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Phosphinines *versus* mesoionic carbenes:
a comparison of structurally related ligands
in Au(I)-catalysis†

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Gold(I) complexes based on a 2,4,6-triarylphosphinine and a mesoionic carbene derivative have been prepared and characterized crystallographically. Although structurally related, both heterocycles differ significantly in their donor/acceptor properties. These opposed electronic characteristics have been exploited in Au(I)-catalyzed cycloisomerization reactions. For the conversion of the standard substrate dimethyl 2-(3-methylbut-2-enyl)-2-(prop-2-ynyl)malonate the results obtained for both Au-catalysts were found to be very similar and comparable to the ones reported in the literature for other carbene- or phosphorus(III)-based Au(I)-complexes. In contrast, a clear difference between the catalytic systems was found for the cycloisomerization of the more challenging substrate *N*-2-propyn-1-ylbenzamide. A combination of the phosphinine-based complex and [AgSbF₆] or [Cu(OTf)₂] leads to a catalytic species, which is more active than the mesoionic carbene-based coordination compound. We attribute these differences to the stronger π -accepting ability of phosphinines in comparison to mesoionic carbenes. The here presented results show for the first time that phosphinines can be used efficiently as π -accepting ligands in Au(I)-catalyzed cycloisomerization reactions.

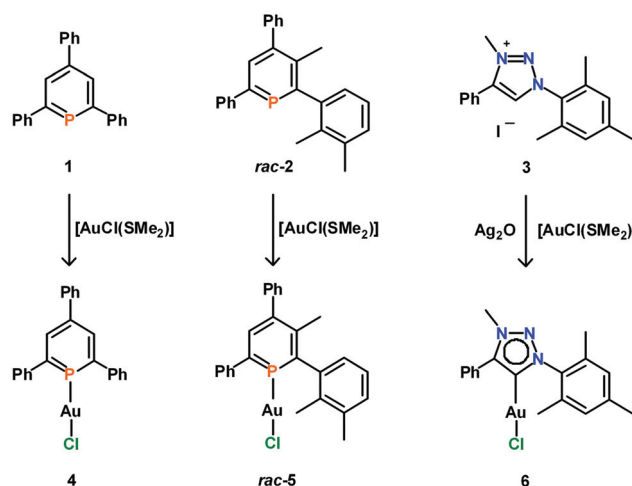
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Introduction

A milestone in the chemistry of low-coordinate phosphorus compounds was reached by Märkl in 1966 with the first successful preparation of 2,4,6-triphenyl- λ^3 -phosphinine (**1**, Scheme 1), which contains a fully unsaturated, six-membered and planar phosphorus heterocycle.¹ The stabilization of otherwise reactive P=C double bonds by their incorporation into aromatic systems opened up the access to formally sp²-hybridized phosphorus(III) compounds with significantly different electronic and steric properties compared to classical P(III)-species. Phosphinines have long been regarded as “chemical curiosities” but state-of-the-art synthetic methodologies allow nowadays their specific derivatization and


Scheme 1 Synthesis of Au(I)-complexes **4**, *rac*-**5** and **6**.

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functionalization.^{2,3} In particular, the 2,4,6-triaryl-substituted derivatives show a considerable kinetic stability and are often inert towards water, oxygen and many acids and bases, which facilitates their preparation and functionalization.

When coordinated to a metal center through the P-atom, phosphinines act as weak σ -donors but rather strong

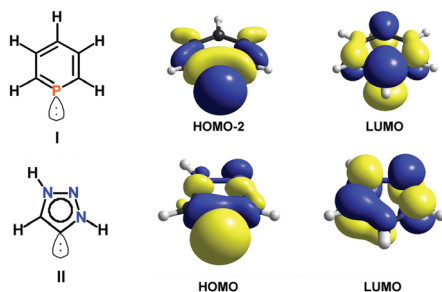


Fig. 1 Phosphinine (I) and mesoionic carbene (II) and the corresponding frontier orbitals HOMO and LUMO.

π -acceptors, due to an energetically low-lying HOMO-2 and LUMO (I, Fig. 1).⁴ This is reflected in Tolman's electronic parameter (TEP) of the 2,4,6-triphenylphosphinine ligand, for which a value of $\chi = 23$ has been determined by IR-spectroscopic measurements on the corresponding complex $[(L)Ni(CO)_3]$.⁵ Depending on the substitution pattern, π -donor properties have also been reported for σ -coordinated phosphinines, originating from the HOMO and HOMO-1 of the π -symmetry.⁶

From the planarity of the P-heterocycle it becomes obvious, however, that the steric demand of such systems is significantly different compared to classical trivalent phosphines. Tolman's steric parameter θ (cone angle), which provides a measure of the volume around a metal center occupied by a ligand, is not appropriate to describe the steric properties of phosphinines. In fact, the occupancy angles α and β along the two orthogonal planes x and y , show that the steric demand in the y plane is relatively small, while it is rather large in the x plane.⁷ On the basis of representative conformations and calculated structures of a 2,4,6-triphenylphosphinine-metal complex, values of $\alpha = 216^\circ$ and $\beta = 54^\circ$ have been determined.⁷ Taking these steric considerations into account, phosphinines are much more similar to their pyridine-analogs, as well as to N-heterocyclic carbenes. Among the latter ones, the triazolylidene-based mesoionic carbenes (MICs) have recently emerged as an important ligand class in the field of coordination- and supramolecular chemistry, molecular materials sciences as well as homogeneous catalysis.⁸ In contrast to phosphinines, however, MICs are rather strong σ -donors, but relatively weak π -acceptors, as obvious from the corresponding HOMO and LUMO (II, Fig. 1).⁸

Despite the fact that phosphinines have been known for 50 years now and possess a rich and versatile coordination chemistry, investigations on their application as ligands in homogeneous catalysis have only been started two decades ago. Studies are limited to only a few examples and Fe-catalyzed cyclotrimerizations and cyclodimerizations, Rh-catalyzed hydroformylations, Rh-catalyzed hydroformylation-cyclization tandem reactions, Ni-catalyzed cycloisomerizations, Rh- and Ir-catalyzed hydrogenations as well as Ir- and Pd-catalyzed hydrosilylations and water-oxidation reactions have so far been investigated.⁹

In this respect, Yoshifuji and co-workers have recently applied phosphalkenes in Au-catalyzed transformations.¹⁰ Apparently, the highly π -accepting properties of these low-coordinate phosphorus compounds are beneficial for increasing the Lewis acidity of the gold centers. Moreover, the soft properties of the phosphorus center in such systems are advantageous for a moderate stabilization of putative cationic Au intermediates. In the cyclotrimerization of 1,6-enynes the formation of vinylcyclopentenes was even observed in the absence of the typical silver co-catalyst. A P,P-hybrid ligand consisting of both a low-coordinate phosphalkene and a classical phosphorus donor was applied in Au(I)-catalysis by Ito and co-workers.¹¹ Again, even in the absence of a Ag-based co-catalyst the cycloisomerization of a 1,6-enyne derivative could be successfully accomplished. The catalytic activity of the digold complexes was primarily attributed to the presence of a formally sp^2 -hybridized phosphorus atom.

