Electronic Supporting Information

Impact of Halogen Bonding Interactions on M–X Bond Activation Pathways: A Perspective

Sritama Maiti[†] [a], *Sreeja Maitra*[†] [a], *Gopal Kanrar* [a], *Koushik Sarkar* [a], *Kausikisankar Pramanik*[*] [b] *and Sanjib Ganguly*[*] [a]

[†] *Authors have equal contribution*

[a] *Department of Chemistry, St. Xavier's College (Autonomous), Kolkata*

[b] *Department of Chemistry, Jadavpur University, Kolkata*

icsgxav@gmail.com

icsg@sxccal.edu

Table S1. Cyclization of the amide (Scheme 1a) in the presence of activators and reference compounds.

Entry	Activator[a]	Conversion[b] to products [%]	k_{rel}[c]
1	None	≤5[d]	-
2	10a[d]	60	1100
3	10b	≤5	10
4	11a[e]	38	660
5	11b	≤5	3
6	12a	≤5	1
7	12b	≤5	-
8	13a	92	3100
9	13b	≤5	18
10	13c	25	330
11	14a	≤5	26
12	$NaBAr^F_4$	95	3500
13	I_2[f]	≤5	-
14	I_2[g]	≤5	-

[a] Activators added in 2 mol% unless indicated otherwise. [b] Conversion determined by ^1H NMR after 3 hours of reaction time, unless indicated otherwise. An error margin of ~5% is assumed. All experiments were reproduced at least twice. [c] Relative initial rates after 70 minutes of reaction time, referenced to **12a** (and rounded to two valid digits). [d] 30 hours reaction time. [e]. The propargylic amide 6 was added to a preformed solution of the activator and the gold complex. Reproduced with permission from ref. 1. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA.

Table S2. Cyclization of malonate ester in the presence of 1 mol% of activators and reference compounds**.**

Entry	Activator[a]	Yield[b] of products [%]	k_{rel}[c]
1	None	≤5[d]	-
2	10a	76	740
3	10b	≤5	14
4	11a	43	420
5	11b	≤5	10
6	12a	≤5	1
7	12b	≤5	10
8	13a	83	830
9	13b	≤5	3
10	14a	≤5	41
11	$NaBAr^F_4$	84	850
12	$TMABAr^F_4$	≤5	5

[a] Activators added in 1 mol%. [b] ^{1}H NMR yield of the products after 40 minutes of reaction time, unless indicated otherwise. An error margin of 5% is assumed. All experiments were reproduced at least twice. [c] Relative initial rates after 20 minutes of reaction time, referenced to **12a** (and rounded to two valid digits). [d] 15 hours reaction time. Reproduced with permission from ref. 1. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA.

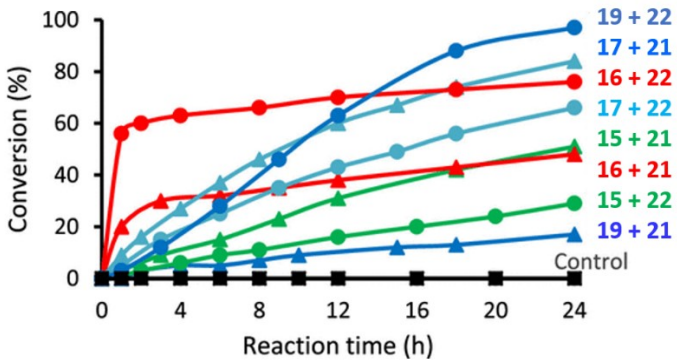


Figure S1. Cyclopropanation of propargyl acetate with vinyl derivative styrene to form cyclopropane as a function of reaction time using gold catalysts and XBDs. Reactions were run at 25 °C, followed by ^{1}H NMR. The runs with the same gold catalyst are shown with the same colour. The control experiments, using 20 mol% gold catalyst **17** without a halogen bond donor, using 20 mol% halogen bond donor **21** without a gold catalyst, using 20 mol% each 1,3-dimesitylimidazolium chloride and gold catalyst **3**, and finally, using 20 mol% gold catalyst **3** with a small amount of HCl, are all shown as black squares. None of the controls gave conversion. Reproduced with permission from ref. 2. Copyright 2022 American Chemical Society.

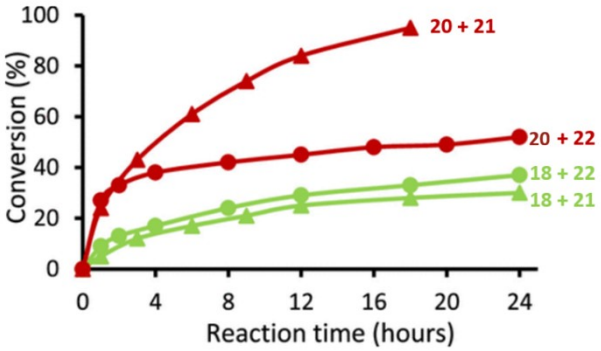


Figure S2. Conversions observed for the cyclopropanation of propargyl acetate (Scheme 1 and Table 1) as a function of reaction time using 7 (triangles) or 8 (circles) to activate gold(III) catalysts 4 (bright green) and 6 (dark red). Reactions were run at 25 °C, and conversion was followed by ^{1}H NMR. Reproduced with permission from ref. 2. Copyright 2022 American Chemical Society.

