variations of M-H and M-E bonds in transition metals,[28] Landis *et al.* stated that *"late metal-heteroatom bond enthalpy variations appear to represent a complex interplay between bond polarity and lone pair interactions"*. More recently, Gunnoe *et al.* addressed computationally this problem and attributed the higher orbital stabilization of E–M compared to E–H bonds to the higher orbital electronegativity of the E group. Moreover, they explained the slope of the M–E *vs*. H-E BDEs correlations as the result of closed-shell dπ-pπ interactions.[29]

Special attention has been paid to fluorinated aryls, R(F),[16,30] because of their very high M–C BDE values. In fact, these groups produce an unusually high stabilizations of the C–M bonds compared to the corresponding C–H bonds, which strongly influences the lower reactivity of R(F)–M bonds and their higher inertia in reactions catalyzed by transition metals.[31]

Here we report calorimetric C–Au^I data for [AuR(PPh$_3$)] complexes. We have used as R groups methyl, alkynyls, and aryls, including several fluoroaryls such as pentafluorophenyl (C$_6$F$_5$, or Pf) and 3,5-dichloro-2,4,6-trifluorophenyl (C$_6$F$_3$Cl$_2$, or Rf). The latter are particularly useful in mechanistic studies because of their informative ^{19}F NMR spectra.[32-37] We also study the strength of the Ph–Au bond in [AuPhL] complexes for L = PPh$_3$, PMe$_3$, PCy$_3$, P(OPh)$_3$ and IPr). The goal of our work is to obtain experimental thermodynamic values directly related to Au–C bond dissociation energies (BDE) in order to provide solid experimental references to computational or kinetic studies. Being a fundamental part of many gold-catalyzed reactions, several kinetic and computational studies on protodearuation processes have been published. Blum *et al.* studied, through competitive kinetics, the protodeauration reaction of vinylgold, alkynylgold, and arylgold complexes and conclud-

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ed, from a Hammett study, the involvement in the transition states (TS) of the corresponding C–C π systems.[38] The reactions were faster for aryls bearing π-donating substituents and, consequently, a transition state was proposed involving hiperconjugation of the Au–C σ bond with the carbon π system, by analogy with the studies of Berwin on the protonolysis of C–M bonds (M: 14 group element other than carbon).[39] They also noticed that strongly donor ligands (such NHC carbenes) increased the reaction rate. The effect of ligands on the protodeauration reaction was further studied by Wang *et al*. They showed that protodeauration is also accelerated by electron-rich phosphine ligands.[12] Computational studies of the protodeauration reaction by BabaAhmadi *et al.* concluded that: *i)* the stronger the Au–C bond, the higher the activation energy; and *ii)* strongly σ donor ligands decrease the protodeauration activation energy.[13] Recently, Nunes dos Santos Comprido *et al.*, have shown that, during the protonolysis, the new C-H bond takes the electron density from the σ-bonding component between gold and the carbon atom.[40]

Since our plan is the experimental study of the thermodynamics of the process and the parameters that affect the C–Au BDEs, our computational reference works are those published by Clot *et al.* on the study of C–H and C–M BDEs. Consequently, we have used the computational methodology reported in these works, and we have expanded the study to the use of extended basis sets.[17,30]

Results

R group effects. The enthalpies associated to the protodeauration reactions of complexes [AuRL] (Eq. 1), have been measured by calorimetry, affording ΔH_{exp} values for different R (Table 1) and L (Table 2) combinations (Table 1, column 5). Roth and Blum showed that the reaction of [AuRL] with acids such HCl in CH_2Cl_2 proceeds to yield initially [AuClL] and the protonolysis product R–H.[38] They did not find any significant kinetic role of the anion of the acid used for protodeauration, and established that stoichiometric protodeauration is achieved with acids with $pK_a < 18$ in DMSO.[41]
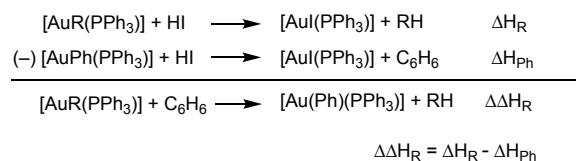
To be suitable for calorimetric determinations a reaction being examined has to be fast, and the final complexes have to be very stable to prevent the contribution of subsequent side reactions (e.g. formation of metallic gold) that would contaminate the meaning of ΔH_{exp} data. After tests with different HX acids such as hydrochloric, triflic or tetrafluoroboric acids, we found that an acid system formed by a mixture of triflic acid and tetrabutylammonium iodide produces the corresponding iodo-gold complexes in very fast and clean reactions (Eq. 1) using CH_2Cl_2 as solvent. The reactions were carried out in the microcalorimeter at 30 °C with the gold complex being in excess.[42] The [AuR(PPh$_3$)] complexes with the R groups listed in Table 1 afforded the experimental ΔH_R values given in the third column.

$$[AuR(PPh_3)] + HI \longrightarrow [AuI(PPh_3)] + RH \qquad (1)$$

The heat released in these reactions consists of several contributions to enthalpy, namely: i) the enthalpy associated to breaking the Au–R and H–I bonds; ii) the enthalpy of formation of the R–H and Au–I bonds; and iii) the changes of solvation energy for the species involved. Assuming that the solvation enthalpies of the organogold complexes are small and quantitatively not very different from each other, all the solvation contributions are practically cancelled by choosing a

reference complex ([AuPh(PPh$_3$)] is our choice) and defining $\Delta\Delta H_R = \Delta H_R - \Delta H_{Ph}$ as shown in Scheme 1.

Scheme 1. Definition of $\Delta\Delta H_R$

[AuR(PPh$_3$)] + HI $\longrightarrow$ [AuI(PPh$_3$)] + RH	ΔH_R	
(–) [AuPh(PPh$_3$)] + HI $\longrightarrow$ [AuI(PPh$_3$)] + C$_6$H$_6$	ΔH_{Ph}	
[AuR(PPh$_3$)] + C$_6$H$_6$ $\longrightarrow$ [Au(Ph)(PPh$_3$)] + RH	$\Delta\Delta H_R$	

$$\Delta\Delta H_R = \Delta H_R - \Delta H_{Ph}$$

Scheme 2. Definition of ΔD_R.

