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Gold *versus* Silver-Catalyzed Intermolecular Hydroaminations of Alkenes and Dienes

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Dedicated to Prof. Avelino Corma on the occasion of his 60th birthday

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Abstract: Comparative studies about the hydroamination of unactivated alkenes and dienes catalyzed by either cationic gold(I) triphenyl phosphite complexes or silver salts were performed using sulfonamides, anilines and carbamates as nucleophiles. Gold-catalyzed reactions generally, need lower loadings than those carried out with silver salts. Simple alkenes react only with sulfonamides and weak aromatic amines such as *p*-nitroaniline, whereas for conjugated dienes carbamates can also be used. Carbon-carbon double bond isomerization is observed only with gold similarly to when triflic acid was used, affording mixtures of regioisomeric products in the same cases. Silver-catalyzed hydroaminations failed with terminal alkenes, except with styrenes. Conjugate dienes can be hydroaminated either at 85 °C in toluene or at room temperature in dichloromethane. Non-conjugated 1,4- and 1,5-dienes suffer double hydroamination leading to saturated *N*-tosylated heterocyclic amines The catalytic cycle for the silver(I)-catalyzed hydroamination process has been computationally analyzed, resembling gold(I)-catalyzed processes, although with some significant differences.

Keywords: alkenes; dienes; gold(I) complexes; silver salts; sulfonamides

Introduction

The catalyzed hydroamination (HA) of alkenes, allenes, dienes and alkynes is a fundamental transformation for the synthesis of acyclic and heterocyclic amines, enamines and imines.[1] Over the last two decades several Brønsted and Lewis acids have shown catalytic activity in atom-economical inter- and intramolecular hydroaminations of unsaturated systems. In spite of this great effort, several aspects should still be improved, especially in intermolecular catalyzed HA processes, such as its suitability for different unactivated alkenes, as well as the isomerization and dimerization of these substrates and the catalyst efficiency.

Several Brønsted acids, such as triflic acid,[2] $PhNH_3B(C_6F_5)_4$,[3] proton-exchange montmorillonite,[4] silicotungstic acid,[5] phosphomolybdic acid supported on silica gel[6] and SO_3H-functionalized ionic liquids[7] have been used for the intermolecular hydroamination of olefins and conjugated dienes. Iodine[8] and *N*-bromosuccinimide[9] have been recently employed for the addition of sulfonamides[8,9] and carbamates[9] to vinylarenes. The acid-catalyzed addition of nitrogenated compounds to alkenes needs an adequate acid-base compatibility for successful reactions; sulfonamides, carboxamides, carbamates and anilines are the most common nucleophilic reagents. Similar considerations can be made when metal salts or complexes are used as catalysts. $Bi(OTf)_3/[Cu(CH_3CN)_4]PF_6$ for 1,3-dienes,[10] $Cu(OTf)_2$/dppe for styrenes, norbornene and cyclohexa-1,3-diene,[11] $FeCl_3$ for styrenes,[12] $InBr_3$,[13] $Zr(OTf)_4$,[14] and Pt(II) complexes activated by $AgBF_4$[15] for acyclic and cyclic alkenes have also been used in HA reactions. Other homogeneous catalysts, such as alkali metal amides,[16] lanthanides,[17] and early (Ti, Zr) transition metals[18] work mainly

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with amines forming metal-amide and metal-imide intermediates in the last case. Late transition metals (Ru, Rh, Pd, Ni, Ir, Au) catalyzed the HA of alkenes mainly with nitrogenated nucleophiles of low basicity, such as anilines, carboxamides and sulfonamides by a C–C activation mechanism.[19]

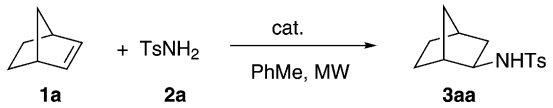
Notable progress has been achieved in this decade using gold-catalyzed processes.[20] Among them intermolecular HA reactions of unactivated alkenes and 1,3-dienes have been performed with electrophilic gold(I) complexes using sulfonamides and carbamates as nucleophiles.[21,22] Recently, we have communicated that (triphenyl phosphite)gold(I) chloride/AgOTf[23] is a more efficient catalyst than the same combination with triphenylphosphine. Performing control experiments we found that AgOTf also catalyzed this intermolecular HA reaction.[24] In this full paper we compare the scope and activities of Au(I) and Ag(I) as catalysts[25] in the intermolecular HA of alkenes and dienes, along with a DFT-based study focused on the elucidation of the reaction mechanism.

Results and Discussion

Catalyst Screening

The hydroamination of norbornene (**1a**) with *p*-toluenesulfonamide (**2a**), in anhydrous toluene under argon using MW heating, was chosen as a model reaction for catalyst screening (Table 1). Gold(I) chloride without and with triphenylphosphine as ligand combined with silver triflate or tetrafluoroborate gave high yields >90% using 5 mol% loading (Table 1, entries 1–4). The reaction time could be decreased from 30 to 15 min when triphenylphosphine was used as ligand. When the loadings of the last two complexes were reduced to 0.1 mol%, compound **3aa** was ob-

Table 1. Catalysts screening for the addition of $TsNH_2$ to norbornene.[a]



1a **2a** **3aa**

Entry	Catalyst [mol%]	Temperature [°C]	Time [min]	Yield [%][b]
1	AuCl/AgOTf (5)	90	30	96
2	AuCl/$AgBF_4$ (5)	85	15	90
3	(Ph_3P)AuCl/AgOTf (5)	85	15	99 (92)
4	(Ph_3P)AuCl/$AgBF_4$ (5)	85	15	99
5	(Ph_3P)AuCl/AgOTf (0.1)	90	30	58
6	(Ph_3P)AuCl/$AgBF_4$ (0.1)	85	15	1
7	$[(BTFP)_3P]$AuCl/AgOTf (5)	85	15	99
8	$[(BTFP)_3P]$AuCl/$AgBF_4$ (5)	85	15	80
9	$[(PhO)_3P]$AuCl/AgOTf (5)	85	15	99
10	$[(PhO)_3P]$AuCl/AgOTf (1)	90	30	99
11	AgOTf (1)	90	30	98 (73)
12	$[(PhO)_3P]$AuCl/AgOTf (0.1)	90	30	99
13	$[(PhO)_3P]$AuCl/AgOTf (0.05)	90	30	94 (90)
14	AgOTf (0.05)	90	30	82
15	$[(PhO)_3P]$AuCl/AgOTf (0.01)	90	30	60
16	$[(PhO)_3P]$AuCl/$AgClO_4$ (1)	90	30	99
17	$AgClO_4$ (1)	90	30	22
18	$[(PhO)_3P]$AuCl/$AgClO_4$ (0.5)	90	30	99
19	$[(PhO)_3P]$AuCl/$AgClO_4$ (0.1)	90	30	78
20	$[(PhO)_3P]$AuCl/$AgClO_4$ (0.05)	90	30	75
21	$[(PhO)_3P]$AuCl/$AgClO_4$ (0.01)	90	30	10
22	$[(PhO)_3P]$AuCl/$AgBF_4$ (1)	90	30	4
23	$AgBF_4$ (1)	90	30	5
24	$[(PhO)_3P]$AuCl/$AgSbF_6$ (1)	90	30	99
25	$AgSbF_6$ (1)	90	30	99 (98)
26[c]	$[(PhO)_3P]$AuCl/AgOTf (0.05)	85	–[d]	75

[a] Reactions were performed with $TsNH_2$ (171 mg, 1 mmol), norbornene (376 mg, 4 mmol), catalyst (see column) in dry toluene (2 mL) under argon in a microwave reactor (70 W, 10 psi) with air stream cooling.
[b] Determined by GC, based on $TsNH_2$. In parenthesis isolated yield after flash chromatography.
[c] Reaction was performed with conventional heating in air without light protection.
[d] 14 h.

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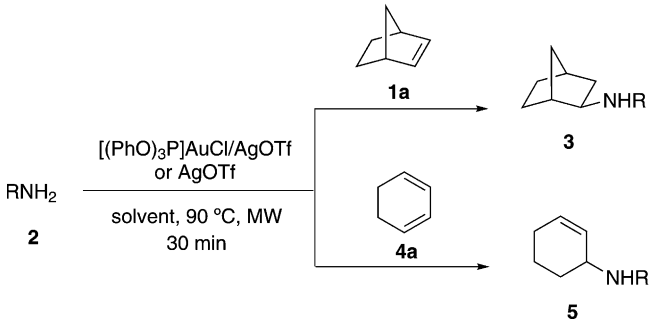
Table 2. Hydroamination of norbornene and 1,3-cyclohexadiene with different nucleophiles.[a]