Inspired by the obvious analogy between phosphalkenes and phosphinines we started to investigate the synthesis and structural characterization of a Au(I) complex, containing a 2,4,6-triarylphosphinine-derivative as the ligand. We report here on a detailed comparison of this coordination compound with a structurally related mesoionic carbene Au(I)-complex in the Au-catalyzed cycloisomerization of dimethyl 2-(3-methylbut-2-enyl)-2-(prop-2-ynyl)malonate as well as *N*-2-propyn-1-ylbenzamide. As phosphinines have never been applied in Au(I)-catalyzed reactions before, we aim to investigate the effect of the significantly different donor/acceptor properties of phosphinines- and MIC-based ligands on the catalytic activity and selectivity of the corresponding Au(I)-complexes.

Results and discussion

Phosphinines readily form coordination compounds with Au(I)-precursors, such as $[Au(CO)Cl]$ or $[AuCl(tht)]$ (tht = tetrahydrothiophene). Even though the first phosphinine-Au(I) complex $[AuCl(C_5H_2P-2,4,6-Ph_3)]$ (4) was prepared by Schmidbaur *et al.* in 1973 from 2,4,6-triphenylphosphinine 1 and $[Au(CO)Cl]$, the X-ray crystal structure determination of 4 has not been reported in the literature until very recently.^{12,13} Recently, only a few crystallographically characterized Au(I)-complexes of differently substituted phosphinines have been published.^{13,14}

2,4,6-Triphenylphosphinine (1) also reacts smoothly with $[AuCl(SMe_2)]$ in CH_2Cl_2 and 4 can be obtained as a slightly yellow solid after evaporation of all volatiles (Scheme 1). Likewise, a racemic mixture of the axially chiral phosphinine *rac*-2 reacts quantitatively with a racemic mixture of the corresponding Au(I)-complex *rac*-5 (Scheme 1). Compound *rac*-5, which was isolated as a bright yellow solid, shows the typical resonance for phosphinine-based transition-metal complexes at $\delta = 164.3$ ppm in the $^{31}P\{^1H\}$ NMR spectrum, which is located upfield from the free ligand (δ (ppm) = 190.6). The Au(I)-coordination compound 6, containing a mesoionic carbene-ligand can be prepared from the triazolium salt 3. Treatment

with Ag_2O and subsequent reaction with $[\text{AuCl}(\text{SMe}_2)]$ give **5** as a white solid in 82% isolated yield (Scheme 1). Single crystals suitable for X-ray diffraction could be obtained from both $\text{Au}(\text{i})$ -complexes *rac*-**5** and **6** and the molecular structures, along with selected bond lengths and distances are depicted in Fig. 2 and 3, respectively.

Similar to the situation observed in the few crystallographically characterized phosphinine- $\text{Au}(\text{i})$ -complexes, the metal center in *rac*-**5** is coordinated in a nearly linear fashion with a $\text{P}-\text{Au}-\text{Cl}$ angle of $174.82(3)^\circ$. The $\text{Au}(1)-\text{P}(1)$ and $\text{Au}(1)-\text{Cl}(1)$ distances of $2.2040(7)$ Å and $2.2674(8)$ Å, respectively, are in line with reported data for such compounds. The slightly shorter $\text{Au}(1)-\text{P}(1)$ bond length compared to the value of $2.235(3)$ Å found in $[\text{AuCl}(\text{PPh}_3)]$ should, however, not be directly related to an enhanced π -backbonding from the metal center to the LUMO of the phosphinine ligand, as the different formal hybridizations of the phosphorus atoms in these compounds do not allow a direct comparison.^{14e} Nevertheless, the rather high value of the internal $\text{C}(1)-\text{P}(1)-\text{C}(5)$ angle of $107.26(14)^\circ$ compared to free phosphinines ($\sim 100^\circ$) reflects significant disruption of the aromaticity upon coordination of the ligand to the $\text{Au}(\text{i})$ -center. Furthermore, the crystallographic characterization of *rac*-**5** nicely reveals that the xylyl-group in

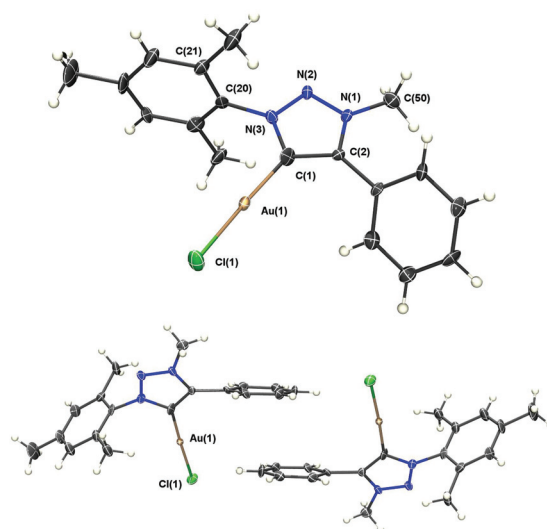


Fig. 3 Top: Molecular structure of **6** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): $\text{C}(1)-\text{Au}(1)$: $1.973(9)$, $\text{Au}(1)-\text{Cl}(1)$: $2.281(2)$, $\text{C}(1)-\text{C}(2)$: $1.395(12)$, $\text{C}(1)-\text{N}(3)$: $1.384(10)$, $\text{N}(3)-\text{N}(2)$: $1.342(9)$, $\text{N}(2)-\text{N}(1)$: $1.317(9)$, $\text{N}(1)-\text{C}(2)$: $1.36(1)$, $\text{N}(3)-\text{C}(20)$: $1.439(11)$, $\text{N}(1)-\text{C}(50)$: $1.463(11)$, $\text{N}(3)-\text{C}(1)-\text{C}(2)$: $102.0(7)$, $\text{C}(21)-\text{C}(20)-\text{N}(3)-\text{C}(1)$: $90.8(8)$. Bottom: Arrangement of **6** in the crystal packing.