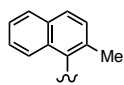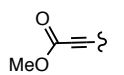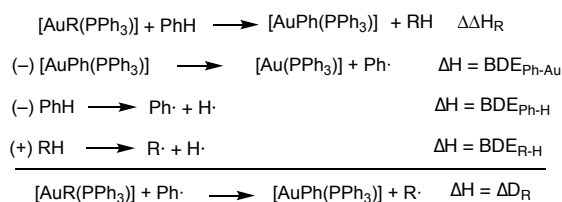|		
[AuR(PPh$_3$)] + PhH $\longrightarrow$ [AuPh(PPh$_3$)] + RH	$\Delta\Delta H_R$
(–) [AuPh(PPh$_3$)] $\longrightarrow$ [Au(PPh$_3$)] + Ph·	$\Delta H = BDE_{Ph-Au}$
(–) PhH $\longrightarrow$ Ph· + H·	$\Delta H = BDE_{Ph-H}$
(+) RH $\longrightarrow$ R· + H·	$\Delta H = BDE_{R-H}$
[AuR(PPh$_3$)] + Ph· $\longrightarrow$ [AuPh(PPh$_3$)] + R·	$\Delta H = \Delta D_R$

Table 1. Calorimetry data for protonolysis of R–Au(PPh$_3$), and dissociation values relative to PhAu(PPh$_3$). vValues in kJmol^{-1}.

Entry	R	ΔH_R	$\Delta\Delta H_R$	BDE[†] R-Au(calcd)	ΔD_{RAu}[&]
1	CH$_3$	-124 ± 3[#]	5 ± 6	281	-20 ± 6
2	4-F-C$_6$H$_4$	-134 ± 2	-5 ± 5	312	-2 ± 5
3	4-Me-C$_6$H$_4$	-129 ± 2	-1 ± 5	305	-1 ± 5
4	Ph	-129 ± 3	0	306	0.0
5	4-MeO-C$_6$H$_4$	-127 ± 2	1 ± 5	306	4 ± 5
6	[naphthyl]-Me	-114.8 ± 0.5	14 ± 4	295	15 ± 4
7	2-F-C$_6$H$_4$	-114 ± 5	15 ± 8	333	24 ± 8
8	2,6-F$_2$C$_6$H$_3$	-75 ± 1	54 ± 4	362	77 ± 4
9	3,5-Cl$_2$-2,4,6-F$_3$C$_6$	-76 ± 1	52 ± 4	398	78 ± 4
10	C$_6$F$_5$	-62 ± 2	67 ± 5	376	93 ± 5
11	C$_6$H$_5$CC	-73.7 ± 0.7	55 ± 4	465	151 ± 4
12	[MeO-C(=O)-C≡C]	-35.9 ± 0.7	93 ± 4	471	177 ± 4

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With [AuPh(PPh$_3$)] taken as zero, $\Delta\Delta H_R$ for the different complexes [AuR(PPh$_3$)] is the heat released (or absorbed) in their reaction with C$_6$H$_6$ (Scheme 1), and gives a relative order of protonolysis reactivity. The $\Delta\Delta H_R$ values are given in Table 1 column 4. From the experimental data it is also possible to calculate relative bond dissociation energies (ΔD_R, Scheme 2), provided that the BDE$_{R-H}$ values are known.[44,45] If no experimental BDE$_{R-H}$ data are available, calculated values are accessible for many R groups (see SI for details).[46]

In addition to our experimental determinations, we have calculated by DFT the R–Au bond dissociation energies for all the complexes in Table 1. From them it is also possible to obtain relative $\Delta D_{R(calcd)}$ values, taking complex [AuPh(PPh$_3$)] as zero (equation 2). The correlation between experimental ΔD_{Rexp} and the calculated value ΔD_{Rcalcd} is shown in Figure 1.

$$\Delta D_{RAu(calcd)} = BDE_{R-Au(calcd)} - BDE_{Ph-Au(calcd)} \qquad (2)$$

Overall, the values in Table 1 show that the strength of C–Au bonds follows the usual trend found for C–M bonds of late transition metal complexes: Csp–Au $\gg$ Csp^2–Au > Csp^3–Au. They also confirm that electron-withdrawing substituents reinforce the C–Au bond, in agreement with previous computational studies.[47,48] The high strength of the Csp–Au bond is a distinctive property of organogold complexes.[49] Liu $et\ al.$ calculated the BDE of the anions [ClAu–CCH]$^-$ and [ClAu–CH$_3$]$^-$, and found than the former is 179.5 kJ mol^{-1} stronger than the second. This difference is very close to our experimental value for the BDE difference between the neutral phenylalkynyl and methyl complexes ([Au(C≡CPh)(PPh$_3$)] BDE is 170.3 larger than [Au(CH$_3$)(PPh$_3$)]; entries 1 and 11 in Table 1). Note that the carboxymethylalkynyl complex in entry 12 provides an even larger 193 kJ mol^{-1} difference, consequence of the stabilization of the negative charge at the carbon. This is discussed below for aryl groups.[49]

The classical representation of ΔD_R vs ΔD_{R-H} ($\Delta D_{R-H} = BDE_{R-H} - BDE_{Ph-H}$) shows for the gold complexes a roughly linear correlation, fitting a line with slope 1.75 (Figure 1). This good correlation is consistent with the idea that [AuL]$^+$ and H$^+$ fragments are considered isolobal.[50]

Our experimental data for substituted aryls show also strong increase of the C–Au energy bond with the electron withdrawing ability of the substituents, which is particularly important for fluorine substituents (these show their own linear correlation with slope 3.8 in Figure 1). The study of this peculiarity in several metal complexes was computationally addressed by Clot $et\ al.$,[30] who showed that the effect can be almost perfectly parameterized to a linear relationship (Eq. 3), where n_{ortho}, n_{meta}, and n_{para} are the number of fluorine atoms in positions $ortho$, $meta$ or $para$ relative to the C–M or C–H carbon atom, and b, c, and d are the parameters that quantify the relative contribution of each fluorine atom. For Rh^{III} complexes they found a good linear fitting for a = -1.0, b = 26.1, c = 3.8, d = 2.5 (b $\gg$ c $\approx$ d. We have found an analogous relationship in our experimental data for fluoroaryl gold complexes, leading

to the correlation $\Delta D_{RF} = -13.27 + 42.64 n_{ortho} + 6.42\ n_{meta} + 8.55\ n_{para}$.

$$\Delta D_R = a + b n_{ortho} + c n_{meta} + d n_{para}\ (kJ\ mol^{-1}) \qquad (3)$$
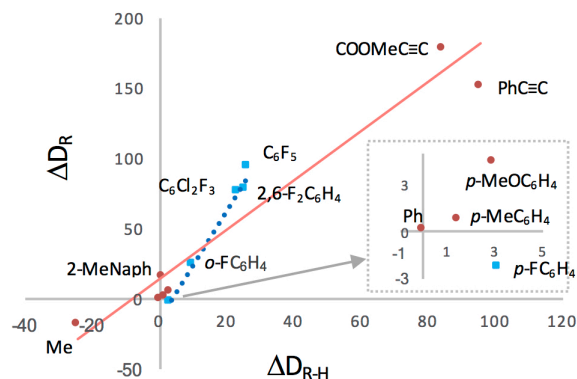

Figure 1. Correlations for the experimental values of ΔD_R vs calculated ΔD_{R-H} (both relative to phenyl). The red line represents the correlation of all the experimental values; the blue line represents the correlation of fluorinated aryls. See Table 1 for details.