Entry	Catalyst[mol%]	RNH_2	Solvent	Product No.	Yield [%][b]
1[c]	Au (0.05)	$TsNH_2$ (**2a**)	PhMe	**3aa**	94 (90)
2[c]	Ag (1)	$TsNH_2$ (**2a**)	PhMe	**3aa**	98 (73)
3[c]	Au (0.1)	4-MeO-$C_6H_4SO_2NH_2$ (**2b**)	PhMe	**3ab**	99 (96[d])
4	Ag (5)	4-MeO-$C_6H_4SO_2NH_2$ (**2b**)	PhMe	**3ab**	32
5	Au (5)	4-NO_2-$C_6H_4SO_2NH_2$ (**2c**)	PhMe	**3ac**	0
6	Au (5)	$MeSO_2NH_2$ (**2d**)	dioxane	**3ad**	(65)
7	Ag (5)	$MeSO_2NH_2$ (**2d**)	dioxane	**3ad**	57
8	Au (5)	*p*-NO_2-$C_6H_4NH_2$ (**2g**)	PhMe	**3ag**	88 (81)
9	Ag (5)	*p*-NO_2-$C_6H_4NH_2$ (**2g**)	PhMe	**3ag**	0
10[e]	Au (0.1)	$TsNH_2$ (**2a**)	PhMe	**5aa**	66
11	Ag (5)	$TsNH_2$ (**2a**)	PhMe	**5aa**	86
12	Au (1)	4-MeO-$C_6H_4SO_2NH_2$ (**2b**)	dioxane	**5ab**	77 (60)
13	Ag (1)	4-MeO-$C_6H_4SO_2NH_2$ (**2b**)	dioxane	**5ab**	0
14	Ag (5)	4-MeO-$C_6H_4SO_2NH_2$ (**2b**)	PhMe	**5ab**	60
15[f]	Au (5)	$MeSO_2NH_2$ (**2d**)	CH_2Cl_2	**5ad**	(75)
16	Ag (5)	$MeSO_2NH_2$ (**2d**)	dioxane	**5ad**	(47)
17	Au (5)	saccharin (**2e**)	PhMe	**5ae**	0
18	Ag (1)	saccharin (**2e**)	PhMe	**5ae**	45 (27)
19[g]	Au (5)	$CBzNH_2$ (**2f**)	$(CH_2Cl)_2$	**5af**	98 (65)
20[g]	Ag (5)	$CBzNH_2$ (**2f**)	$(CH_2Cl)_2$	**5af**	99 (96)
21	Au (5)	*p*-NO_2-$C_6H_4NH_2$ (**2g**)	PhMe	**5ag**	56 (52)
22	Ag (5)	*p*-NO_2-$C_6H_4NH_2$ (**2g**)	PhMe	**5ag**	25

[a] Reactions were performed with amide (1 mmol), alkene or diene (4 mmol), catalyst (see column) in dry solvent (2 mL) under Ar in a microwave reactor (70 W, 10 psi) at 90 °C for 30 min with air stream cooling.
[b] Determined by GC, based on RNH_2. In parenthesis isolated yield after flash chromatography.
[c] 1.2 equiv. of norbornene (**1a**) were used.
[d] After recrystallization from hexane/EtOAc.
[e] 1.2 equiv. of cyclohexa-1,3-diene (**4a**) were used.
[f] Reaction performed at room temperature during 24 h.
[g] Under conventional thermal conditions at 50 °C during 23 h.

tained in only 58% and 1% yields, respectively, (Table 1, entries 5 and 6). When the more electron-withdrawing ligand tris[3,5-bis(trifluoromethyl)phenyl]phosphine[26] was used for the preparation of the LAuCl complex and AgOTf or $AgBF_4$ as silver salts, 99% and a lower 80% yield were obtained, respectively (Table 1, entries 7 and 8). A less expensive strong π-acceptor phosphorus ligand such as triphenyl phosphite was used for gold(I) chloride[27] and AgOTf[26] as silver salt. In this case quantitative yields of **3aa** with 5 mol% and even with 1 mol% loadings were obtained, although with the reaction time increasing from 15 to 30 min (Table 1, entries 9 and 10). The same gold complex without a silver salt gave negligible yields. Silver triflate gave 98% yield using the same conditions as with $[(PhO)_3P]AuCl/AgOTf$ (Table 1, compare entries 10 and 11). The loading of the gold catalyst formed by $[(PhO)_3P]AuCl/AgOTf$ could be decreased to 0.1 and 0.05 mol% providing **3aa** in high yields. However, with only 0.01 mol% loading the yield dropped down to 60% (Table 1, entries 12, 13, and 15). These results indicate that triphenyl phosphite was a more efficient ligand than the phosphines (Table 1, compare entry 5 with 12 and 13). Silver triflate provided a lower (82%) yield compared to when the gold complex was used, both in

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0.05 mol% loading (Table 1, compare entries 13 and 14).

The use of 1 mol% of silver perchlorate either combined with $[(PhO)_3P]AuCl$ or alone, gave 99% and 22% of **3aa**, respectively (Table 1, entries 16 and 17). The loadings of the phosphite ligand and $AgClO_4$ were decreased to 0.5, 0.1, 0.05 and 0.01 mol% giving product **3aa** in quantitative yield only in the first case (Table 1, entries 18–21). From these results it can be concluded that AgOTf is a more efficient salt than $AgClO_4$ for this transformation. On the other hand, $AgBF_4$ failed with or without the gold(I) complex (Table 1, entries 22 and 23). However, $AgSbF_6$ showed a good efficiency using 1 mol% loading (Table 1, entries 24 and 25). Under conventional heating the best reaction (Table 1, entry 13) needed 14 h giving a lower 75% yield (Table 1, entry 26).

Nucleophile Screening

When different amides such as sulfonamides and carbamates were allowed to react with norbornene (**1a**) in the presence of $[(PhO)_3P]AuCl$/AgOTf or simple AgOTf as catalysts, only electron-rich sulfonamides were appropriate nucleophiles for this HA (Table 2, entries 1–7). The HA with *p*-toluenesulfonamide (**2a**) worked with both Au and Ag catalysts, but a higher loading must be used in the latter case (Table 2, entries 1 and 2). However, the addition of *p*-methoxybenzenesulfonamide (**2b**) only took place efficiently when using 0.1 mol% of the gold complex (Table 2, entries 3 and 4), whereas in the case of *p*-nitrobenzenesulfonamide (**2c**), the Au-catalyzed HA failed (Table 2, entry 5). For the HA with methanesulfonamide (**2d**), the catalyst loading should be increased to 5 mol% and dioxane instead of toluene must be used as solvent due to solubility problems. Again, the gold complex showed better catalytic performance than the silver salt, affording product **3ad** in 65% yield (Table 2, entries 6 and 7). A weak basic amine such as *p*-nitroaniline (**2g**) could be used only for the gold-catalyzed HA of **1a** providing **3ag** in 81% yield using a 5 mol% catalyst loading (Table 2, entries 8 and 9). In general, gold-catalyzed HA needed a lower catalyst loading than the silver counterparts but only in the case of norbornene.

Cyclohexa-1,3-diene (**4a**) was used as a representative conjugate diene for the HA reaction with different sulfonamides, carbamates and *p*-nitroaniline as nucleophiles working under microwave heating at 90 °C during 30 min (Table 2, entries 10–22). In the case of *p*-toluenesulfonamide (**2a**), 0.1 mol% of Au catalyst and 5 mol% of AgOTf were used affording product **5aa** in 66% and 86% yields, respectively (Table 2, entries 10 and 11).

Similar experiments were carried out with *p*-methoxybenzenesulfonamide (**2b**) and methanesulfonamide (**2d**) as nucleophiles in dioxane or dichloromethane affording products **5ab** and **5ad**, respectively, in moderate yields (Table 2, entries 12–16). The reaction of **4a** with *p*-methoxybenzenesulfonamide (**2b**) catalyzed by AgOTf failed in dioxane and was carried out in toluene (Table 2, entry 14). The HA with saccharin (**2e**) only took place with 1 mol% of AgOTf giving **5ae** in a modest 27% yield (Table 2, entries 17 and 18). Benzyl carbamate (**2f**) could be added to cyclohexadiene (**4a**) using either Au or Ag as catalysts, but under conventional heating at 50 °C for *ca.* 1 d in 1,2-dichloroethane as solvent, yielding 65% or 96% of product **5af**, respectively (Table 2, entries 19 and 20). In the case of *p*-nitroaniline compound **5ag** was obtained in 52% yield using the gold catalyst, compared to a modest 25% yield when using Ag, in both cases

Table 3. Hydroamination of alkenes with $TsNH_2$ catalyzed by either by $[(PhO)_3P]AuCl$/AgOTf or AgOTf and by TfOH.[a]

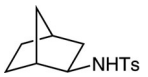
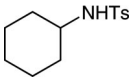
Entry	Alkene	No.	Solvent	Catalyst (mol%)	Temperature [°C]	Time	Product	No.	Yield [%][b]
1		**1a**	PhMe	Au (0.05)	85	14 h		**3aa**	(99)
2			PhMe	Ag (0.5)	85	4 h			96[c] (99)
3			PhMe	Au (0.05)	90	30 min[d]			90[c] (94)
4			PhMe	Ag (1)	90	30 min[d]			73 (98)
5			PhMe	TfOH (0.1)	90	30 min[d]			8
6			CH_2Cl_2	Au (5)	25	24 h			3
7			CH_2Cl_2	Ag (5)	25	24 h			(99)
8			CH_2Cl_2	TfOH (1)	25	24 h			91[2c]
9		**1b**	PhMe	Au (2)	85	24 h		**3ba**	64 (84)
10			PhMe	Ag (2)	85	14 h			38 (50)
11			PhMe	TfOH (1)	85	22 h			58[2c]
12			neat	Au (5)	90	30 min[d]			(35)
13			neat	Ag (5)	90	30 min[d]			71 (88)
14			neat	Au (2)	85	14 h			84 (95)
15			neat	Ag (2)	85	14 h			(21)