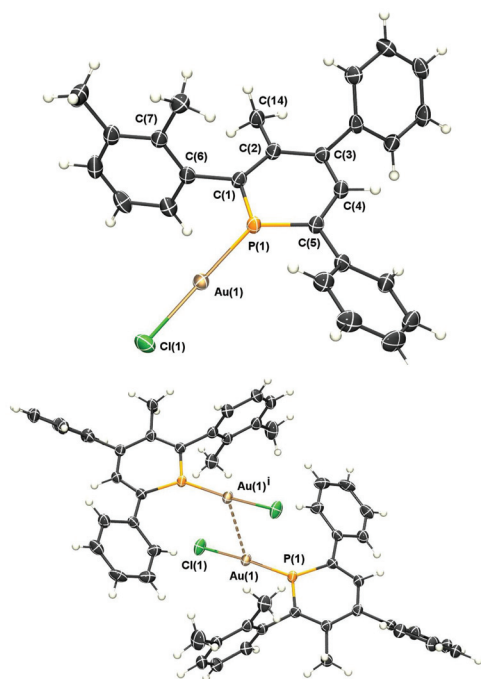


Fig. 2 Top: Molecular structure of *rac*-**5** in the crystal. Displacement ellipsoids are shown at the 50% probability level. A THF solvent molecule is omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): $\text{P}(1)-\text{Au}(1)$: $2.2040(7)$, $\text{Au}(1)-\text{Cl}(1)$: $2.2674(8)$, $\text{P}(1)-\text{C}(1)$: $1.715(3)$, $\text{P}(1)-\text{C}(5)$: $1.721(3)$, $\text{C}(1)-\text{C}(2)$: $1.391(4)$, $\text{C}(2)-\text{C}(3)$: $1.412(4)$, $\text{C}(3)-\text{C}(4)$: $1.399(4)$, $\text{C}(4)-\text{C}(5)$: $1.379(4)$, $\text{C}(2)-\text{C}(14)$: $1.508(4)$, $\text{C}(1)-\text{C}(6)$: $1.504(4)$, $\text{C}(1)-\text{P}(1)-\text{C}(5)$: $107.26(14)$, $\text{C}(7)-\text{C}(6)-\text{C}(1)-\text{C}(2)$: $-79.4(4)$. Bottom: Arrangement of *rac*-**5** in the crystal packing. $\text{P}(1)-\text{Au}(1)-\text{Cl}(1)$: $174.82(3)^\circ$, $\text{Au}(1)\cdots\text{Au}(1)^i$: $3.2960(2)$ Å. Symmetry code i : $1-x, 1-y, 1-z$. The $\text{Au}\cdots\text{Au}$ contact is indicated by a dotted line.

the α -position of the heterocyclic framework is rotated out of the C_5P -plane with an interplanar angle of as much as $77.93(14)^\circ$. This effect can not only be attributed to the coordination of the ligand to the metal center, but also to the presence of the methyl-group in the 5-position ($\text{C}(14)$), which leads to atropisomerism and the formation of a racemic mixture of *rac*-**5**. This phenomenon has also been detected for the free axially chiral phosphinine *rac*-**2**, for which a rotational barrier of $\Delta G^\ddagger_{298} = 109.5 \pm 0.5 \text{ kJ mol}^{-1}$ and a half-life-time of $t_{1/2} = 9.6 \pm 2.1 \text{ d}$ have been determined by us before.¹⁵

A closer look at the packing of *rac*-**5** in the crystal lattice reveals an antiparallel aggregation of enantiomeric pairs (Fig. 2, bottom). The $\text{Au}\cdots\text{Au}$ distances of only $3.2960(2)$ Å point to significant auriphilic interactions between neighboring molecules. A crossed arrangement of phosphinine- $\text{Au}(\text{i})$ -complexes with weak auriphilic interactions has been observed by Siemeling *et al.* in $[\text{AuCl}(\text{C}_5\text{H}_2\text{P}-2,6-\text{Me}_2-4-\text{Ph})]$ ($\text{Au}\cdots\text{Au} = 3.60$ Å), while a parallel organization of two $[\text{AuCl}\{\text{C}_5\text{H}_2\text{P}-2,4-\text{Ph}_2-6-[\text{C}_6\text{H}_3-3,4-(\text{OMe})_2]\}]$ complexes has been observed by Gudat and co-workers.^{13,14c} In the latter compound, no $\text{Au}\cdots\text{Au}$ -contacts are present, instead weak $\text{Au}\cdots\text{Cl}$ interactions were observed ($\text{Au}\cdots\text{Cl} = 3.387$ Å).

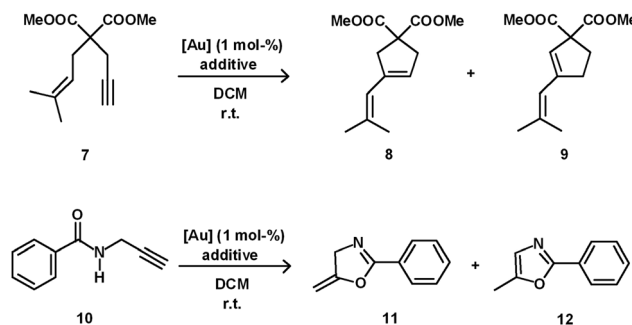
The molecular structure of the mesoionic-carbene-containing $\text{Au}(\text{i})$ -complex **6** in the crystal shows the expected quasi-linear coordination geometry around the metal center with a $\text{Cl}(1)-\text{Au}(1)-\text{C}(1)$ angle of $176.7(2)^\circ$. The $\text{Au}(1)-\text{C}(1)$ and $\text{Au}(1)-\text{Cl}(1)$ distances of $1.973(9)$ Å and $2.181(2)$ Å are very similar to those observed in other $\text{Au}(\text{i})$ -triazolyliene complexes.¹⁶ Moreover, with a torsion angle of $\text{C}(21)-\text{C}(20)-\text{N}(3)-\text{C}(1) = 90.8(8)^\circ$, the sterically demanding mesityl-group is located almost perfectly perpendicular to the triazolyliene ring. A closer look

at the packing of **6** in the crystal shows that no aurophilic interactions between adjacent coordination compounds are present. On the other hand, π - π -interactions (centroid-centroid-distance: 3.870 Å, shift distance: 1.644 Å) between the phenyl-substituents of neighbouring complexes can be detected (Fig. 3, bottom).