Our calculated BDE$_{Rcalcd}$ values, with the same computational methodologies used by Clot $et\ al.$ (two procedures),[48] show a reasonably good correlation with the experimental values (Figure 2), and lead to a correlation with the fluorine substituted groups: $\Delta D_{RFcalcd} = -16.66 + 39.61\ n_{ortho} -8.22\ n_{meta} + 25.43\ n_{para}$ (Figure 2).[51]
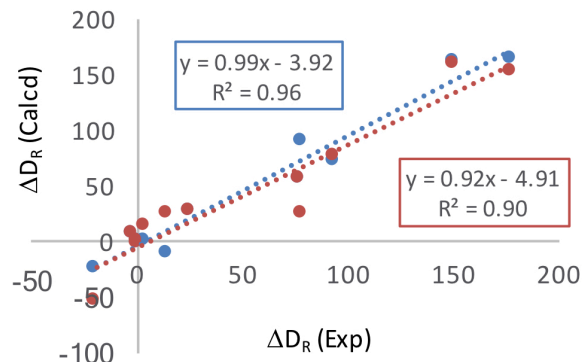

Figure 2. Correlations between calculated and calorimetry based experimental BDE values. Blue points and line: calculated with B3PW31/6-31G(d,p); Red points and line: calculated with B3PW31/cc-pvtz and dispersion function gd3bj. Each experimental value should be correlated to one blue and one red point; note that sometimes the two overlap (then only the red point is observed).

The stabilizing effect of the fluorine substituents in the aryls has been explained as a negative hyperconjugation of electron density into the σ*(C–F) orbital.[30] This stabilizes negative charge at the C$_{ipso}$, increasing the contribution of ionic interactions to the C–Au bond and the BDE value. Analysis of the

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NBO second order perturbations show some donation of electron density from the σ Au–C bond to the σ* C–F orbital, as well as an increment of electron transfer from the σ Au–C to the σ* C-C orbital when these ring carbons are fluorinated.

Ligand influences. The effect of the auxiliary ligand on the protonolysis enthalpy of [AuPhL] with HI has been studied for different ligands (Eq. 4). The calorimetric data (Table 2) indicate a strong increase of the heat released in each experiment in the order $P(OPh)_3 \gg PPh_3 \approx PMe_3 > IPr > PCy_3$, with energy spanning a range of about 50 kJ mol^{-1}. Neglecting solvation contributions, these data can be assigned to the enthalpy difference of (I–Au–L) – (Ph–Au–L) for each ligand. The π back-donating ability of Au^I in its carbonyl and carbene complexes has been deeply studied,[52-56] and it is widely accepted that it is very small, so it barely influences the bond strengths. It has been shown also that the bulkiness of the ligands does not affect their ability to coordinate to linear gold(I) either.[11] Consequently, the differences of enthalpy observed must be mostly related to the σ-donating ability of all the ligands (Ph$^-$, I$^-$, and L), which is the origin of the elongation and weakening of the bonds trans to each other. This phenomenon is known as *trans-influence* of the ligands, and is a matter of polarization of the electron clouds of the bonds. The trans influence series of the ligands involved is: I$^-$ < Ph$^-$ ≈ phosphines ≈ NHC.[57] Since the trans influence is I$^-$ < Ph$^-$, shorter (and stronger) Au–L bonds are formed in [AuIL] than in [AuPhL]. Not unexpectedly, this difference in stabilization by L coordination is bigger the stronger the σ-donor the L ligands. Also the C–Au and Au–I bonds are affected by the trans influence of ligands L, and the overall result is that both bonds, L–Au and Au–C, in [AuPhL] are weakened when the σ-donor ability of L increases, more than L–Au and I–Au are in [AuIL]. Table 2 gathers also, for the ligands studied, the calculated differences between BDE LAu–I and BDE LAu–Ph. These increase with the σ-donor ability of the ligand, running parallel to the enthalpy values, and confirm a stabilization of complexes L–Au–I compared to L–Au–Ph that is larger for better σ-donor ligands.
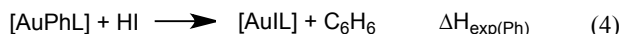
$$[AuPhL] + HI \longrightarrow [AuIL] + C_6H_6 \qquad \Delta H_{exp(Ph)} \qquad (4)$$

Table 2. Experimental calorimetric data for the protonolysis of [AuPhL] (kJ mol^{-1}) and calculated differences between BDE Au-I relative to Au–I for several ligands.

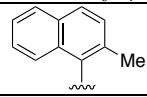| Ligand	P(OPh)$_3$	PPh$_3$	PMe$_3$	IPr	PCy$_3$
$-\Delta H_R$	-86 ± 4	-129 ± 3	-129 ± 3	-135 ± 3	-140 ± 2
BDE$_{Au-Ph}$ – BDE$_{Au-I}$	-31.8	-40.2	-39.9	-40.1	-44.7

Study of Sn/Au transmetalation reactions. The protonolysis reaction AuRL + HX can be used to compare other transmetalation reactions AuRL + E–X (E = a suitable electrophile) that produce Ar–X and E–R. Our interest in the Sn/Au transmetalation comes primarily from the gold-cocatalyzed reaction that we developed to accelerate slow or non-operative couplings involving bulky aryls,[36,58,59] The dramatic positive effect of gold in this bimetallic catalysis is that the double transmetalation Sn/Au and Au/Pd skips the sterically hindered Sn/Pd direct transmetalation in the case of bulky aryls. We found that the thermodynamics of the Sn/Au transmetalation is very dependent on the R group and on the halogen being transferred.[34,58] The transmetalation between organogold and organotin reagents plays also a role in other catalytic processes, and its mechanism has been studied.[60-64] Here we measure the reaction of [AuR(PPh$_3$)] complexes with ISnBu$_3$ (Eq. 6). The reactions were carried out at 30 °C (See Experimental Section), with the organotin complex in large excess in order to make the reactions fast enough to be measured by calorimetry. The results are gathered in Table 3.

$$[AuR(PPh_3)] + SnIBu_3 \rightarrow [AuI(PPh_3)] + SnRBu_3 \quad \Delta H \qquad (6)$$
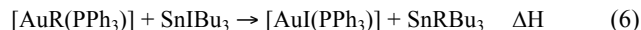
Again the enthalpy of the reaction depends on the BDE balance for the M–R/M'–I exchanges. The enthalpy difference between SnIBu$_3$ and [AuI(PPh)] is a constant for all the reactions. Hence the effect of Sn–R *vs* Au–R bonds can be measured for different R groups, which affords $\Delta H_{R(SnAu)}$ in Table 3, 3rd row. The table shows that the heat involved in the Au/Sn transmetalations is, generally, very small compared to the heats of protonolysis of the same Au–C bonds. More useful is to define the differences between R groups, $\Delta\Delta H_{R(SnAu)} = \Delta H_{R(SnAu)} - \Delta H_{Ph(SnAu)}$, taking the case of Ph as zero, whereupon the contribution of the two iodides disappears and the values reflect and compare differences in Au–C BDEs for different R groups (Table 3, 4th row). In other words, $\Delta\Delta H_{R(SnAu)}$ represents the thermodynamic tendency to produce transmetalation between [AuR(PPh$_3$)] and SnBu$_3$Ph. The data show that this reaction is strongly exothermic for R = Me, which prefers to be on tin than on Au (Au–Me is weak) and clearly endothermic for R = C≡CPh, due to the strong Au-alkynyl bonds (see BDE in Table 1).