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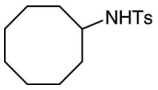
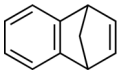
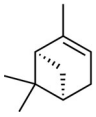
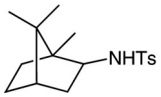
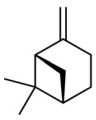
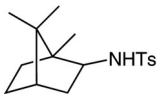
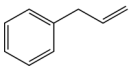
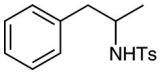
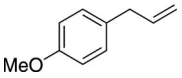
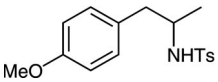
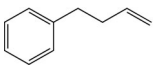
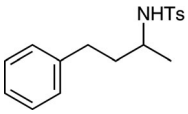
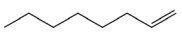
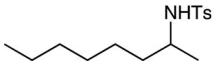
Table 3. (Continued)

Entry	Alkene	No.	Solvent	Catalyst (mol%)	Temperature [°C]	Time	Product	No.	Yield [%][b]
16		**1c**	PhMe	Au (1)	85	24 h		**3ca**	75 (98)
17			PhMe	Ag (4)	85	14 h			(4)
18		**1d**	PhMe	Au (1)	90	30 min[d]		**3da**	90 (98)
19			PhMe	Ag (1)	90	30 min[d]			25 (53)
20		**1e**	neat	Au (5)	85	14 h		**3ea**	70 (98)
21			neat	Ag (5)	85	14 h			79 (98)
22			neat	TfOH (1)	85	14 h			(66)
23		**1f**	neat	Au (5)	85	14 h		**3ea**	60 (98)
24			neat	Ag (5)	85	14 h			(0)
25			neat	TfOH (1)	85	14 h			(57)
26		**1g**	PhMe	Au (5)	85	14 h		**3ga**	(61)
27			PhMe	Ag (5)	85	14 h			(72)
28			PhMe	TfOH (5)	85	14 h			70[2c]
29			PhMe	Au (5)	90	30 min[d]			66 (78)
30			PhMe	Ag (5)	90	30 min[d]			58 (76)
31		**1h**	PhMe	Au (5)	85	24 h		**3ha**	68 (80)[e]
32			PhMe	Ag (5)	85	24 h			(0)
33			PhMe	Au (5)	90	30 min[d]			(59)[f]
34		**1i**	PhMe	Au (5)	85	24 h		**3ia**	65 (99)[g]
35			PhMe	Ag (5)	85	24 h			0
36			PhMe	Au (5)	90	30 min[d]			91 (95)[g]
37			PhMe	Ag (5)	90	30 min[d]			(0)
38			PhMe	TfOH (5)	90	30 min[d]			75 (97)[h]
39		**1j**	PhMe	Au (5)	85	14 h		**3ja**	73 (78)[i]
40			PhMe	Ag (5)	85	14 h			0
41			PhMe	Au (5)	90	30 min[d]			34
42			PhMe	Ag (5)	90	30 min[d]			0
43		**1k**	PhMe	Au (5)	85	14 h		**3ka**	26 (27)
44			PhMe	Ag (5)	85	14 h			1
45			neat	Au (5)	85	14 h			91 (98)[j]
46			neat	Ag (5)	85	14 h			0

[a] Reactions were performed with $TsNH_2$ (171 mg, 1 mmol), alkene (4 mmol), catalyst (see column) in dry solvent (2 mL) or under solvent-free conditions under conventional or MW heating and argon atmosphere.
[b] Isolated yield after flash chromatography. In parenthesis isolated crude yield determined by GC based on $TsNH_2$.
[c] Isolated yield after recrystallization.
[d] Under microwave heating (70 W, 10 psi) with air stream cooling.
[e] 19% of *N*-tosyl-1-phenyl-1-propanamine was also obtained.
[f] 45% of *N*-tosyl-1-phenyl-1-propanamine was also obtained.
[g] 9% of *N*-tosyl-1-(*p*-methoxyphenyl)-1-propanamine was also obtained.
[h] 25% of *N*-tosyl-1-(*p*-methoxyphenyl)-1-propanamine was also obtained.
[i] 2.2% of *N*-tosyl-1-phenyl-2-butanamine and 0.4% of *N*-tosyl-1-phenyl-1-butanamine were also obtained.
[j] 33% of *N*-tosyl-3-octanamine and 22% of *N*-tosyl-4-octanamine were also obtained.

with a 5 mol% loading (Table 2, entries 21 and 22). In general, the conjugate diene **4a** showed higher reactivity than norbornene with a wider scope concerning nucleophiles. Gold- and silver-catalyzed HA reactions of cyclohexa-1,3-diene showed similar efficiency, gold only failing when saccharin was used as nucleophile.

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Au- *vs.* Ag-Catalyzed Hydroamination of Alkenes

The scope of the gold *versus* silver-catalyzed HA of different cyclic and acyclic alkenes was studied with *p*-toluenesulfonamide (**2a**) under conventional or microwave heating (Table 3). Several experiments were also carried out to make comparisons with TfOH-catalyzed hydroaminations either previously described or performed by us under the same conditions. In the case of norbornene (**1a**) the HA took place in >94% yield either in the presence of the gold complex (0.05 mol%) or silver salt (0.5–1 mol%), both at 85 °C under conventional heating and under microwave irradiation at 90 °C (Table 3, entries 1–4). However, TfOH gave only 8% of **3aa** under MW heating (Table 3, entry 5). Hydroaminations at room temperature took place only using 5 mol% of AgOTf or 1 mol% of TfOH,[2c] affording **3aa** in quantitative yields, whereas Au failed under these reaction conditions (Table 3, compare entries 6–8).

For the HA of cyclohexene (**1b**) in toluene, 2 mol% of gold or silver catalysts were used under heating at 85 °C achieving 64% or 38% yield, respectively, of product **3ba** (Table 3, entries 9 and 10), whereas a 58% yield was obtained when using 1 mol% of TfOH as catalyst (Table 3, entry 11).[2c] Under solvent-free conditions, silver was a better catalyst than gold under MW heating, whereas gold was better than silver under conventional heating (Table 3, entries 12–15). The highest yield (84%) for compound **3ba** was obtained by conventional heating under solvent-free conditions using the gold complex (2 mol%) as catalyst (Table 3, entry 14).

Cyclooctene (**1c**) showed a lower reactivity than cyclohexene and could be hydroaminated with *p*-toluenesulfonamide using 1 mol% of the gold catalyst (Table 3, entry 16). 1,4-Dihydro-1,4-methanonaphthalene (**1d**)[29] was also hydroaminated at 85 °C under MW heating to afford product **3da** in higher 90% yield using 1 mol% of gold, whereas only a 25% yield was obtained in the case of the silver salt (Table 3, entries 18 and 19).

(+)-α-Pinene (**1e**) and (−)-β-pinene (**1f**) afforded the same racemic *N*-tosylisobornylamine (**3ea**)[30] using the cationic gold complex (5 mol%) as catalyst, but only under solvent-free conditions and heating at 85 °C (Table 3, entries 20 and 23). However, AgOTf was an efficient catalyst only in the case of **1e**, the HA failing in the case of **1f** (Table 3, entries 21 and 24). Under the same neat conditions and in the presence of 1 mol% of TfOH, **3ea** was obtained in 66% and 57% yield, respectively, although accompanied by secondary products derived from **1e** and **1f** (Table 3, entries 22 and 25). It can be proposed that **1e** after the coordination to Au or Ag at the *endo*-face gave rise to a tertiary carbocation that suffeed a typical 1,2-Wagner–Meerwein shift to afford the corresponding isobornyl cation. In order to explain the racemization process, this isobornyl cation should suffer a metallotropy if the metal is in an *endo*-position. Final attack of the *p*-toluenesulfonamide to the less hindered *exo*-position followed by protonolysis provided racemic **3ea** and regeneration of the catalyst (Scheme 1). In the case of **1f**, after the coordination to the cationic gold complex, subsequent rearrangement would result in the formation of two isobornyl cations by prototropy which, after subsequent nucleophilic *exo*-attack by the *p*-toluenesulfonamide and protonolysis, would give rise to racemic **3ea**. In general, cyclic alkenes can be hydroaminated by both gold and silver catalysts, except for exocyclic alkenes such as β-pinene, which did not react when AgOTf was used as catalyst.

Styrene (**1g**) gave product **3ga** in moderate yields either under conventional or MW heating with both gold and silver catalysts and TfOH[2b] in toluene (Table 3, entries 26–30). However, the homologous allylbenzene (**1h**) reacted with *p*-toluenesulfonamide only under gold catalysis (Table 3, entries 31–33).

Compound **3ha** was mainly obtained together with its regioisomer *N*-tosyl-1-phenyl-1-propanamine in a 4/1 ratio when heating to 85 °C, (Table 3, entry 31). Similarly, *p*-methoxyallylbenzene (**1i**) gave product **3ia** and its regioisomer *N*-tosyl-1-(*p*-methoxyphenyl)-1-propanamine in a *ca.* 10/1 and 4/1 ratio, respectively, only under gold or TfOH catalysis (Table 3, entries 34, 36, and 38). However, AgOTf was inefficient under both conditions (Table 3, entries 35 and 37). 4-Phenylbut-1-ene (**1j**) was efficiently hydroaminated in toluene at 85 °C using 5 mol% of the gold complex to provide compound **3ja** together with small amounts of *N*-tosyl-1-phenylbut-2-amine and -1-amine (Table 3, entry 39). Nevertheless, when MW heating was used, very poor results were obtained (Table 3, entry 41), again the silver-catalyzed reactions failed (Table 3, entries 40 and 42). For other terminal acyclic alkenes, such as oct-1-ene (**1k**), the HA took place in high yield only under solvent-free conditions using the gold complex as catalyst (Table 3, entries 43–46). In this case, product **3ka** was obtained together with regioisomeric sulfonamides at the 3- and 4-positions of the aliphatic skeleton, in 2/1.5/1 ratio.