Having characterized the Au(I)-complexes of both a phosphinine and a mesoionic carbene crystallographically, we decided to make some considerations about the steric properties of both the substituted heterocycles. As mentioned above, the Tolman cone-angle is not suitable to describe the steric properties of planar ligands sufficiently. Especially for N-heterocyclic carbenes, the % V_{bur} (% buried volume) has, on the other hand, emerged as a reasonably good molecular descriptor for the steric bulk of such systems.¹⁷ As these parameters have not been evaluated for the planar phosphinines so far, we determined the % V_{bur} for phosphinines **1** and *rac*-**2** as well as for the mesoionic carbene computationally and found values of 33.1% (**1**), 33.8% (*rac*-**2**) and 31.8% for the mesoionic carbene ligand. Apparently, the methyl groups of the xyllyl-substituent in *rac*-**2** do not significantly influence the direct environment around the metal center compared to 2,4,6-triphenylphosphinine **1**, as they are relatively far from the coordination site due to the enforced orientation by the methyl-group C(14). The value of % V_{bur} = 31.8% for the mesoionic carbene is comparable to similar NHC-ligands, which are obviously less bulky than phosphinines.

Inspired by the work of Yoshifuji and Ito on the application of phosphalkenes as low-coordinate phosphorus-ligands in Au(I)-mediated transformations, we decided to compare the coordination compound *rac*-**5** with **6** in the Au(I)-catalyzed cycloisomerization reaction of dimethyl 2-(3-methylbut-2-enyl)-2-(prop-2-ynyl)malonate (**7**) and *N*-2-propyn-1-ylbenzamide (**10**). As described above, both complexes are structurally related but differ significantly in the electronic properties of the corresponding ligands. Interestingly, although a few Au(I)-complexes have been described in the literature before (*vide supra*), π -accepting phosphinines have never been applied as ligands in Au(I)-catalyzed transformations. On the other hand, π -accepting phosphites, in combination with Au(I)-precursors, often show remarkable catalytic activities in such reactions.¹⁸ However, the corresponding complexes usually suffer from a considerable thermal and kinetic instability and consequently electron donating phosphines are preferentially the ligands of choice. Also, several reports on the use of N-heterocyclic carbenes (including mesoionic carbenes) as strongly σ -donating ligands in Au(I)-catalyzed reactions have been reported in the literature.^{16,20} For comparison reasons, the Au(I)-complex **4**, containing the 2,4,6-triphenylphosphinine ligand **1**, was also included in our studies.

We first investigated the cycloisomerization of **7** towards the cyclopentene-derivatives **8** and **9** in dichloromethane at room temperature and under the exclusion of light as gold-complexes can be light-sensitive (Scheme 2).¹⁹ Although often neglected in the literature, it is absolutely necessary to explore the influence of the used gold-precursor as well as the additive



Scheme 2 Au(I)-catalyzed cycloisomerization of **S1** and **S2**.

in the cycloisomerization reaction under identical reaction conditions (blind-reactions). Compound **7** is frequently used as a standard substrate in Au(I)-catalyzed reactions, as it can easily be converted with high conversions to the corresponding products **8** and **9**, respectively.^{16a,c,20c}

The standard additive AgSbF₆ does not show any conversion of the substrate within 24 h (Table 1, entry 1). In contrast, the alternative additive [Cu(OTf)₂], already leads almost quantitatively (98% conversion) and exclusively to product **8** within 24 h (entry 2).²¹ In the absence of any additive, the Au(I)-precursor [AuCl(SMe₂)] also catalyzes the reaction of **7** to **8**, although with only 75% conversion within 24 h (entry 3). A combination of [AuCl(SMe₂)] and the additive [AgSbF₆] generates a catalyst with moderate activity (>99% conversion after 8 h) but with a different selectivity, as a product ratio of the two cyclopentene-derivatives of **8** : **9** = 1 : 2 can be observed.

Next, we turned our attention to the influence of the ligands on the catalytic reactions and applied the Au(I)-complexes *rac*-**5** and **6** in the Au(I)-mediated cycloisomerization of **7**. Apparently, no difference in activity and selectivity can be noticed between [AuCl(SMe₂)] alone and the phosphinine-based complex *rac*-**5** (entries 3 and 5). In the absence of any

Table 1 Cycloisomerization of substrate **7** into the products **8** and **9**

Entry	Precatalyst	Additive	Time	Conversion [%]	Product ratio [8 : 9]
1	—	[AgSbF ₆]	24 h	0	—
2	—	[Cu(OTf) ₂]	24 h	98	1 : 0
3	[AuCl(SMe ₂)]	—	24 h	75	1 : 0
4	[AuCl(SMe ₂)]	[AgSbF ₆]	8 h	>99	1 : 2
5	<i>rac</i> - 5	—	24 h	75	1 : 0
6	6	—	24 h	40	1 : 0
7	<i>rac</i> - 5	[AgSbF ₆]	5 min	>99	1 : 0
8	4	[AgSbF ₆]	5 min	>99	1 : 0
9	6	[AgSbF ₆]	15 s	96	1 : 0
		[AgSbF ₆]	1 min	>99	1 : 0
		[AgSbF ₆]	10 min	>99	2 : 3
10	<i>rac</i> - 5	[Cu(OTf) ₂]	30 min	>99	1 : 0
11	6	[Cu(OTf) ₂]	2.5 h	>99	1 : 0
12	[AuCl(PPh ₃)]	[AgSbF ₆]	30 min	>99	1 : 0
13	[AuCl(P(OR) ₃)]	[AgSbF ₆]	5 min	>99	Mixture