Table 3. Experimental calorimetry data for the reaction: [AuR(PPh$_3$)] + SnIBu$_3$ → [AuI(PPh$_3$)] + SnRBu$_3$ ΔH_{exp} (eq. 6) All the values are in kJ mol^{-1}.

Entry	R	$\Delta H_{R(SnAu)}$	$\Delta\Delta H_R$
1	CH$_3$	–100 ± 2	-81±3
2	4-F-C$_6$H$_4$	–9.2 ± 0.6	9.8±1.6
3	4-Me-C$_6$H$_4$	–21.8± 0.6	–2.8±1.6
4	Ph	–19 ± 1	0±3
5	4-MeO-C$_6$H$_4$	–26 ± 1	-7±2
6	(naphthyl-Me)	–18 ± 2	1±3
7	C$_6$H$_5$CC	–7.5 ± 0.4	11.5±1.4

The values for aryls reflect the expected variations depending on the electronic influence of the aryl substituents. Moreover, it also shows that the reaction is almost thermoneutral for R = 2-methyl-naftyl group, in spite of the about 10 kJ mol^{-1} lower BDE Au–R bond for this group than for Au–Ph. This means that the Sn-(2Methyl-naftyl) BDE is about 10 kJ mol^{-1} lower than expected if we considered exclusively its electronic properties. This is in fact a very nice confirmation of the unfavorable steric hindrance effect when a bulky group is incorporated to a SnBu$_3$ fragment. Consequently, the transmetalation of bulky groups from Sn to Au(I) is enthalpically favored compared to the transmetalation of electronically similar smaller groups. The

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same reason favors transmetalation to linear Au(I), where this hindrance is released, better than to more crowded Pd(II) complexes,[36,65] which is the basis of the gold co-catalyzed Stille reaction.

Conclusions. The energy of C–Au^I bonds in neutral [AuRL] complexes show strong dependence on the carbon atom features, with BDE values spanning from 280 kJ mol^{-1} to more than 470 kJ mol^{-1}. The Csp–Au^I bonds are particularly strong. The nature of the auxiliary ligand L has also a clear effect that arises, not only from the differences in C–Au bond lengths and strengths, but also from the different bond lengths and strengths of the Au–L bonds, depending on whether in the corresponding complex L is in front of R or in front of I. The latter effect is due to the very different "trans influence" of R$^-$ and I$^-$. The protonolysis enthalpies with HI span more than 50 kJ mol^{-1}, depending on the ligand L. This can introduce a very large thermodynamic variability on some gold catalyzed reactions that finish with an irreversible protonolysis of the C–Au^I bond, such as the cyclizations of polyynes and other poly-unsaturated molecules.

The reaction of transference of an R group from Au^I to SnBu$_3$ produces a comparatively small release of heat when compared with the Au–R protonolysis with HI, but the order of reactivity stands the same for common R groups. Thus the transmetalation from Sn to Au^I, occurring in the Stille gold cocatalyzed process is unfavorable. However, bulky R groups produce comparatively weaker C–Sn bonds due to steric hindrance in RSnBu$_3$, and their transmetalation benefits from this bond weakening provided that the reaction rates are facilitated by accessible transition states mediated by gold.[36]

Experimental section. All reactions were carried out under nitrogen atmosphere using Schlenk techniques. Solvents were dried using a solvent purification system (SPS) or standard procedures.[66] NMR spectra were recorded on a Bruker AV 400 or an Agilent 500 instrument. Chemical shifts were reported in ppm from tetramethylsilane (^{1}H and ^{13}C), CCl$_3$F (^{19}F), or 85% H$_3$PO$_4$ (^{31}P). Coupling constant were reported in Hertzs (Hz). In the ^{19}F and ^{31}P spectra measured in non-deuterated solvents, a coaxial tube containing acetone-d$_6$ was used to maintain the lock ^{2}H signal. Solution calorimetry measurements were made using an OMNICAL SuperCRC 20-250-2.4 calorimeter located inside a glove box. Unless specified, all compounds were used from commercial sources and used without further purification. The gold complexes [Au(CH$_3$)(PPh$_3$)],[34] [Au(C$_6$F$_5$)(PPh$_3$)],[67] Au(C$_6$H$_5$)(PPh$_3$)],[68] [Au(C≡CC$_6$H$_5$)(PPh$_3$)],[69] [Au(4-F-C$_6$H$_4$)(PPh$_3$)],[54] [Au(2-MeC$_{10}$H$_6$)(PPh$_3$)],[69] [Au(C$_6$Cl$_2$F$_3$)(PPh$_3$)],[69] [Au(4-MeC$_6$H$_4$)(PPh$_3$)],[70] [Au(4-OMeC$_6$H$_4$)(PPh$_3$)],[70] [Au(C$_6$H$_5$)(PMe$_3$)],[35] [Au(C$_6$H$_5$)(PCy$_3$)],[35] [Au(2,4-F$_2$C$_6$H$_3$)(PPh$_3$)],[71] [Au(MeOCOC≡C)(PPh$_3$)],[72] and [Au(C$_6$H$_5$)(IPr)][73] were prepared as reported in the literature. All other compounds were synthesized as described below:

[AuPh(P(OPh)$_3$)]. A two-necked flask was charged with [AuCl(P(OPh)$_3$)] (275 mg, 0.502 mmol) and 20 mL of Et$_2$O. A 1.9 M solution of phenyllithium in Et$_2$O (0.315 mL, 0.6 mmol) was added dropwise under stirring at -78 ºC. The mixture was stirred during 1 hour at -78 ºC and was stirred for 4 hours at room temperature. Then three drops of Et$_2$O were added to quench the reaction. The solvents were evaporated and the residue was dissolved in dichloromethane, the solution was filtered through celite, concentrated and crystallized by addition of n-hexane at -60 ºC. Yield 794.5 mg (95 %). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.65 – 7.59 (m, 6H), 7.49 – 7.40 (m, 5H), 7.40 – 7.30 (m, 6H), 7.22 – 7.12 (m, 3H). ^{31}P NMR (202 MHz, CDCl$_3$) δ 148.10. ^{13}C {^{1}H}NMR (126 MHz, CDCl$_3$): 156.6, 150.2, 129.9, 129.4, 125.60, 121.3, 119.9, 115.5. Cald. For C$_{24}$H$_{20}$AuO$_3$P: C, 49.33; H, 3.45. Found: C, 49.45; H, 3.43.