It can be concluded that in the case of monosubstituted olefins only styrenes were reactive in both Au and Ag catalysis, whereas AgOTf gave very poor catalytic activity with the alkyl-substituted ones. This different behaviour between Au and Ag is probably due to the fact that terminal alkenes are less prone to suffer HA due to competitive C=C isomerization in acid-catalyzed reactions.

When 0.5 mL of 4-phenyl-but-1-ene (**1j**) was allowed to react with the gold complex (0.05 mmol) or with AgOTf (0.05 mmol) overnight at 85 °C, only the former produced isomerization of the C=C double

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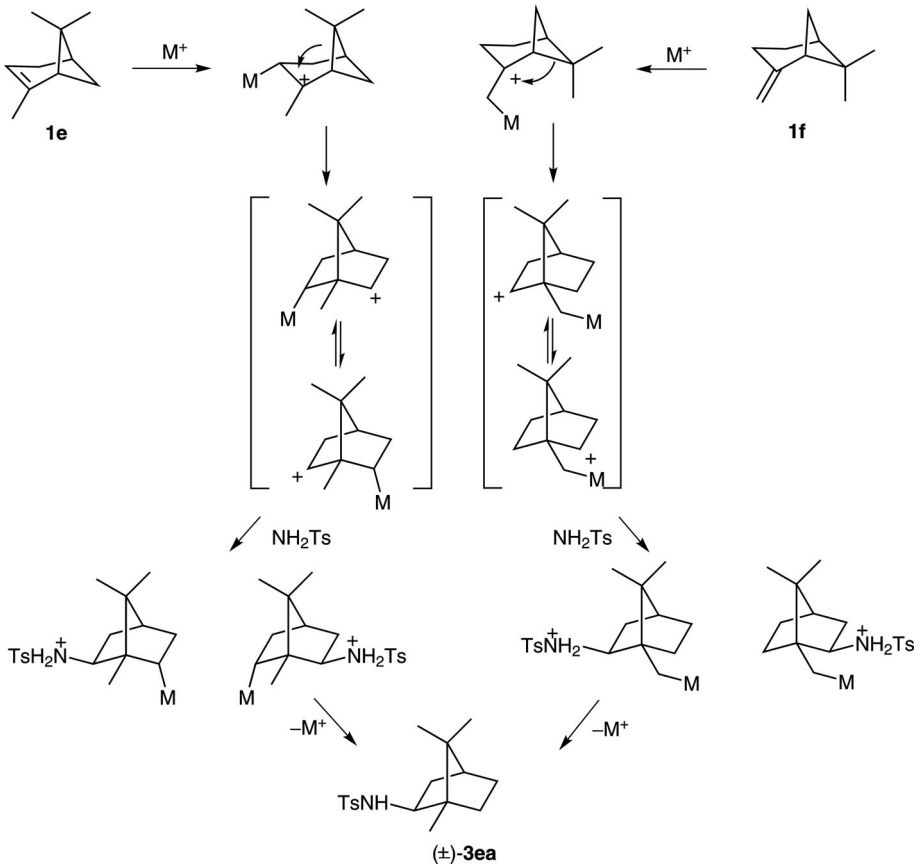

Scheme 1. Postulated mechanisms for the formation of compound **3ea**.

bond giving a 3/1 mixture of 4-phenylbut-1-ene and 4-phenylbut-2-ene. In addition to the inability of AgOTf to isomerize alkenes, we have observed much cleaner reactions with Ag than with Au, because only gold afforded alkene dimerization by-products. The reason why only Au promotes the double bond migration is still unclear and further investigation is needed. It can be proposed that, after coordination of cationic Au or Ag with the C=C double bond, gold forms better covalent sigma bonds with the C atom than silver[31] generating the corresponding vicinal carbenium cation. Alternatively, TfOH can be employed as catalyst giving similar results to those with the Au complex but affording more secondary by-products.

Au- *vs.* Ag-Catalyzed Hydroaminations of Dienes

Hydroamination of dienes was also performed with *p*-toluenesulfonamide as nucleophile (Table 4). Conjugated 1,3-dienes showed a higher reactivity than alkenes using both catalysts either under heating or at room temperature, except for cycloocta-1,3-diene (**4b**) (Table 4, entries 1–28). Cyclohexa-1,3-diene (**4a**) was hydroaminated in toluene under conventional and MW heating using low catalyst loadings (Table 2, entries 1, 2 and 4). However, when AgOTf was used as catalyst under the latter conditions 5 mol% was necessary to provide **5aa** in good yield (Table 2, entry 5). In the case of using TfOH, **5aa** was obtained in 63% yield using 1 mol% loading at 50 °C (Table 4, entry 3).[2c] Working under room temperature conditions, the use of 1 mol% of gold complex in dichloromethane as solvent afforded **5aa** in 90% yield (Table 4, entries 6 and 7). As mentioned above, cycloocta-1,3-diene (**4b**) gave moderate yields of product **5ba** only under heating at 85 °C and in toluene as solvent (Table 4, entries 8–12). Acyclic dienes, such as penta-1,3-diene (**4c**) and 3-methylpenta-1,3-diene (**4d**), were successfully hydroaminated under the three sets of reaction conditions (Table 4, entries 13–28). In addition, diene **4c** was used as a *Z/E*: 1/1.8 diastereomeric mixture and afforded product **5ca** mainly as the *E*-diastereomer (Table 4, entries 13–18), especially under room temperature conditions (Table 4, entries 17 and 18). Working under room temperature conditions, TfOH provided **5ca** in similar yield (Table 4, entry 19). Moreover, similar results were observed in the case of 3-methylpenta-1,3-diene (**4d**) that is available commercially as a *Z/E*: 1/2.5 diastereomeric mixture (Table 4, entries 20–28). Furthermore, the corresponding hydroamination with *p*-tol-

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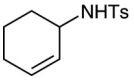
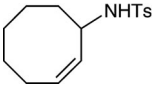
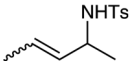
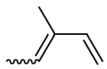
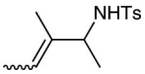
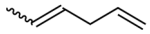
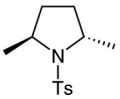
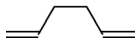
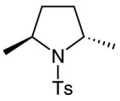
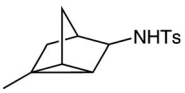
Table 4. Hydroamination of dienes with $TsNH_2$ catalyzed by either by $[(PhO)_3P]AuCl/AgOTf$ or AgOTf and by TfOH.[a]

Entry	Diene	No.	Solvent	Cat.alyst (mol%)	Temperature [°C]	Time	Product	No.	Yield [%][b]	*Z/E* Ratio[c]
1		**4a**	PhMe	Au (0.1)	85	14 h		**5aa**	(68)	
2			PhMe	Ag (0.1)	85	14 h			76 (87)	
3			PhMe	TfOH (1)	50	25 h			63[2c]	
4			PhMe	Au (0.1)	90	20 min[d]			(66)	
5			PhMe	Ag (5)	90	30 min[d]			(86)	
6			CH_2Cl_2	Au (1)	25	24 h			90 (99)	
7			CH_2Cl_2	Ag (1)	25	24 h			49 (58)	
8		**4b**	PhMe	Au (1)	85	14 h		**5ba**	51 (64)	
9			PhMe	Ag (1)	85	14 h			52 (66)	
10			PhMe	TfOH (1)	85	22 h			58[2c]	
11			neat	Au (1)	85	14 h			(14)	
12			neat	Ag (1)	85	14 h			(9)	
13		**4c**[e]	PhMe	Au (0.1)	85	14 h		**5ca**	(85)	1/5
14			PhMe	Ag (0.1)	85	14 h			73 (88)	1/4.3
15			PhMe	Au (0.1)	90	30 min[d]			85 (97)	1/7
16			PhMe	Ag (0.1)	90	30 min[d]			(52)	1/11
17			CH_2Cl_2	Au (1)	25	24 h			65 (99)	1/16
18			CH_2Cl_2	Ag (1)	25	24 h			(66)	1/26
19			CH_2Cl_2	TfOH (1)	25	24 h			55 (77)	1/8
20		**4d**[f]	PhMe	Au (0.1)	85	14 h		**5da**	77 (98)	1/6
21			PhMe	Ag (0.1)	85	14 h			73 (88)	1/8
22			PhMe	TfOH (0.1)	85	24 h			(21)	1/49
23			PhMe	Au (0.1)	90	30 min[d]			85 (97)	1/6
24			PhMe	Ag (0.1)	90	30 min[d]			(90)	1/11
25			PhMe	TfOH (0.1)	90	30 min[d]			(51)	1/21
26			CH_2Cl_2	Au (1)	25	24 h			86 (99)	1/49
27			CH_2Cl_2	Ag (1)	25	24 h			(66)	1/49
28			CH_2Cl_2	TfOH (1)	25	24 h			59 (93)	1/49
29		**4e**	neat	Au (5)	85	14 h		**6a**	83 (79)[g]	
30			neat	Ag (5)	85	14 h			(27)[h]	
31		**4f**	PhMe	Au (5)	85	14 h		**6a**	(47)	
32			neat	Au (5)	85	14 h			44 (56)[i]	
33			neat	Ag(5)	85	14 h			(3)	
34			neat	TfOH (5)	85	14 h			(23)	
35		**4j**	neat	Au (2)	90	30 min[d]		**7a**	70 (96)	
36			neat	Ag (2)	90	30 min[d]			0	
37			neat	TfOH (1)	90	30 min[d]			(94)	
38			neat	Au (2)	85	14 h			(98)	
39			neat	TfOH (1)	85	14 h			(98)	
40		**4k**	neat	Au (5)	85	14 h		**8a**	44 (61)	
41			neat	Ag (5)	85	14 h			54 (85)	
42			neat	TfOH (1)	85	14 h			(70)	