Conditions: catalyst precursor: 1 mol%, additives: 1 mol% [AgSbF₆], 5 mol% [Cu(OTf)₂], dichloromethane, room temperature. P(OR)₃ = tris(2,4-di-*tert*-butylphenyl)phosphite.

additive, the MIC-based complex **6** also shows the conversion of **7** exclusively to **8**, although with only 40% conversion within 24 h (entry 6). In the presence of the additive $[\text{AgSbF}_6]$, a clear difference in the catalytic reactions can finally be observed. In the presence of the silver additive, both phosphinine-based coordination compounds *rac*-**5** and **4** exhibit very high catalytic activity and the almost quantitative transformation (>99%) of the substrate exclusively into **8** can already be detected after 5 min (entries 7 and 8). The combination of the mesoionic NHC-containing complex **6** and $[\text{AgSbF}_6]$ also leads to a very active and selective catalyst. As a matter of fact, it turned out that $6/[\text{AgSbF}_6]$ cycloisomerizes **7** already with 96% conversion within 15 s, while >99% conversion is achieved after 1 min (entry 9). In both catalytic runs, **8** has been formed exclusively. However, we noticed that after the full conversion of **7** into **8**, isomerization of **8** to **9** occurs in the presence of *rac*-**5**/ $[\text{AgSbF}_6]$ and $6/[\text{AgSbF}_6]$, respectively, and a ratio of **8**:**9** = 2:3 can be found after 10 min. Similar observations for the isomerization of the product in the presence of Au(I)-species have been observed before.^{16c}

We further investigated the cycloisomerization of **7** with *rac*-**5** and **6** in the presence of the alternative additive $[\text{Cu}(\text{OTf})_2]$. In both cases rather active and selective catalysts are generated as well and the almost quantitative formation (>99% conversion) of **8** exclusively was found after 30 min (*rac*-**5**/ $[\text{Cu}(\text{OTf})_2]$) and 2.5 h (**6**/ $[\text{Cu}(\text{OTf})_2]$), respectively (entries 10 and 11). Finally, we carried out the cycloisomerization reaction of substrate **7** with the standard precatalysts $[\text{AuCl}(\text{PPh}_3)]$ and $[\text{AuCl}(\text{P}(\text{OR})_3)]$ ($\text{P}(\text{OR})_3$ = tris(2,4-di-*tert*-butylphenyl)phosphite) under the same reaction conditions. Interestingly, we found that the combination $[\text{AuCl}(\text{PPh}_3)]/[\text{AgSbF}_6]$ is much less active than the phosphinine- or NHC-based Au(I)-catalysts (entry 12). Although the system $[\text{AuCl}(\text{P}(\text{OR})_3)]/[\text{AgSbF}_6]$ is, on the other hand, rather active (entry 13), the phosphite-based catalyst apparently produces a mixture of **9** and other unidentified reaction products.

To summarize the results described above, the following observations have been made: as already reported in the literature, the substrate dimethyl 2-(3-methylbut-2-enyl)-2-(prop-2-ynyl)malonate (**7**) can readily be converted into the corresponding cyclopentene-derivatives **8** and **9**. It is thus not surprising that high conversions of **7** are observed, even if only the additive $[\text{Cu}(\text{OTf})_2]$, the Au(I)-precursor $[\text{AuCl}(\text{SMe}_2)]$, or a combination of both $[\text{AuCl}(\text{SMe}_2)]$ and $[\text{AgSbF}_6]$ are used. Moreover, the neutral coordination compounds *rac*-**5** and **6** also lead to a significant catalytic activity, although no full conversions were achieved. The higher activity of *rac*-**5** with respect to **6** might be attributed to the π -accepting property of the phosphinine-ligand, which might facilitate the coordination of the unsaturated substrate to the metal center. Fast and selective catalytic reactions occur when using **4**, *rac*-**5**, and **6** in combination with the additives $[\text{AgSbF}_6]$ and $[\text{Cu}(\text{OTf})_2]$, respectively, while the phosphinine-containing catalyst turned out to be superior to $6/[\text{Cu}(\text{OTf})_2]$. Interestingly, a comparison with the standard precursors $[\text{AuCl}(\text{PPh}_3)]$ and $[\text{AuCl}(\text{P}(\text{OR})_3)]$ revealed that both phosphinine- and NHC-based catalysts

show a better performance in terms of the activity and selectivity. For this particular substrate, however, the catalytic results are very similar to the ones reported in the literature for other carbene- or phosphorus(III)-based Au(I)-complexes.^{16a,c,20c,22} At this point, we assume that the additives $[\text{AgSbF}_6]$ and $[\text{Cu}(\text{OTf})_2]$ function according to their well-documented role, that means the elimination of AgCl or CuCl_2 , respectively, under the formation of a cationic Au(I)-complex, although we do not have any structural or spectroscopic evidence at the moment. Studies on these specific coordination compounds are currently under investigation in our laboratories.

Apparently, the difference in activity observed for the transformation of **7** into **8** and **9** by *rac*-**5**/ $[\text{AgSbF}_6]$ and $6/[\text{AgSbF}_6]$ is very small. As mentioned above, this can be attributed to the fact that this particular substrate can easily be converted, even when using the precursors alone. Consequently, we chose the more challenging substrate *N*-2-propyn-1-ylbenzamide (**10**) in order to better evaluate the catalytic properties of these coordination compounds. Studies carried out by Hashmi and co-workers showed that **10** can be converted both to the oxazoline (**11**) and to the oxazole (**12**), using Au(I) as well as Au(III) catalysts.²³ In particular, Au(I) complexes containing phosphines or normal N-heterocyclic carbenes as ligands turned out to be effective catalysts for this particular cycloisomerization reaction, although the conversion of **10** to **11/12** proceeds generally slower compared to the conversion of **7** to **8/9**.²⁴ Even though amides are very weak acids, we first wanted to exclude the reaction of the N-H-functionality with the phosphinine-complex *rac*-**5**, as the addition of reactive O-H and N-H bonds across the P=C-double bond in phosphinine-based coordination compounds has frequently been observed before.²⁵ We thus added *N*-2-propyn-1-ylbenzamide to a solution of *rac*-**5** in dichloromethane and investigated the reaction mixture by means of $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, showing no sign of any reaction of the substrate with the coordinated ligand.