[Au(2-FC$_6$H$_4$)(PPh$_3$)]. A two-necked flask was charged with 105 µL (0.969 mmol) of 1- bromo-2-fluorobenzene and 50 mL of dry THF. The mixture was cooled down to -78 ºC and 0.75 mL (1.212 mmol) of a 1.6 M solution of n-BuLi in hexane were added dropwise. The reaction was stirred for 1h and 400 mg (0.808 mmol) of [AuCl(PPh$_3$)] were subsequently added. The cooling bath was removed and the mixture was stirred at room temperature for 4 hours. Next, a few drops of wet THF were added. The solvents were evaporated and then a saturated aqueous solution of NH$_4$Cl (30 mL) was added. The aqueous layer was decanted and extracted with Et$_2$O (3x30 mL). All the organic layers were combined, washed with brine (3x60 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure and the resulting yellow solid was dissolved in CH$_2$Cl$_2$ and filtered. The compound crystallized from this solution by slow addition of n-hexane under stirring. Yield 350 mg (78 %). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.62 (m, 6H), 7.59 – 7.54 (m, 1H), 7.53 – 7.42 (m, 9H), 7.15 – 7.08 (m, 2H), 7.04 (m, 1H). ^{31}P NMR (202 MHz, CDCl$_3$) δ 43.50 (d, J = 8.4 Hz). ^{19}F NMR (470 MHz, CDCl$_3$) δ -89.70 (m). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 168.19 (dd, J_{C-P} =3.5 Hz , J_{C-F} = 228.8 Hz), 154.97 (dd, J_{C-P} = 52.2 Hz , J_{C-F} =111.56 Hz), 140.1 (d, J_{C-P} = 20 Hz), 134.4 (d, J_{C-P} = 13.8 Hz), 131.2 (d, J_{C-P} = 2.5 Hz), 130.74 (d, J_{C-P} = 50.9 Hz) 129.0 (d, J_{C-P}= 11.0 Hz), 127.0 (d, J_{C-P}= 7.2 Hz), 123.5 (dd, J_{C-F} = 6Hz, J_{C-P} = 2.5 Hz), 113.7 (dd, J_{C-F} = 30 Hz, J_{C-P} = 3.4 Hz).Cald. For C$_{24}$H$_{19}$AuFP: C, 52.0; H, 3.45. Found: C, 51.88; H, 3.32.

Calorimetry experiments.
A typical measurement of protodeauration was made as follows: In the calorimeter thermostated at 30 ˚C the sample and reference vials were charged with a solution of [AuPh(PPh$_3$)] (27.02 mg, 0.05 mmol) in 4 mL, and with 4 mL of neat CH$_2$Cl$_2$ respectively. The syringes, in both vials, were charged with 0.3 mL of a solution 0.2M of I(NBu$_4$) and with 0.3 mL of a solution 0.2M of HOTf in CH$_2$Cl$_2$, in order to produce 0.6 mL of a solution 0.1M on acid and on iodide. After thermal equilibration the reagents were injected simultaneously in both vials. When the heat flow ceased (40 minutes approximately) the sample vial was opened and its contents were examined by ^{19}F or ^{1}H and ^{31}P NMR to confirm quantitative conversion to the desired product. The enthalpy of reaction (ΔH$_R$) with all species in solution was measured as 6.95 J (-129 kJ/mol), is based on the average of three independent determinations.
For the reaction of [AuMe(PPh$_3$)] the calorimeter was thermostated at –3 ˚C.
A typical measurement of the transmetalation reaction was made as follows: The sample and reference vials of the calorimeter that had been thermostated at 30 ˚C, were charged with a solution of [AuPh(PPh$_3$)] (100 mg, 0.185 mmol) in 4 mL, and with 4 mL of neat THF respectively. The syringes were charged with 0.6 mL (1 mmol) of the stock solution of tributyltin iodide in THF 1.67M. After thermal equilibration

the reagents were injected simultaneously in both vials. When the heat flow ceased (40 minutes approximately) the sample vial was opened and its contents were examined by ^{19}F or ^{1}H and ^{31}P NMR to confirm quantitative conversion to the desired product. The enthalpy of reaction (ΔH_R) with all species in solution was measured as 3.63 J (-19 kJ/mol and is based on the average of three independent determinations.

Computational Section. All the calculations were carried out by means of the Density Functional Theory using the dispersion corrected hybrid functional B3PW91, implemented in the Gaussian09 program.[74] Gold atoms were represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set, augmented by an f polarization function.[75] The phosphorus and chlorine atoms were represented by RECP from the Stuttgart group and the associated basis set, augmented by a d polarization function.[76] The C, H, O and F atoms were described using the double-ζ 6-31G(d,p).[77] The calculation was also performed using triple-ζ cc-pvtz basis set, and empirical dispersion gd3bj.[78] Geometry optimizations were performed in vacuum and without imposing any constraint. The nature of all the stationary points was further verified through vibrational frequency analysis.

ASSOCIATED CONTENT

Supporting Information. The supporting information contains: Experimental and computational methods (11 pages). This Supporting Information is available free of charge on the ACS Publications website as PDF file.

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript. / ‡These authors contributed equally. (match statement to author names with a symbol)

REFERENCES

1 Li, Z.; Brouwer, C.; He, C. Gold-Catalyzed Organic Transformations. *Chem. Rev.* **2008**, *108*, 3239–3265.
2 Hashmi, A: S. K. Gold-Catalyzed Organic Reactions. *Chem. Rev.* **2007**, *107*, 3180–3211.