[a] Reactions were performed with $TsNH_2$ (171 mg, 1 mmol), diene (4 mmol), catalyst (see column) in dry solvent (2 mL) or under solvent-free conditions under conventional or MW heating and argon atmosphere.
[b] Isolated yield after flash chromatography. In parenthesis isolated crude yield determined by GC based on $TsNH_2$.
[c] Determined by ^1H NMR over the crude product.
[d] Under microwave heating (70 W, 10 psi) with air stream cooling.
[e] *Z/E*: 1/1.8.
[f] *Z/E*: 1/2.5.
[g] *cis/trans*: 1/2.75.
[h] *cis/trans*: 1.5/1.
[i] *cis/trans*: 1/2.2.

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uenesulfonamide afforded product **5da** mainly or exclusively as the *E* diastereomer, Au and Ag giving similar results under the three sets of reaction conditions. However, TfOH afforded lower yields than the Au- or Ag-catalyzed processes (Table 4, entries 22, 25, and 28).

In the case of the non-conjugated hexa-1,4-diene (**4e**), the reaction must be heated under solvent-free conditions affording a 1/2.75 mixture of *cis/trans*-2,5-dimethylpyrrolidine (**6a**) in good yield when the gold complex was used as catalyst (Table 4, entries 29 and 30). The same product **6a** was obtained starting from hexa-1,5-diene (**4f**) but in lower yield, the reaction taking place only under gold catalysis at 85 °C either in toluene or under solvent-free conditions (Table 4, entries 31 and 32). However, silver failed in this case and TfOH gave a low yield of product **6a** (Table 4, entries 33 and 34).

5-Vinylnorborn-2-ene (**4j**) gave tricyclic heterocycle **7a** only under gold catalysis and neat conditions either by conventional or MW heating (Table 4, entries 35 and 38), the reaction failing when using AgOTf as catalyst (Table 4, entry 36). The same product **7a** was obtained in the presence of 1 mol% of triflic acid either under MW or conventional thermal conditions in 94% and 98% crude yields, respectively (Table 4, entries 37 and 39). The structure of this hydroamination product was determined by X-ray diffraction analysis of the methanesulfonamide derivative **7d**,[32] which was obtained in 70% yield by heating at 85 °C, under the same reaction conditions (Figure 1).

Compounds **7** could be formed by successive isomerization of **4j** through cationic intermediates **A–C** (Scheme 2). After the attack of the sulfonamide on intermediate **C**, the first hydroamination product **D** could be formed, which suffers anti-Markonikov intramolecular hydroamination to provide product **7**.

Finally, when 5-methylenebicyclo[2.2.1]hept-2-ene (**4k**) was allowed to react with *p*-toluenesulfonamide (**1a**), the tricyclic product **8a** was obtained in moderate yield under solvent-free conditions or conventional heating at 85 °C either under gold or silver catalysis in 44% and 54% yields, respectively (Table 4, entries 40 and 41). In addition, compound **8a** was obtained in 70% crude yield by using 1 mol% of TfOH at 85 °C during 14 h (Table 4, entry 42). For the structure assessment of tricyclic compound **8a**, the corresponding crystalline methanesulfonamide derivative **8d** was prepared in 74% yield using 5 mol% AgOTf as catalyst under heating at 85 °C for 14 h, and was submitted to X-ray diffraction analysis (Figure 2).[33]

This type of structure **8** has been previously described in the Ritter reaction of 5-methylenebicyclo-[2.2.1]hept-2-ene (**4k**) with acetonitrile giving the corresponding acetamide.[34] Its formation can be explained by binding of the cationic gold or silver species to the methylene moiety affording intermediate **A** which, after intramolecular cyclization, leads to intermediate **B**. After the final addition of the sulfon-

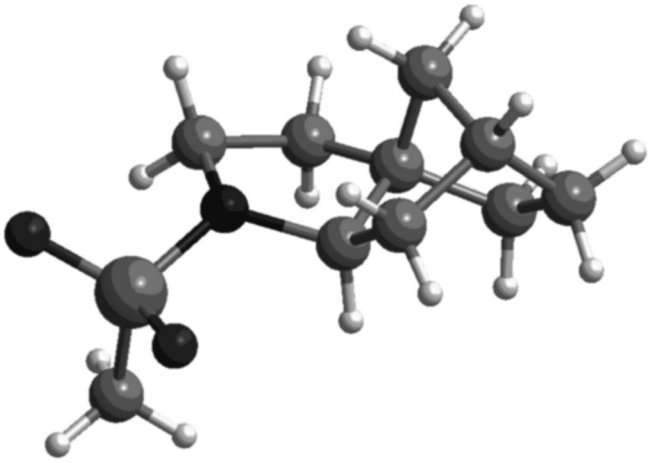
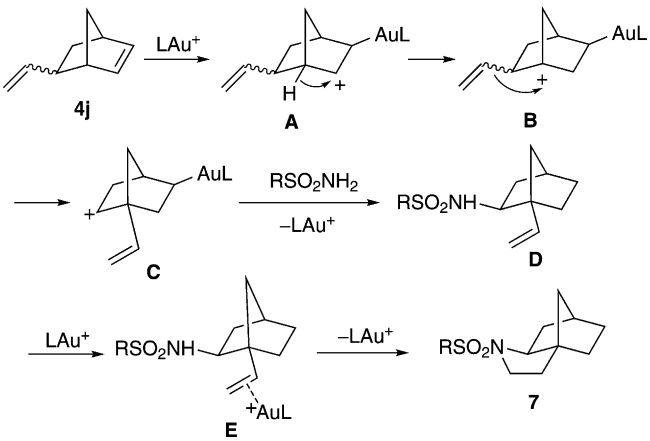


Figure 1. X-ray structure of compound **7d**.



Scheme 2. Postulated mechanism for the formation of compound **7**.

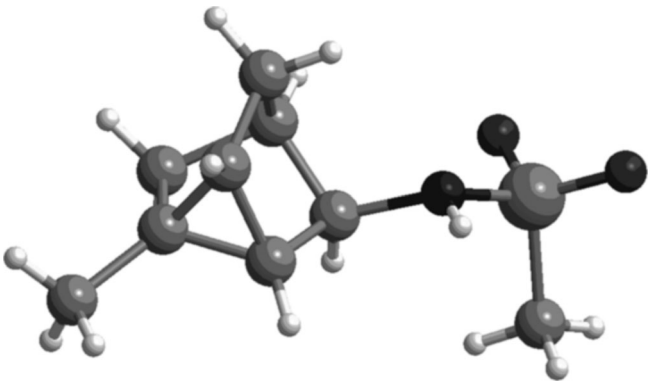


Figure 2. X-ray structure of compound **8d**.

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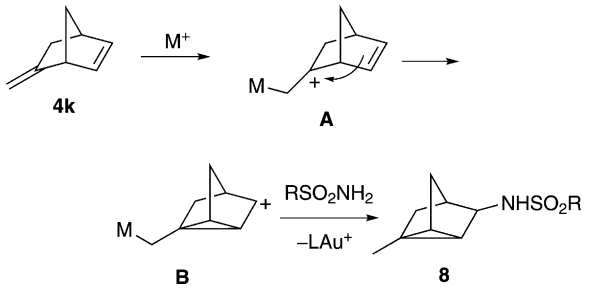
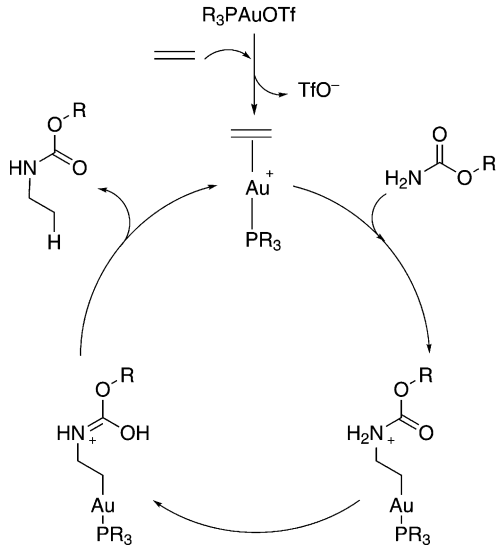


Scheme 3. Postulated mechanism for the formation of compound **8**.