Once again, we first tried to carry out the cycloisomerization reaction of **10** solely with the additives. Indeed we observed only a low conversion of **10** (5%) exclusively to **11** after 24 h in the presence of $[\text{Cu}(\text{OTf})_2]$, while no reaction at all was detected with $[\text{AgSbF}_6]$ (Table 2, entries 1 and 2). As anticipated, in contrast to the situation observed for **7**, the Au(I)-precursor $[\text{AuCl}(\text{SMe}_2)]$ also does not show any reactivity towards **10** (entry 3). Only a combination of $[\text{AuCl}(\text{SMe}_2)]$ and $[\text{AgSbF}_6]$ leads to a low conversion (15%) within 24 h with a ratio of **11**:**12** = 9:1 (entry 4).

In the absence of any additive, the neutral coordination compounds *rac*-**5** and **6** also show moderate to low catalytic activity in the cycloisomerization of **10**, while the MIC-based complex is less active than the phosphinine-based complex *rac*-**5** (entries 5 and 6). Once again, we assume that the higher activity of *rac*-**5** with respect to **6** is due to the stronger π -accepting property of the phosphinine ligand, which could facilitate the coordination of the unsaturated substrate to the metal center as the first step in the catalytic cycle. Most strikingly, however, a clear contrast not only to the situation observed for the cycloisomerization of **7**, but also between the

Table 2 Cycloisomerization of substrate **10** into the products **11** and **12**

Entry	Precatalyst	Additive	Time [h]	Conversion [%]	Product ratio [11 : 12]
1	—	[AgSbF ₆]	24	0	—
2	—	[Cu(OTf) ₂]	24	5	1 : 0
3	[AuCl(SMe ₂)]	—	24	0	—
4	[AuCl(SMe ₂)]	[AgSbF ₆]	24	15	9 : 1
5	<i>rac</i> - 5	—	24	75	1 : 3
6	6	—	62	25	1 : 0
7	<i>rac</i> - 5	[AgSbF ₆]	3	>99	98 : 2
8	6	[AgSbF ₆]	62	94	95 : 5
9	<i>rac</i> - 5	[Cu(OTf) ₂]	8	>99	98 : 2
10	6	[Cu(OTf) ₂]	62	92	96 : 4
11	[AuCl(PPh ₃)]	[AgSbF ₆]	7	>99	96 : 4
12	[AuCl(P(OR) ₃)]	[AgSbF ₆]	11	>99	98 : 2
13	4	—	24	25	0 : 1
14	4	[AgSbF ₆]	24	40	80 : 20

Conditions: catalyst precursor: 1 mol%, additives: 1 mol% [AgSbF₆], 5 mol% [Cu(OTf)₂], dichloromethane, room temperature. P(OR)₃ = tris(2,4-di-*tert*-butylphenyl)phosphite.

two coordination compounds *rac*-**5** and **6** can now be noticed in the presence of an additive. In combination with [AgSbF₆], a very active catalytic species is formed from complex *rac*-**5** and >99% conversion and a good selectivity towards the oxazoline **11** is achieved already after 3 h (entry 7). On the other hand, the MIC-based catalyst **6**/[AgSbF₆] is less active, as 94% conversion can be detected only after 62 h (entry 8). A similar result is obtained with the additive [Cu(OTf)₂], again showing a superior performance of the phosphinine-based Au(I)-complex with respect to **6**/[Cu(OTf)₂], even though the reaction with both catalysts is much slower with this additive (entries 9 and 10).

In contrast to the observations made with substrate **7**, the catalytic activities and selectivities of [AuCl(PPh₃)]/[AgSbF₆] and [AuCl(P(OR)₃)]/[AgSbF₆] (P(OR)₃ = tris(2,4-di-*tert*-butylphenyl)phosphite) are similar (entries 11 and 12) compared to the phosphinine-based catalyst. We followed the cycloisomerization reaction over time for the best performing catalytic systems (entries 7, 8, 11 and 12) and analyzed the conversion of the substrate by means of ¹H NMR spectroscopy during specific time intervals. The corresponding conversion-over-time plot is depicted in Fig. 4, from which the turnover frequencies of TOF = 91 h⁻¹ (*rac*-**5**/[AgSbF₆]), TOF = 91 h⁻¹ ([AuCl(PPh₃)]/[AgSbF₆]), TOF = 49 h⁻¹ ([AuCl(P(OR)₃)]/[AgSbF₆]) and TOF = 5 h⁻¹ (**6**/[AgSbF₆]) could be determined at 20% conversion. These values nicely demonstrate that the activity of the phosphinine-containing catalytic system is comparable with the reported data of state-of-the-art cationic phosphorus-based gold catalysts used for this particular substrate.²⁶

Having demonstrated that phosphinine *rac*-**2** can act successfully as a π -accepting phosphorus ligand in gold-catalyzed reactions, we also investigated coordination compound **4**, which is based on the simple 2,4,6-triphenylphosphinine ligand **1**, in the cycloisomerization reaction of **10**. In the absence of any additive, **4** shows much lower activity compared to *rac*-**5** (25% versus 75% conversion after 24 h, entries 13 and

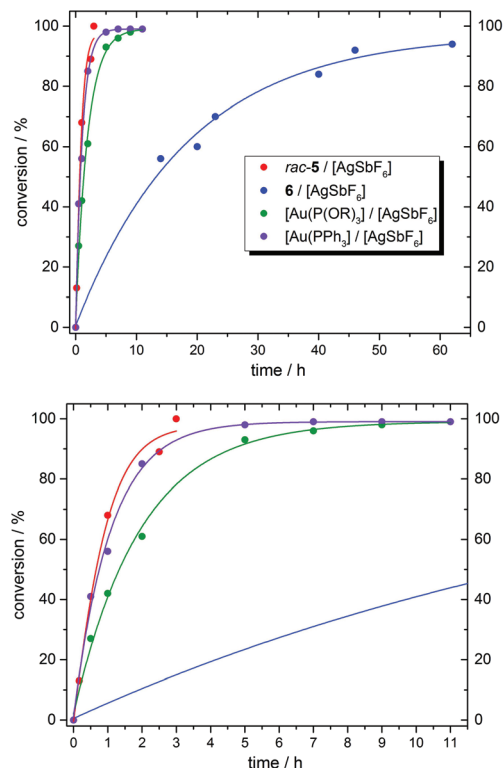


Fig. 4 Conversion-over-time plot for the cycloisomerization of **S2** with the catalytic system *rac*-**5**/[AgSbF₆] (entry 7), **6**/[AgSbF₆] (entry 8), [AuCl(PPh₃)]/[AgSbF₆] (entry 11) and [AuCl(P(OR)₃)]/[AgSbF₆] (P(OR)₃ = tris(2,4-di-*tert*-butylphenyl)phosphite) (entry 12).