3 Jiménez-Núñez, E.; Echavarren, A. M.; Jiménez-Núñez, E.; Echavarren, A. M. Gold-Catalyzed Cycloisomerizations of Enynes: A Mechanistic Perspective. *Chem. Rev.* **2008**, *108*, 3326–3350.
4 Gorin, D. J.; Sherry, B. D.; Toste, F. D. Ligand Effects in Homogeneous Au Catalysis. *Chem. Rev.* **2008**, *108*, 3351–3378.
5 Marion, N.; Nolan, S. P.; Mba, M.; Toste, F. D.; Sánchez, F.; Sánchez, F.; Nolan, S. P. N-Heterocyclic Carbenes in Gold Catalysis. *Chem. Soc. Rev.* **2008**, *37*, 1776.
6 Hashmi, A: S. K. Homogeneous Gold Catalysis Beyond Assumptions and Proposals—Characterized Intermediates. *Angew. Chem. Int. Ed.* **2010**, *49*, 5232-5241.
7 Rudolph, M.; Hashmi, A. S. K.; Zhu, Y.; Zhang, F.; Yu, B.; Li, C.-C.; Luo, T.; Yang, Z. Gold Catalysis in Total Synthesis—an Update. *Chem. Soc. Rev.* **2012**, *41*, 2448–2462.
8 Dorel, R.; Echavarren, A. M. Gold(I)-Catalyzed Activation of Alkynes for the Construction of Molecular Complexity. *Chem. Rev.* **2015**, *115*, 9028–9072.
9 Qian, D.; Zhang, J.; Sun, N.; Zhao, J.; Liu, Y.; Li, Y.; Zhang, J.; Tang, W.; Hours, A.; Lesage, D.; et al. Gold-Catalyzed Cyclopropanation Reactions Using a Carbenoid Precursor Toolbox. *Chem. Soc. Rev.* **2015**, *44*, 677–698.
10 Ahrland, S.; Balzamo, S. Thermodynamics of the Complex Formation in Pyridine between Gold(I) and Ligands Coordinating via N, P, As or Sb. *Inorg. Chim. Acta* **1988**, *142*, 285–289.
11 Fortman, G. C.; Nolan, S. P. Solution Calorimetric Study of Ligand Exchange Reactions in the [Au(L)Cl] System (L = Phosphine and Phosphite). *Organometallics* **2010**, *29*, 4579–4583.
12 Wang, W.; Hammond, G. B.; Xu, B. Ligand Effects and Ligand Design in Homogeneous gold(I) Catalysis. *J. Am. Chem. Soc.* **2012**, *134*, 5697–5705.
13 BabaAhmadi, R.; Ghanbari, P.; Rajabi, N. A.; Hashmi, A. S. K.; Yates, B. F.; Ariafard, A. A Theoretical Study on the Protodeauration Step of the Gold(I)-Catalyzed Organic Reactions. *Organometallics* **2015**, *34*, 3186–3195.
14 Halpern, J. Determination and Significance of Transition Metal-Alkyl Bond Dissociation Energies. *Acc. Chem. Res.* **1982**, *15*, 238–244.
15 Xue, X. S.; Ji, P.; Zhou, B.; Cheng, J. P. The Essential Role of Bond Energetics in C-H Activation/Functionalization. *Chem. Rev.* **2017**, *117*, 8622–8648.
16 Eisenstein, O.; Milani, J.; Perutz, R. N. Selectivity of C–H Activation and Competition between C–H and C–F Bond Activation at Fluorocarbons. *Chem. Rev.* **2017**, *117*, 8710–8753.
17 Balcells, D.; Clot, E.; Eisenstein, O. C-H Bond Activation in Transition Metal Species from a Computational Perspective. *Chem. Rev.* **2010**, *110*, 749–823.
18 Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. Relative Metal-Hydrogen, -Oxygen, -Nitrogen, and -Carbon Bond Strengths for Organoruthenium and Organoplatinum Compounds; Equilibrium Studies of Cp*(PMe$_3$)$_2$RuX and (DPPE)MePtX Systems. *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456.
19 Schock, L. E.; Seyam, A. M.; Marks, T. J A new approach to measuring absolute metal-ligand bond disruption enthalpies in organometallic compounds. The [(CH$_3$)$_3$SiC$_5$H$_4$]$_3$ U-system; *Polyhedron*, **1988**, 7 (16), 1517-1529.
20 Halpern, J. Determination of Transition Metal-Alkyl Bond Dissociation Energies from Kinetic Measurements. *Polyhedron* **1988**, *7* (16–17), 1483–1490.
21 Holland, P. L.; Andersen, R. A.; Bergman, R. G.; Huang, J.; Nolan, S. P. Monomeric Cyclopentadienylnickel Methoxo and Amido Complexes: Synthesis, Characterization, Reactivity, and Use for Exploring the Relationship between H-X and M-X Bond Energies. *J. Am. Chem. Soc.* **1997**, *119*, 12800–12814.

[22] Schock, L. E.; Marks, T. J. Organometallic Thermochemistry. Metal Hydrocarbyl, Hydride, Halide, Carbonyl, Amide, and Alkoxide Bond Enthalpy Relationships and Their Implications in Pentamethyl-cyclopentadienyl and Cyclopentadienyl Complexes of Zirconium and Hafnium. *J. Am. Chem. Soc.* **1988**, *110*, 7701–7715.

[23] Jones, W. D.; Hessell, E. T. Photolysis of Tp'Rh(CN-neopentyl)(.eta.2-PhN:C:N-Neopentyl) in Alkanes and Arenes: Kinetic and Thermodynamic Selectivity of [Tp'Rh(CN-Neopentyl)] for Various Types of Carbon-Hydrogen Bonds. *J. Am. Chem. Soc.* **1993**, *115*, 554–562.

[24] Wick, D. D.; Jones, W. D. Energetics of Homogeneous Intermolecular Vinyl and Allyl Carbon−Hydrogen Bond Activation by the 16-Electron Coordinatively Unsaturated Organometallic Fragment [Tp'Rh(CNCH$_2$CMe$_3$)]. *Organometallics* **1999**, *18*, 495–505.

[25] Bennett, J. L.; Wolczanski, P. T. Selectivities in Hydrocarbon Activation: Kinetic and Thermodynamic Investigations of Reversible 1,2-RH-Elimination from (silox)$_2$((t)Bu$_3$SiNH)TiR (Silox = (t)Bu$_3$SiO). *J. Am. Chem. Soc.* **1997**, *119*, 10696–10719.

[26] Jones, W. D. On the Nature of Carbon-Hydrogen Bond Activation at Rhodium and Related Reactions. *Inorg. Chem.* **2005**, *44*, 4475–4484.

[27] Bulls, A. R.; Bercaw, J. E.; Manriquez, J. M.; Thompson, M. E. Relative Bond Dissociation Energies for Early Transition Metal Alkyl, Aryl, Alkynyl and Hydride Compounds. Equilibration of Metallated Cyclopentadienyl Derivatives of Peralkylated Hafnocene and Scandocene with Hydrocarbons and Dihydrogen. *Polyhedron* **1988**, *7* (16–17), 1409–1428.

[28] Uddin, J.; Morales, C. M.; Maynard, J. H.; Landis, C. R. Computational Studies of Metal-Ligand Bond Enthalpies across the Transition Metal Series. *Organometallics* **2006**, *25* (23), 5566–5581

[29] Devarajan, D.; Gunnoe, T. B.; Ess D. H. Theory of Late-Transition-Metal Alkyl and Heteroatom Bonding: Analysis of Pt, Ru, Ir, and Rh Complexes. *Inorg. Chem.* **2012**, *51*, 6710−6718.