Scheme 4. Catalytic cycle for the Au(I)-catalyzed hydroamination.

amide and proton transfer regenerating the catalyst, product **8** is formed (Scheme 3).

Au *vs.* Ag Hydroamination Reaction Mechanism

Theoretical analysis is a valuable tool for understanding reaction mechanisms as shown, for instance, in other Au-catalyzed reactions.[35] The reaction mechanism for the $PR_3Au(I)$-catalyzed hydroamination has been computationally studied by some of us.[22] The main reaction steps for this process in the case of ethylene (see Scheme 4) can be summarized as follows: (i) substitution of the counterion by the alkene at the coordination sphere of the gold center, giving rise to the catalytically active species; (ii) nucleophilic attack of the amide on the coordinated alkene forming an Au-alkyl species; (iii) proton transfer from the nucleophile to the newly formed alkyl ligand. The last one is the most striking step within the overall catalytic cycle. The direct proton transfer was found to be energetically prohibitive. A deeper analysis of the mechanism revealed that when a tautomerization process takes place on the added nucleophile the energy barrier for the overall proton transfer process is much lower. The tautomerization takes place on the nucleophile (a carbamate in the studied case) once it is added to the double bond. The energy barrier for the tautomerization process alone was found to be quite high. Nevertheless, the presence of triflate anion was shown to dramatically decrease the energy barrier for this step. Subsequent proton transfer from the tautomer to the C atom generates the final product. Substitution of the product by a new reactant alkene closes the catalytic cycle. The hydroamination reaction catalyzed by TfOH has been also computationally analyzed.[22b] The reaction mechanism was shown to be rather similar with the H^+ activating the double bond, but with the nucleophilic attack and the proton transfer taking place concertedly. Such a study on a model olefin also showed that the energy barrier for the TfOH-catalyzed reaction was somewhat higher than that for the Au(I)-catalyzed process.

Experimental attempts to isolated the cationic $[(PhO)_3P]AuOTf$ complex failed. However, from ^{31}P NMR spectra could be stablished that the signal from the covalent complex $[(PhO)_3P]AuCl$ at $\delta =$ 109.93 ppm was moved to 95.11 when AgOTf was added. The formation of $[(PhO)_3P]Au^+(CH_3CN)$ (m/z=548) was better detected by ESI-MS in reaction of $[(PhO)_3P]AuCl$ with AgOTf in acetonitrile.[23] The weak interaction between $[(PhO)_3P]Au^+$ and the triflate anion would facilitate the coordination of the C=C double bond to the metal center. The coordination of the vinyl ($CH=CH_2$) group of diene **4d** to $[(PhO)_3P]Au^+$ was observed by ^{13}C NMR.[23] This coordination took place mainly with the *E*-diastereomer because the corresponding signal from the diene appears at lower fields.[23]

The reaction mechanism for the Ag(I)-catalyzed hydroamination of dienes has been analyzed by means of DFT calculations. The computational analysis was initially performed taking the AgOTf molecule as the active catalyst, 3-methylpenta-1,3-diene as a model substrate and methanesulfonamide as a nucleophile. The initial step analyzed corresponds to a 3-methylpenta-1,3-diene coordination to the AgOTf catalyst giving rise to a linear species. The next step should involve the nucleophilic addition of the sulfonamide to the coordinated diene. Nevertheless, the product of this nucleophilic attack could not be located on the potential energy surface. All geometry optimizations starting from a structure with the N–C bond already formed, spontaneously lead to the rupture of this bond and the regeneration of the separated reactants. These results suggest that a neutral AgOTf molecule is not a catalytic species, since nucleophilic addition does not take place. Besides AgOTf, other cationic species as Ag^+, $[Ag(diene)]^+$ and

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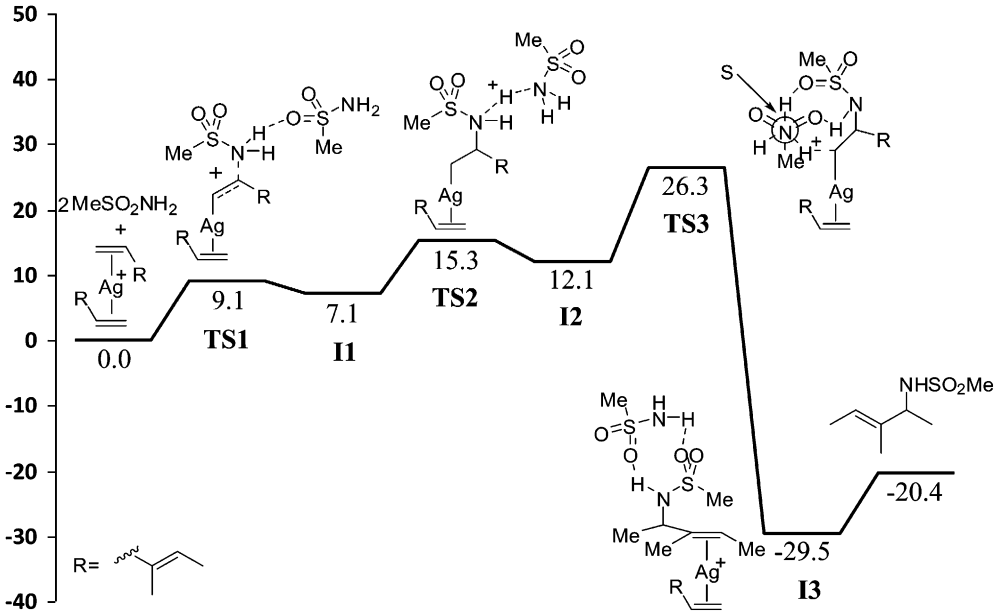

Figure 3. Reaction energy profile for the Ag(I)-catalyzed hydroamination of dienes (energies in kcal mol^{-1}).

$[Ag(diene)_2]^+$ can also be present in solution and could, in principle, be active catalysts for the process. The complex $[Ag(diene)_2]^+$ is by far the most stable species among the cationic Ag(I) species present in solution; Ag-diene bond dissociation energy in $[Ag(diene)_2]^+$ is 21.1 kcal mol^{-1}. In addition, diene concentration in the reaction media is high enough to displace the equilibrium position to the formation of $[Ag(diene)_2]^+$ species. According to this, the latter species was selected for the theoretical analysis of the reaction mechanism, even though the mechanism should be quite similar for all cationic species.

The presence of counterions or Lewis bases in the reaction media can play a significant role in proton transfer processes.[36] In order to evaluate the effects of the base on the proton transfer process, an additional base molecule (sulfonamide) was explicitly incorporated into the calculations. The reaction energy profile for this process is shown in Figure 3.

The initial step (once the diene binds to the metal center) corresponds to the nucleophilic attack of the sulfonamide on the coordinated diene. The energy barrier for this process is 9.1 kcal mol^{-1} whereas the formed intermediate lies 7.1 kcal mol^{-1} over the reactants. The reaction must involve a proton transfer from the sulfonamide to the C atom directly bonded to the metal atom. The direct proton transfer is too energy demanding, with an energy barrier of 49.6 kcal mol^{-1}. A proton-transfer agent has to participate in the reaction, and the sulfonamide represents by far the best candidate in solution for this purpose.

Hence, a proton transfer process including an additional sulfonamide was investigated.[36] Calculations show that the proton transfer takes place in two steps. In the first one the proton goes to the second sulfonamide. The relative energy barrier for this step is 8.2 kcal mol^{-1}. The last step involves the proton transfer from the base to the C atom coordinated to metal center. The relative energy barrier for the last step is 14.2 kcal mol^{-1}, therefore becoming the rate-determining step for this reaction. The overall energy barrier for the reaction is 26.3 kcal mol^{-1}. The formation of the final product coordinated to metal center is exothermic by 29.5 kcal mol^{-1}. Calculations suggest that in solution the reaction takes place in three steps: nucleophilic addition and two proton transfer steps using the nucleophile as a proton shuttle. The transition states are depicted in the Figure 4, respectively.

For the case of Au(I)-catalyzed HA process it was found that the nucleophile (carbamate) performs a tautomerization during the reaction. The analogous mechanism was evaluated for the case of sulfonamide acting as the nucleophile and an Ag(I) species as the catalyst. As previously described, the initial step corresponds to the nucleophilic addition. Then, the tautomerization process might take place on the bonded nucleophile. The direct tautomerization process is too energy demanding to be a feasible step within the reaction mechanism, having a global energy barrier of 63.0 kcal mol^{-1}. Alternatively, as in the case of the gold system, the tautomerization process may be catalyzed by the presence of a base. Thus, a second molecule of the base (sulfonamide) was explicitly included in the theoretical calculations. In this case the tautomerization takes place in one step in solution, the sulfonamide acting as a proton shuttle. The overall energy barrier in this case is 28.0 kcal mol^{-1}. The global energy barrier in this reaction mechanism is somewhat higher in energy than the previous one, which suggests that the most favourable reaction