5). Even in the presence of [AgSbF₆] only 40% conversion is achieved with **4** after 24 h (entry 14). Moreover, only a low product-selectivity of **11** : **12** = 80 : 20 was observed. The evaluation of the electronic properties of **1** in comparison to *rac*-**2** reveals that **1** is slightly more π -accepting than *rac*-**2** (χ = 23 for **1**, versus χ = 21 for *rac*-**2**, based on the A₁ stretching band in the IR spectrum of the corresponding [LNi(CO)₃] complexes, see the ESI†), which should lead to an even higher catalytic activity of **4**/[AgSbF₆]. However, at this point, we assume that 2,4,6-triphenylphosphinine (**1**) forms a kinetically less stable Au(I) complex than phosphinine-derivative *rac*-**2**, probably due to both electronic and steric effects.

To summarize the results obtained with substrate **10**, we can draw the following conclusions: in comparison to substrate **7**, the cycloisomerization of **10** to **11** and **12** is indeed much more difficult to achieve. Additives or gold-precursors either show no or only a little conversion to the corresponding oxazoline or oxazole. In the presence of [AgSbF₆] or [Cu(OTf)₂], the phosphinine-based complex *rac*-**5** forms a very active and selective catalyst, while the oxazoline-derivative is the major product. However, the right substitution-pattern of the 2,4,6-triarylphosphinine ligand seems to be essential for the formation of a stable catalyst. In contrast, the electron-donating mesoionic carbene-ligand leads to catalytic Au(I)-species, which shows a lower activity.

Experimental

General procedures, materials and instrumentation

[AuCl(SMe₂)],²⁷ **1**,^{1,28} **2**,¹⁵ **3**,²⁹ **4**¹² and the substrates **7**³⁰ and **10**³¹ were prepared as described previously in the literature. Commercially available chemicals were used as purchased, unless otherwise noted. The solvents used for metal complex synthesis and the catalytic runs were dried and distilled under nitrogen and degassed by common techniques prior to use. Column chromatography was performed over Silica 60 M (0.04–0.063 mm) or aluminium oxide, neutral 60A (50–200 µm). ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on a JEOL ECS 400 spectrometer by using the chemical shift of the solvent as an internal standard. Mass spectrometry was performed on an Agilent 6210 ESI-TOF.

Synthesis of the gold phosphinine complex *rac*-5. [AuCl(SMe₂)] (48.2 mg, 0.164 mmol) was dissolved in CH₂Cl₂ (2 mL) and was added dropwise to a solution of *rac*-**2** (60 mg, 0.164 mmol) in CH₂Cl₂ (3 mL). The resulting solution was stirred for 1 hour at room temperature. The reaction mixture was then filtered over Celite and the solvent was removed *in vacuo*. The remaining solid was washed two times with Et₂O and dried *in vacuo* yielding a pale yellow solid (60.1 mg, 72%).

¹H NMR (400 MHz, CD₂Cl₂): δ = 8.14 (d, *J*_{H-P} = 20.3 Hz, 1H), 7.75 (m, 2H), 7.49 (m, 4H), 7.45 (m, 1H), 7.41 (m, 2H), 7.26 (m, 3H), 7.13 (m, 1H), 2.39 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H) ppm. ¹³C{¹H} NMR (400 MHz, CD₂Cl₂): δ = 162.07 (d, *J* = 29.9 Hz), 157.68 (d, *J* = 24.2 Hz), 145.98 (d, *J* = 26.5 Hz), 145.41 (d, *J* = 10.1 Hz), 142.41 (d, *J* = 4.6 Hz), 139.19 (d, *J* = 11.7 Hz), 139.13 (d, *J* = 10.1 Hz), 138.58 (d, *J* = 19.6 Hz), 138.41 (d, *J* = 1.8 Hz), 135.30 (d, *J* = 8.0 Hz), 131.01 (d, *J* = 2.8 Hz), 129.77 (s), 129.59 (d, *J* = 2.3 Hz), 129.41 (d, *J* = 6.1 Hz), 129.09 (s), 128.75 (s), 128.73 (s), 128.65 (s), 128.61 (s), 128.48.78 (s), 126.24 (d, *J* = 2.1 Hz), 21.13 (d, *J* = 6.1 Hz), 20.87 (s), 17.17 (s) ppm. ³¹P{¹H} NMR (400 MHz, CD₂Cl₂): δ = 164.3 ppm.

Synthesis of the gold carbene complex **6.** A mixture of the triazolium salt **3** (1 equiv., 113.42 mg, 0.3 mmol) and silver(i) oxide (0.5 equiv., 34.76 mg, 0.15 mmol) was stirred in absolute dichloromethane (30 mL) at room temperature for 17 h under exclusion of light. Then [AuCl(SMe₂)] (1 equiv., 88.19 mg, 0.3 mmol) was added. After stirring the mixture for another 24 h at room temperature under exclusion of light, the reaction mixture was filtered over Celite, washed with dichloromethane and the solvent was evaporated. The residue was re-resolved in dichloromethane (3 mL) and precipitated with pentane (100 mL). The precipitate was collected by filtration, passed through a short pad of SiO₂ and this was eluted with dry CH₂Cl₂. Evaporation of the solvent and its precipitation again gives the complex **6** as a white solid with a yield of 82% (124.44 mg, 0.244 mmol). Single crystals suitable for X-ray diffraction analysis were obtained by condensing hexane onto a concentrated solution of the complex in dichloromethane at room temperature.

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 7.78–7.74 (m, 2H, aryl-*H*), 7.58–7.54 (m, 3H, aryl-*H*), 7.00 (s, 2H, aryl-*H*), 4.23 (s, 3H, N-CH₃), 2.36 (s, 3H, CH₃), 2.07 (s, 6H, 2 × CH₃) ppm. ¹³C

{¹H} NMR (101 MHz, CDCl₃, 25 °C) δ = 160.6 (carbene-*C*), 147.2, 140.8, 135.6, 134.3, 130.6, 129.8, 129.6, 129.4, 126.2 (all aryl-*C*), 38.2 (N-CH₃), 21.6, 17.8 (all alkyl-*C*) ppm. HRMS (ESI): Calcd for [C₁₈H₁₉AuClN₃] [(M + Na)⁺] *m/z* 532.0825, found 532.0801.