[30] Clot, E.; Mégret, C.; Eisenstein, O.; Perutz, R. N. Exceptional Sensitivity of Metal-Aryl Bond Energies to Ortho-Fluorine Substituents: Influence of the Metal, the Coordination Sphere, and the Spectator Ligands on M–C/H–C Bond Energy Correlations. *J. Am. Chem. Soc.* **2009**, *131*, 7817–7827.

[31] Albéniz, A. C.; Casares, J. A. Palladium-Mediated Organofluorine Chemistry, *Adv. Organomet. Chem.* **2014**, *62*, 1–110.

[32] Espinet, P.; Albéniz, A. C.; Casares, J. A.; Martínez-Ilarduya, J. M. ^{19}F NMR in Organometallic Chemistry. Applications of Fluorinated Aryls. *Coord. Chem. Rev.* **2008**, *252*, 2180–2208.

[33] Pérez-Temprano, M.; Casares, J. A.; Lera, Á. R. De; Álvarez, R.; Espinet, P.; Strong Metallophilic Interactions in the Palladium Arylation by Gold Aryls, *Angew. Chem. Int. Ed.*, **2012**, 51, 4917 – 4920 .

[34] Carrasco, D.; Pérez-Temprano, M. H.; Casares, J. A.; Espinet, P. Cross Alkyl-Aryl versus Homo Aryl-Aryl Coupling in Palladium-Catalyzed Coupling of Alkyl-gold(I) and Aryl-Halide. *Organometallics* **2014**, *33*, 3540-3545.

[35] Carrasco, D.; García-Melchor, M.; Casares, J. A.; Espinet, P. Dramatic Mechanistic Switch in Sn/Au I Group Exchanges: Transmetalation vs. Oxidative Addition. *Chem. Commun.* **2016**, *52*, 4305–4308.

[36] Delpozo, J.; Carrasco, D.; Pérez-Temprano, M. H.; García-Melchor, M.; Álvarez, R.; Casares, J. A.; Espinet, P. Stille Coupling Involving Bulky Groups Feasible with Gold Cocatalyst. *Angew. Chem. Int. Ed.* **2013**, *52*, 2189-2193.

[37] Pérez-Temprano, M. H.; Casares, J. A.; Espinet, P. Bimetallic Catalysis Using Transition and Group 11 Metals: An Emerging Tool for C-C Coupling and Other Reactions. *Chem. Eur. J.* **2012**, *18*, 1864–1884.

[38] Roth, K. E.; Blum, S. A. Relative Kinetic Basicities of Organogold Compounds. *Organometallics* **2010**, *29*, 1712–1716.

[39] Berwin, H. J.; The Influence of σ-π Conjugation on the Rate of Protodemetallation Reactions. *J.C.S. Chem. Comm.* **1972**, 237-239.

[40] Nunes dos Santos Comprido, L.; Klein, J. E. M. N.; Knizia, G.; Kästner, J.; Hashmi, A. S. K. On the Accessible Reaction Channels of Vinyl Gold(I) Species: π-and σ-Pathways. *Chem. Eur. J.* **2017**, *23*, 10901-10905.

[41] Bordwell, F. G. Equilibrium acidities in dimethyl sulfoxide solution. *Acc. Chem. Res.* **1988**, *21*, 463.

[42] The experiment was carried out by injecting the solution of triflic acid/(NBu$_4$)I simultaneously on both the reaction and the reference reactors, in order to compensate for the heat of dilution of the acid and the ionic species. However this does not compensate the changes on the solvation of reagents and products.

[43] The gold complex is not stable enough at 30˚C, and some decomposition to metallic gold is observable at this temperature. In addition, the measurement at lower temperature increases very much the solubility of the released methane in organic solvents minimizing the error due to the transference of methane to the gas phase and the heat involved.

[44] BDE is the homolytic bond dissociation energy. We have used this value instead of the heterolytic dissociation energy following the methodology described by Clot et al in reference 30. They have shown that both dissociation energies correlate with M–C BDE, but the homolytic value provides more accurate correlations.

[45] Note that the absolute value of BDE$_{Au-R}$ cannot be obtained from the experimental values unless BDE$_{Au-I}$ was known, which is not the case. Since the calculation by DFT of BDE$_{Au-I}$ would have lead to a more uncertain value than the calculation of BDE$_{C-H}$, we have chosen this approximation.

[46] BDE C–H have been calculated using the methodology described in reference 30.

[47] BabaAhmadi, R.; Ghanbari, P.; Rajabi, N. A.; Hashmi, A. S. K.; Yates, B. F.; Ariafard, A. A Theoretical Study on the Protodeauration Step of the Gold(I)-Catalyzed Organic Reactions. *Organometallics* **2015**, *34*, 3186–3195.

[48] Clot, E.; Mégret, C.; Eisenstein, O.; Perutz, R. N. Validation of the M-C/H-C Bond Enthalpy Relationship through Application of Density Functional Theory. *J. Am. Chem. Soc.* **2006**, *128*, 8350–8357.

[49] Liu, H.-T.; Xiong, X.-G.; Diem Dau, P.; Wang, Y.-L.; Huang, D.-L.; Li, J.; Wang, L.-S. Probing the Nature of Gold–carbon Bonding in Gold–alkynyl Complexes. *Nat. Commun.* **2013**, *4*, 2223.

[50] Raubenheimer H. G.; Schmidbaur, H. Gold Chemistry Guided by the Isolobality Concept. *Organometallics*, **2012**, *31*, 2507–2522

[51] The values obtained with an extended basis set and including dispersion lead to the correlation: y=23.29+ 12.44 n$_{orto}$ +23.82 n$_{meta}$ - 19.29 n$_{para}$ (see figure 2 and SI for details).

[52] Dias, H. V. R.; Dash, C.; Yousufuddin, M.; Celik, M. A.; Frenking, G. Cationic Gold Carbonyl Complex on a Phosphine Support. *Inorg. Chem.* **2011**, *50*, 4253–4255.

[53] Joost, M.; Estévez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. Enhanced π-Backdonation from Gold(I): Isolation of Original Carbonyl and Carbene Complexes. *Angew. Chemie Int. Ed.* **2014**, *53*, 14512–14516.