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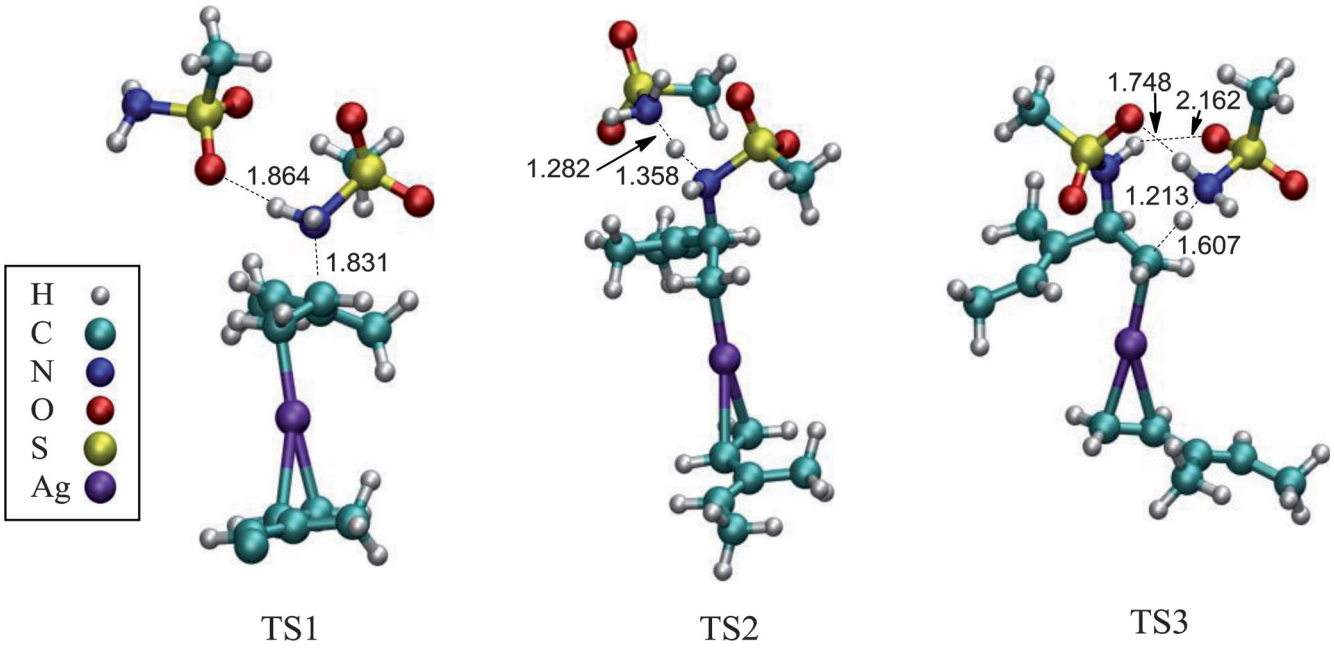
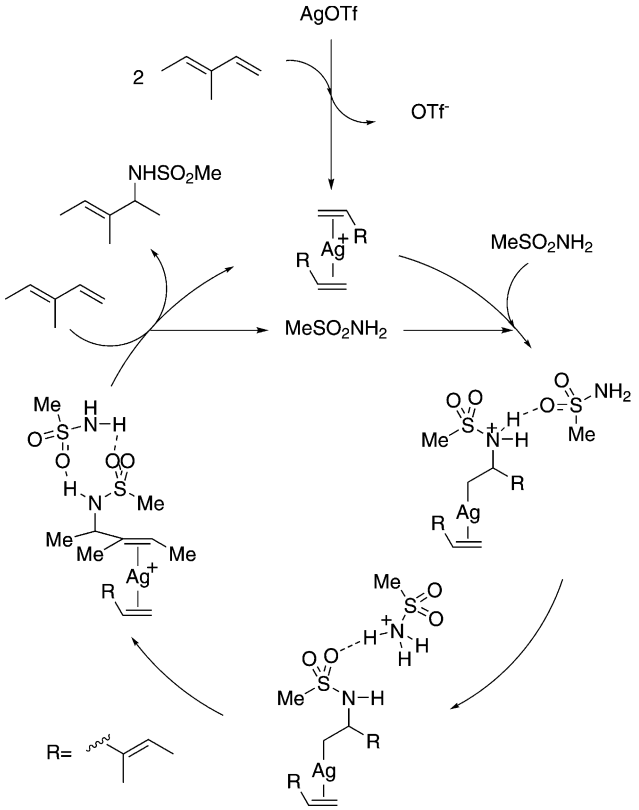


Figure 4. Geometries of the transitions states: TS1 nucleophilic addition, TS2 proton transfer to the base, and TS3 proton transfer to C atom, respectively (distances in Å).

mechanism involves a proton-transfer catalyzed by the presence of the base without including tautomerization.[38] This behaviour is different from that found for the Au(I) catalyst using a system with a carbamate as a nucleophile.

The energy difference[22] between the tautomeric intermediates in the case of Au(I)-carbamate system was 1.6 kcal mol^{-1}, nearly isoenergetic, whereas for the case of Ag(I)-sulfonamide the energy difference between the tautomeric structures is 16.5 kcal mol^{-1}. The origin of these differences can be related on one hand to the nature of the nucleophile. Thus, the energy difference between the tautomers in their isolated structures[22] is 12.7 kcal mol^{-1} for carbamate and 12.2 kcal mol^{-1} for sulfonamide, respectively; therefore, tautomerization of the isolated molecules has similar energetic requirements. The nature of the metal center is playing an important role for stabilizing the tautomeric intermediates and they go in opposite directions: Au(I) is able to stabilize the less stable tautomer by 14.3[22] kcal mol^{-1}, whereas Ag(I) destabilizes the less stable tautomer by 4.3 kcal mol^{-1}. Thus, the nature of the metal center is also affecting the relative energies of the intermediates in both reaction mechanisms.

According to the results obtained, the proposed catalytic cycle for the Ag(I)-catalyzed hydroamination is shown in Scheme 5. The catalytic cycle can be divided into the following steps: formation of the Ag(I) cationic species, N-nucleophilic addition and a stepwise proton transfer giving rise to the final product and regenerating the catalyst. Alternatively, the



Scheme 5. Catalytic cycle for the Ag(I)-catalyzed hydroamination.

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proton transfer may go through the tautomeric intermediate, although this process is more energetically demanding.

Conclusions

It has been found that $[(PhO)_3P]AuCl/AgOTf$ or just AgOTf afforded good catalytic efficiency in the hydroamination of alkenes with sulfonamides and *p*-nitroaniline. The gold catalyst showed a wider scope than the silver salt, which was unable to catalyze the hydroamination of terminal alkenes. The hydroamination of conjugate dienes can be performed with sulfonamides, *p*-nitroaniline, and carbamates as nucleophiles, either in gold- or silver-catalyzed reactions. In the case of non-conjugated 1,4- or 1,5-dienes the inter- and intramolecular hydroaminations gave the saturated heterocyclic compounds. Regarding the reaction mechanism, gold- and silver-catalyzed hydroamination processes have related reaction mechanisms albeit including significant differences. The initial step corresponds to the formation of a cationic species by substituting the counterion with the diene, which is followed by the nucleophilic addition step. Then, two successive proton transfer steps assisted by a second nuclephile molecule give rise to the final product and regenerate the catalytic species. In the case of the gold-catalyzed reaction the last step was found to follow a tautomerization process (using carbamate as nucleophile) and the presence of TfO^- was found to be crucial for assisting such a process. Nevertheless, for the case of the silver-catalyzed reaction using sulfonamide as a nucleophile, the tautomerization process, even if it is energetically accessible, it is not required. The proton transfer using the nucleophile as a proton shuttle is found to be the most favourable process.

Experimental Section

Computational Methods

The model selected for calculation was AgOTf as catalyst, $CH_3SO_2NH_2$ as nucleophile and 3-methylpenta-1,3-diene as the diene. The geometry optimizations have been carried by DFT calculations with the program package Gaussian09[39] and the B3LYP[40] combination of functionals. The SDD[41] pseudo-potential was employed for the silver centre, and the standard 6-31G(d) basis set was used for the other atoms. Energies have been obtained by means of single point calculations at the M06 level using the same SDD pseudo-potential, including a series of f-functions for the metal center and the extended 6-311G(d,p) basis set for the other atoms. The effect of the bulk solvent (dichloromethane) was estimated by the application of the polarizable continuum model (PCM)[42] as implemented in Gaussian 09 [ε(dichloromethane) = 8.93]. All energies given in the text correspond to those including the effect of the bulk solvent, which were obtained by adding the contribution of the Gibbs energy of solvation to the gas phase total energies with the larger basis set.

In the case of the transition states, normal coordinate analysis has been used to calculate the imaginary frequencies, and for each transition structure we calculated the intrinsic reaction coordinate (IRC) routes towards the corresponding minima. If the IRC calculations failed to reach the energy minima on the potential energy surface, we performed geometry optimizations from the final phase of the IRC path.

Hydroamination of Alkenes and Dienes; General Procedure

To a mixture of gold complex and or silver salt (see Table 1, Table 2, Table 3, and Table 4) and nitrogenated nucleophile (1 mmol) in dry solvent (2 mL, see Table 1, Table 2, Table 3, and Table 4) was added the alkene or 1,3-diene (4 mmol) with magnetic stirring in a sealed tube under argon atmosphere in the dark. For neat experiments (Table 3 and Table 4) no solvent was added. After the corresponding reaction time under the conditions indicated in Table 1, Table 2, Table 3, and Table 4 (for microwave heating the vessel was sealed with a pressure lock and the mixture was heated at 90 °C in a CEM Discover MW reactor at 70 W, 10 psi with air stream cooling during 30 min), the reaction mixture was cooled at room temperature and water (2 mL) and brine (2 drops) were added. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (2 × 10 mL). All organic phases were mixed, dried with $MgSO_4$ and evaporated. Pure products were obtained by recrystallization or by flash chromatography.