General procedure for the catalytic cycloisomerization with **4** and *rac*-5

A solution of [LAuCl] (0.0084 mmol, 1 mol%) and the additive [AgSbF₆] (1 equiv.) or [Cu(OTf)₂] (5 equiv.) in dichloromethane was added to the substrate (0.84 mmol) in CH₂Cl₂ (5 mL in total). The solution was stirred at room temperature in the dark for a given time. Samples were taken after different reaction times. For this, a little sample was taken with a syringe and filtered over a little plug of silica in the case of [Cu(OTf)₂], or Celite in the case of [AgSbF₆] and the plugs were eluted with dichloromethane. The solvent was removed *in vacuo* and conversions were detected by ¹H NMR spectroscopy.

General procedure for the catalytic cycloisomerization with **6**

To a solution of catalyst **6** (0.51 mg, 0.001 mmol, 1 mol%) and additive [AgSbF₆] (1 mol%, 1 equiv.) or [Cu(OTf)₂] (5 mol%, 5 equiv.) in absolute dichloromethane (1 mL) was added **7** (23.8 mg, 0.1 mmol) or **10** (15.9 mg, 0.1 mmol). The reaction mixture was stirred at room temperature for a given time. Hexadecane was added as the internal standard in the beginning to the reaction mixture in the case of **10**. Samples were taken after different reaction times. For this, a little sample was taken with a syringe and filtered over a little plug of silica in the case of [Cu(OTf)₂], or Celite in the case of [AgSbF₆] and the plugs were eluted with dichloromethane. The solvent was removed *in vacuo* and conversions were detected by ¹H NMR spectroscopy (for **10** with hexadecane as the internal standard and for **7** in direct comparison of the integrals).

X-ray crystal structure determination of *rac*-5

Crystals suitable for X-ray diffraction were obtained by the slow diffusion of pentane into a solution of *rac*-**5** in THF.

C₂₆H₂₃AuClP...C₄H₈O, *F*_w = 670.93, yellow block, 0.48 × 0.48 × 0.21 mm³, triclinic, *P* $\bar{1}$ (no. 2), *a* = 9.8535(1), *b* = 10.2395(1), *c* = 13.9713(2) Å, α = 109.0598(7), β = 91.5964(6), γ = 93.8629(5)°, *V* = 1327.47(3) Å³, *Z* = 2, *D*_x = 1.679 g cm⁻³, μ = 5.72 mm⁻¹. 19 592 reflections were measured on a Nonius KappaCCD diffractometer with a rotating anode and graphite monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)_{max} = 0.65 Å⁻¹. The HKL2000 software³² was used for the integration of the intensities. Multiscan absorption correction and scaling was performed with SADABS³³ (correction range 0.14–0.43). 6051 reflections were unique (*R*_{int} = 0.033), of which 5590 were observed [*I* > 2σ(*I*)]. The structure was solved with Direct Methods using SHELXS-97.³⁴ Least-squares refinement was performed with SHELXL-2014³⁵ against *F*² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 310 parameters were refined with no restraints. *R*₁/*wR*₂

$[I > 2\sigma(I)]: 0.0236/0.0534$. R_1/wR_2 [all refl.]: $0.0273/0.0547$. $S = 1.053$. Residual electron density between -1.28 and $1.46 \text{ e } \text{\AA}^{-3}$. Geometry calculations and checking for a higher symmetry were performed with the PLATON program.³⁶

CCDC 1503378 contains the supplementary crystallographic data for this paper.

X-ray crystal structure determination of 6

Single crystals suitable for X-ray diffraction analysis were obtained by condensing hexane onto a concentrated solution of the complex in dichloromethane at room temperature. X-Ray data were collected on a Bruker Smart AXS system. Data were collected at 140(2) K using graphite-monochromated Mo K α radiation ($\lambda_{\alpha} = 0.71069 \text{ \AA}$). The strategy for the data collection was evaluated by using the Smart software. The data were collected by the standard ' ω scan techniques' and were scaled and reduced using SAINT+ and SADABS software. The structures were solved by direct methods using SHELXS-97 or SHELXS_2014/7 and refined by full matrix least-squares, refining on F^2 . Non-hydrogen atoms were refined anisotropically.⁷ If they are noted, bond lengths and angles were measured with Diamond Crystal and Molecular Structure Visualization Version 3.1.

CCDC 1015504 contains the supplementary crystallographic data for this paper.

Conclusions

We have synthesized and structurally characterized Au(I)-complexes containing either a 2,4,6-triarylphosphinine or a mesoionic carbene derivative as the ligand. Both compounds show the expected quasilinear coordination geometry around the Au(I)-center, while significant aurophilic interactions between neighboring molecules are present in the complex containing the low-coordinate phosphorus heterocycle. From the crystallographic data, % buried volumes of $\%V_{\text{bur}} = 33.8$ and $\%V_{\text{bur}} = 31.8$ have been derived for the phosphinine- and carbene-based coordination compounds, respectively.

Because both ligand systems differ significantly in their donor/acceptor properties, we have further exploited these opposed electronic characteristics in the Au(I)-catalyzed cycloisomerization of dimethyl 2-(3-methylbut-2-enyl)-2-(prop-2-ynyl)malonate and the more challenging substrate *N*-2-propyn-1-ylbenzamide. It turned out that the phosphinine-based catalytic system is more active and selective than the mesoionic carbene-based one in the cycloisomerization reaction of *N*-2-propyn-1-ylbenzamide. The here presented results show for the first time that particularly sterically demanding 2,4,6-triarylphosphinine-derivatives can be used efficiently as π -accepting ligands in Au(I)-catalyzed transformations. These observations corroborate the general idea of the better performance of π -accepting ligands in gold(I) catalysis. While there is likely no "one-fits-all" ligand in catalysis, it will be intriguing to see whether the combination of mesoionic carbenes with phosphinines can generate strongly π -accepting bidentates,

which might deliver extraordinarily potent ligands for gold(I) catalysis.

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