Table S3. Reactivity of Gold Complexes (Au) **15**−**20** upon Activation with Halogen Bond Donors (Activator) **21** and **22** in cyclopropanation.[a]

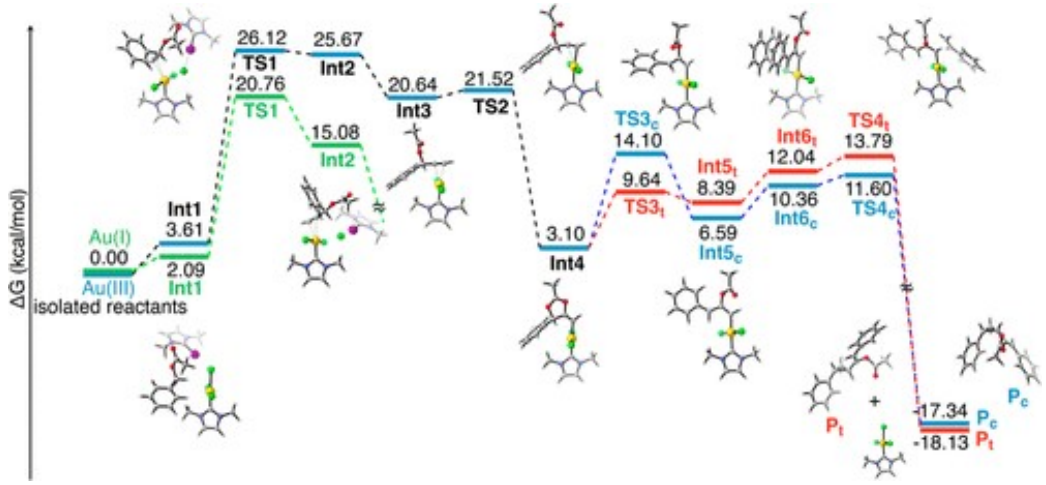
Activator	Au complex	Conversion[b]	k_{rel}[c]
21	15	31	3.2
21	16	38	3.9
21	17	60	5
21	18	25	2.6
21	19	10	1
21	20	84	8.8
22	15	16	1.7
22	16	70	7.3
22	17	43	4.5
22	18	29	3.0
22	19	63	6.6
22	20	45	4.7
none	17	0[d]	-
21	none	0[d]	-
IMes-Cl	17	0[d]	-
HCl	17	0[d]	-

[a] Reactions were performed with 20 mol% of activators **21** and **22** and gold complexes **15**−**20** in CD_2Cl_2 at 25 °C, [Au] = [XBD] = 0.015 M. Both cis and trans isomers of cyclopropanation product are formed, and the reported conversions are given as the sum of those of the isomers. The isomerization is a slow background reaction that takes place in the presence of gold complexes. [b] Conversion. [c] Relative reaction rates measured by ^{1}H NMR at 12 h reaction time (before isomerization). [d] Control experiment. Under "classical" activation conditions, using 5 mol% $AgSbF_6$ to activate the 5 mol% gold complexes, the reactions reach full conversion within 5 min, regardless of the type of gold catalyst used.

Table S4. Conversion of the alkyne and styrene to Cyclopropane (Scheme 1) Using Gold Complexes **15−20** (Au) in Combination with Activator **23** and the Corresponding Relative Reaction Rates (k_{rel}).[a]

Au	Conversion[b]	K_{rel}[c]
1	80	10
2	48	6
3	88	11
4	8	1
5	51	6.4
6	18	2.3

[a] Reactions were performed with 0.5 mol% halogen bond donor **23** and gold complexes **15−20** (0.0015 M each), 0.30 M the alkyne, and 0.60 M styrene in CD_2Cl_2 at 25 °C, monitoring the conversions by ^1H NMR. [b] Conversions. [c] Relative reaction rates (k_{rel}) following 60 min reaction time are shown. As a consequence of the short reaction times, no cis to-trans isomerization was observed. Reproduced with permission from ref. 2. Copyright 2022 American Chemical Society.



Scheme S1. Simplified models of the gold(I/III) catalysts **17/18** were used due to the time limitations of DFT calculations. Following **Int4**, the reaction route leading to the *trans* product is shown in red whereas that to the *cis* product in blue. Relative stabilities are given in kcal/mol, with respect to the energy of the isolated fragments of the reactants. Computations were done at the B3LYP-D3BJ/Def2-TZVP. Reproduced with permission from ref. 2. Copyright 2022 American Chemical Society.

References

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2. H. F. Jónsson, D. Sethio, J. Wolf, S. M. Huber, A. Fiksdahl and M. Erdélyi, *ACS Catal.*, 2022, **12**, 7210–7220