4-Methyl-*N*-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)benzenesulfonamide (3ea): White solid; mp 209 °C (CH_2Cl_2); R_f 0.47 (hexane/ethyl acetate: 4/1); IR (KBr): $\nu = 3276$, 2956, 1323, 1158, 1095, 1024, 923, 814, 706, 681 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.77$ (s, 3H), 0.78 (s, 3H), 0.86 (s, 3H), 0.96–1.05 (m, 2H), 1.45–1.70 (m, 5H), 2.43 (s, 3H), 3.11 (td, $J = 8.2$, 5.71 Hz, 1H), 4.46 (d, $J = 8.7$ Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.74 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.1$, 20.1, 20.3, 21.5, 26.8, 36.3, 40.0, 44.9, 47.0, 48.5, 61.2, 127.1, 129.6, 138.1, 143.1; MS (EI): *m/z* (%) = 307 (4) [M^+], 155 (31), 153 (11), 152 (100), 136 (13), 135 (50), 133 (19), 121 (20), 109 (30), 108 (11), 107 (20), 106 (12), 95 (52), 93 (35), 92 (12), 91 (86), 79 (18), 77 (13), 69 (10), 67 (18), 65 (25); HR-MS: $m/z = 307.1644$, calcd. for $C_{17}H_{25}NO_2S$ $[M]^+$: 307.1606.

1-Tosyloctahydro-3a,6-methanoindole (7a): Yellow oil; R_f 0.40 (hexane/ethyl acetate: 4/1); IR (KBr): $\nu = 2956$, 2868, 1342, 1305, 1163, 1095, 1042, 821, 658 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.08$–1.11 (m, 2H), 1.40–1.53 (m, 2H), 1.58–1.62 (m, 3H), 1.73–1.80 (m, 1H), 1.83 (dd, $J = 9.3$, 3.4 Hz, 1H), 1.98–2.11 (m, 1H), 2.30 (s, 1H), 2.43 (s, 3H), 2.97 (dd, $J = 9.3$, 4.4, 1H), 3.42 (td, $J = 13.8$, 2.4 Hz, 1H), 3.59 (td, $J = 14.1$, 9.2 Hz, 1H), 7.32 (d, $J = 11.1$ Hz, 2H), 7.70 (d, $J = 11.0$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.5$, 27.4, 28.3, 30.0, 38.1, 39.8, 41.4, 49.9, 56.4, 67.9, 127.5, 129.5, 134.5, 143.1; MS (EI): *m/z* (%) = 291 (100) [M^+], 290 (36), 263 (61), 250 (42), 249 (13), 237 (18), 236 (98), 155 (41), 136

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(91), 109 (13), 108 (20), 95 (21), 92 (12), 91 (96), 81 (36), 80 (15), 79 (23), 67 (28); HR-MS $m/z = 291.1283$, calcd. for $C_{16}H_{21}NO_2S$ $[M]^+$: 291.1293.

1-(Methylsulfonyl)octahydro-3a,6-methanoindole (7d): White solid; mp 115 °C (hexane/CH_2Cl_2); R_f 0.14 (hexane/ethyl acetate: 4/1); IR (KBr): $\nu = 2958$, 2865, 1450, 1369, 1332, 1239, 1139, 1050, 972, 779, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.15$ (d, $J = 12.6$ Hz, 1H), 1.25–1.30 (m, 2H), 1.57–1.61 (m, 1H), 1.62–1.69 (m, 2H), 1.75–1.93 (m, 4H), 2.33 (s, 1H), 2.81 (s, 3H), 3.21–3.24 (m, 1H), 3.56–3.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 28.2$, 28.3, 30.0, 35.1, 38.0, 39.5, 41.7, 49.7, 56.7, 68.0; MS (EI): *m/z* (%) = 216 (4%) [M^+], 215 (28), 186 (35), 174 (16), 173 (21), 160 (100), 136 (46), 135 (22), 108 (10), 95 (12), 82 (17), 81 (31), 80 (13), 79 (23), 67 (22): HR-MS $m/z = 215.0989$, calcd. for $C_{10}H_{17}NO_2S$ $[M]^+$: 215. 0980.

4-Methyl-*N*-(1-methyltricyclo[2.2.1.0^{2,6}]heptan-3-yl)benzenesulfonamide (8a): Yellow oil; R_f 0.31 (hexane/ethyl acetate: 4/1); IR (KBr): $\nu = 3279$, 2946, 2867, 1428, 1331, 1089, 870, 814, 662 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.77$ (d, $J = 4.9$ Hz, 1H), 0.92 (d, $J = 4.9$ Hz, 1H), 1.10 (s, 3H), 1.14–1.17 (m, 1H), 1.30 (d, $J = 11.1$ Hz, 1H), 1.53 (d, $J = 10.8$ Hz, 1H), 1.81 (d, $J = 9.3$ Hz, 1H), 2.42 (s, 3H), 3.28 (dt, $J = 7.32$, 1.64 Hz, 1H), 4.89 (d, $J = 7.12$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.78 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.4$, 17.7, 20.3, 21.5, 21.8, 30.5, 36.6, 37.2, 59.2, 127.0, 129.6, 138.1, 143.1; MS (EI): *m/z* (%) = 277 (4) [M^+], 122 (78), 120 (11), 107 (13), 106 (66), 105 (100), 95 (10), 94 (10), 92 (11), 91 (67), 81 (11), 80 (22), 79(20), 77 (16), 65 (18); HR-MS: $m/z = 277.1128$, calcd. for $C_{15}H_{19}NO_2S$ $[M]^+$: 277.1136.

***N*-(1-Methyltricyclo[2.2.1.0^{2,6}]heptan-3-yl)methanesulfonamide (8d):** White solid; mp 81 °C (hexane); R_f 0.16 (hexane/ethyl acetate: 4/1); IR (KBr): $\nu = 3287$, 2941, 1317, 1302, 1288, 1151, 1089, 982, 869, 765 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.03$ (q, $J = 5$ Hz, 2H), 1.20 (s, 3H), 1.28 (q, $J = 10.6$ Hz, 2H), 1.43–1.47 (m, 1H), 1.55–1.59 (m,1H), 2.04 (s, 1H), 2.98 (s, 3H), 3.49 (d, $J = 7.3$ Hz, 1H), 4.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.4$, 17.8, 20.5, 22.1, 30.5, 37.1, 37.2, 41.5, 59.4; MS (EI): *m/z* (%) = 201 (4) [M^+], 122 (34), 120 (16), 107 (17), 106 (76), 105 (100), 95 (14), 94 (16), 93 (18), 92 (18), 91 (31), 81 (13), 80 (36), 79 (36), 78 (23), 67 (13). HR-MS: $m/z = 201.0816$, calcd. for $C_9H_{15}NO_2S$ $[M]^+$: 201.0823.

Other Known Compounds Prepared

N-(Bicyclo[2.2.1]hept-2-yl)-4-methylbenzenesulfonamide (**3aa**),[21c] *N*-(bicyclo[2.2.1]hept-2-yl)-4-methoxybenzenesulfonamide (**3ab**),[21c] *N*-(bicyclo[2.2.1]hept-2-yl)-4-nitrobenzenesulfonamide (**3ac**),[43] *N*-(bicyclo[2.2.1]hept-2-yl)-methanesulfonamide (**3ad**),[4] *N*-(bicyclo[2.2.1]heptan-2-yl)-4-nitrobenzenesulfonamide (**3g**),[4] *N*-(cyclohexyl)-4-methylbenzenesulfonamide (**3ba**),[21c] *N*-(cyclooctyl)-4-methylbenzenesulfonamide (**3ca**),[21c] 4-methyl-*N*-(1,2,3,4-tetrahydro-1,4-methanonaphthalen-2-yl)benzenesulfonamide (**3da**),[44] 4-methyl-*N*-(octan-2-yl)benzenesulfonamide (**3ka**),[21c] 4-methyl-*N*-(1-phenethyl)benzenesulfonamide (**3ga**),[21c] 4-methyl-*N*-(1-phenethyl)benzenesulfonamide (**3ha**),[21c] *N*-[2-(4-methoxyphenyl]-1-methylethyl)-4-methylbenzenesulfonamide (**3ia**),[21c] 4-methyl-*N*-(4-phenylbutan-2-yl)benzenesulfonamide (**3ja**),[4] *N*-(cyclohex-2-enyl)-4-methylbenzenesulfonamide (**5aa**),[45] *N*-(cyclohex-2-enyl)-4-methoxybenzenesulfonamide (**5ab**),[10] 2-(cyclohex-2-en-1-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (**5ae**),[46] benzyl cyclohex-2-en-1-ylcarbamate (**5af**),[47] *N*-(cyclohex-2-en-1-yl)-4-nitroaniline (**5ag**),[48] *N*-(cyclohex-2-enyl)methanesulfonamide (**5ad**),[49] (*Z*)-*N*-(cyclooct-2-en-1-yl)-4-methylbenzenesulfonamide (**5ba**),[50] (*E*)-4-methyl-*N*-(pent-3-en-2-yl)benzenesulfonamide (**5ca**),[51] (*E*)-4-methyl-*N*-(3-methylpent-3-en-2-yl)benzenesulfonamide (**5da**).[21b]

Acknowledgements

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