[54] Li, Z.-F.; Yang, X.-P.; Hui-Xue, L.; Guo, Z. Electronic Structure of Gold Carbonyl Compounds RAuL (R = CF$_3$, BO, Br, Cl, CH$_3$, HCC, Mes$_3$ P, SIDipp; L = CO, N $_2$, BO) and Origins of Aurophilic Interactions in the Clusters [RAuL]. *Organometallics* **2014**, *33*, 5101–5110

[55] Wang, J.; Cao, X.; Lv, S.; Zhang, C.; Xu, S.; Shi, M.; Zhang, J. Synthesis and Structures of Gold and Copper Carbene Intermediates in Catalytic Amination of Alkynes. *Nat. Commun.* **2017**, *8*, 1–10.

[56] Nunes Dos Santos Comprido, L.; Klein, J. E. M. N.; Knizia, G.; Kästner, J.; Hashmi, A. S. K. Gold(I) Vinylidene Complexes as Reactive Intermediates and Their Tendency to π-Backbond. *Chem. Eur. J.* **2016**, *22*, 2892–2895.

[57] Sokolov, A. Y.; Sizova, O. V. Quantum-Chemical Study of Trans Influence in gold(I) Linear Complexes. *Russ. J. Gen. Chem.* **2010**, *80*, 1223–1231.

[58] delPozo, J.; Casares, J. A.; Espinet, P. The Decisive Role of Ligand Metathesis in Au/Pd Bimetallic Catalysis. *Chem. Commun.* **2013**, *49*, 7246–7248.

[59] Carrasco, D.; Garcia-Melchor, M.; Casares, J. A., Espinet, P. Dramatic mechanistic switch in Sn/Au-I group exchanges: transmetalation vs. oxidative addition. *Chem Commun.* **2016**, *23*, 4305-4308.

[60] Hirner, J. J.; Shi, Y.; Blum, S. A. Organogold Reactivity with Palladium, Nickel, and Rhodium: Transmetalation, Cross-Coupling, and Dual Catalysis. *Acc. Chem. Res.*, **2011**, *44*, 603–613.

[61] Chen, Y.; Chen M.; Liu, Y. Gold-Catalyzed Cyclization of 1,6-Diyne-4-en-3-ols: Stannyl Transfer from 2-Tributylstannylfuran Through Au/Sn Transmetalation. *Angew. Chem.* **2012**, *51*, 6181-6186.

[62] Canovese, L.; Levi, C.; Visentin, F.; Santo, C.; Bertolasi, V. Transmetalation between Au(I) and Sn(IV) complexes. The reaction mechanism in non-coordinating and coordinating polar solvents. *Inorg. Chim Acta.* **2013**, *404*, 105-112.

[63] Kinashi, N.; Sakaguchi, K.; Katsumura, S.; Shinada, T. Preparation of E-alpha-stannyl-beta-trimethylsilylethynylacrylate, building block for polyconjugated ylidenebutenolide and its derivatives, by novel E-selective ethynylstannylation of propiolate. *Tetr. Lett.* **2016**, *57*, 129-132.

[64] Kinashi N.; Sakaguchi K.; Katsumura S.; Shinada T. Preparation of E-a-stannyl-b-trimethylsilylethynylacrylate, building block for polyconjugated ylidenebutenolide and its derivatives, by novel E-selective ethynylstannylation of propiolate. *Tetr. Lett.* **2016**, *57*, 129–132.

[65] In order to make the transmetalation of the aryl from tin to gold thermodynamically feasible, chlorine has to be used as halogen for the exchange instead of iodine. See reference 36

[66] Perrin, D. D.; Armarego, W.F.F. Purification of Laboratory Chemicals, 3rd ed.; Pergamon Press: Oxford, U.K.,**1988**.

[67] Usón, R.; Laguna, A.; Sanjoaquin, J. L. Reactions of complexes of gold(I) with bis(pentafluorophenyl)thallium(III) halides. *J. Organomet. Chem.* **1974**, *69*, 361-365.

[68] M. Peña-López, M. Ayán-Varela, L. A. Sarandeses and J. Pérez Sestelo; Palladium-catalyzed cross-coupling reactions of organogold(I) phosphanes with allylic electrophiles, *Org. Biomol. Chem.*, **2012**, *10*, 1686-1694.

[69] Pérez-Temprano, M. H.; Casares, J. A.; Espinet, P. Bimetallic Catalysis Using Transition and Group 11 Metals: An Emerging Tool for C-C Coupling and Other Reactions. *Chem. Eur. J.* **2012**, *18*, 1864–1884.

[70] Weber, D. ; Jones, T. D.; Adduci, L. L.; Gagné, M. R. Strong Electronic and Counterion Effects on Geminal Digold Formation and Reactivity as Revealed by Gold(I)–Aryl Model Complexes, *Angew. Chem. Int. Ed.*, **2012**, *51*, 2452–2456.

[71] Cornella, J.; Rosillo-Lopez, M.; Larrosa, I. A Novel Mode of Reactivity for Gold(I): The Decarboxylative Activation of (Hetero)Aromatic Carboxylic Acids; *Adv. Synth. Catal.*, **2011**, *353*, 1359–1366.

[72] Yam, V. W-W.; Cheung, K.-L.; Cheng, E. C.-C.; Zhu, N.; Cheung K-K. Syntheses and luminescence studies of mixed-metal gold(I)–copper(I) and –silver(I) alkynyl complexes. The "turning-on" of emission upon d[10] metal ion encapsulation, *Dalton Trans.*, **2003**, *9*, 1830-1835.

[73] Max M. Hansmann, Frank Rominger, Michael P. Boone, Douglas W. Stephan, and A. Stephen K. Hashmi; Reactivity of Organogold Compounds with B(C6F5)3: Gold–Boron Transmetalation via σ-B/π-Au Species, *Organometallics*, **2014**, *33*, 4461–4470.

[74] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

[75] Dolg, M.; Stoll, H.; Preuss, H.; Pitzer, R.M. Relativistic and correlation effects for element 105 (hahnium, Ha): a comparative study of M and MO (M = Nb, Ta, Ha) using energy-adjusted ab initio pseudopotentials. *J. Phys. Chem.* **1993***, 97*, 5852-5859.

[76] Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Ab initio* pseudopotentials for Hg through Rn. H. *Mol. Phys.* **1991**, *74*, 1245-1263.

[77] Hariharan, P.C.; Pople, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta* **1973**, *28*, 213 -222.

[78] Dunning, T. H. Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen**.** *J. Chem. Phys.* **1989**, *90*, 1007-1023.

The figure shows the increase on BDE (Bond Dissociation Energy) relative to Au-Ph bond in [AuR(PPh$_3$)] complexes for several R groups. The bond strength Au-R has qualitatively the same electronic dependence on the nature of R than H-R strength, being gold more sensitive to changes than hydrogen. The effect is particularly important for fluoroaryl and alkynyls, for which the Au-R BDE increases much more than H-R BDE.

$$[AuR(PPh_3)] + Ph\cdot \longrightarrow [AuPh(PPh_3)] + R\cdot \qquad \Delta H = \Delta D_R$$