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Ylide-Functionalized Phosphines: Strong Donor Ligands for Homogeneous Catalysis

*Thorsten Scherpf, Christopher Schwarz, Lennart T. Scharf, Jana-Alina Zur, Andreas Helbig, and Viktoria H. Gessner**

Dedicated to Professor Dietmar Stalke on the occasion of his 60th birthday

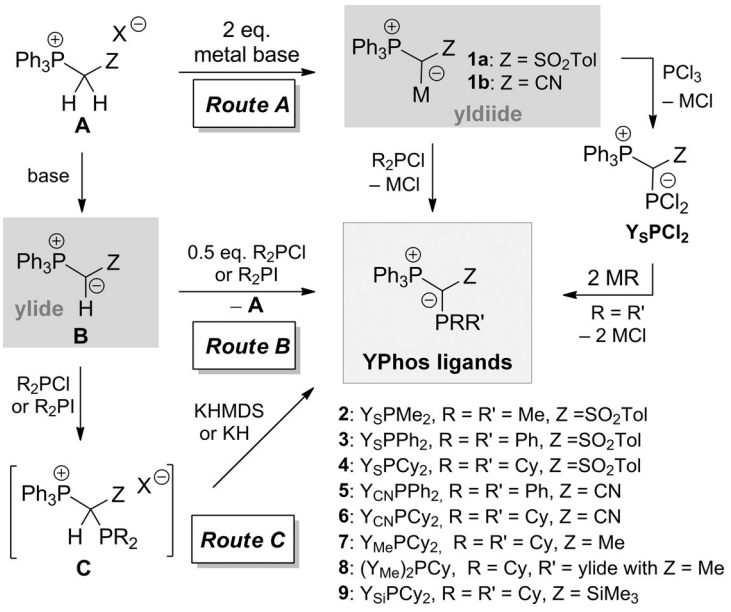
Abstract: *Phosphines are important ligands in homogenous catalysis and have been crucial for many advances, such as in cross-coupling, hydrofunctionalization, or hydrogenation reactions. Herein we report the synthesis and application of a novel class of phosphines bearing ylide substituents. These phosphines are easily accessible via different synthetic routes from commercially available starting materials. Owing to the extra donation from the ylide group to the phosphorus center the ligands are unusually electron-rich and can thus function as strong electron donors. The donor capacity surpasses that of commonly used phosphines and carbenes and can easily be tuned by changing the substitution pattern at the ylidic carbon atom. The huge potential of ylide-functionalized phosphines in catalysis is demonstrated by their use in gold catalysis. Excellent performance at low catalyst loadings under mild reaction conditions is thus seen in different types of transformations.*

Phosphines are the text book examples for ligands in transition-metal chemistry. Many advances in coordination chemistry relate to the developments of these ligands, particularly in homogenous catalysis.[1,2] Important advantages of phosphine ligands are their versatile electronic and steric properties. Their tailoring allows the requirements for different metal centers to be matched and to control the reactivity and properties of the corresponding metal complexes. Various measures are available to determine the donor strength and steric demand (e.g. the Tolman electronic parameter (TEP),[3,4] cone angle, and buried volume[5]), thus facilitating the choice of the right ligand for a given application as well as the design of novel phosphine ligands.[6,7] Although in the past two decades N-heterocyclic carbenes (NHCs)—owing to their generally higher electron-releasing properties—have garnered extensive research interest as ligand systems, phosphines are still indispensable owing to their facile accessibility and their electronic and steric versatility. Hence, until today, many transition-metal catalyzed reactions still rely on the use of phosphine ligands.[8,9] This also holds true for other important fields of applications such as organocatalysis,[10] frustrated Lewis pair (FLP) chemistry[11] or the development of new catalytic transformation.[9,12] Owing to this versatile applicability, the development of new phosphine ligands remain focus of research activities.[13] For instance, it was shown that by adjustment of the substitution pattern the donor capacity of phosphine ligands can compete or even surpass that of NHCs. As such, Carrow reported on the preparation of Ad_3P[14] while Dielmann and co-workers introduced imidazolin-2-ylidenamino substituents which enabled CO_2 binding.[15] Nonetheless, further modifications of the steric and electronic parameters are required to improve complex and catalyst stabilities as well as activities in order to meet future requirements and present needs in catalytic transformations.[16]

During our research program on ylide ligands we became interested in the synthesis of ylide-functionalized phosphines (YPhos). We envisioned that these phosphines should exhibit unusually strong donor properties due to the extra π-donation from the ylide substituent to the phosphorus atom. Herein, we show that indeed ylide-functionalization results in a novel class of highly electron-rich phosphines with outstanding properties for catalytic applications. This is demonstrated by the high catalytic activity of their gold complexes in a series of transformations.

The introduction of ylide substituents in phosphine ligands is easily accomplished via three alternative routes, all starting from readily accessible phosphonium salts **A** (Scheme 1). The three methods include 1) double deprotonation of **A** to a metallated ylide **1** and its subsequent reaction with one equivalent of a halophosphine (Route A), 2) reaction of the corresponding ylide **B** with half an equivalent of a dialkylhalophosphine (Route B) and 3) deprotonation of an α-phosphino substituted phosphonium salt **C** (Route C).[17] The efficiency of each method depends on the substituent Z

[*] T. Scherpf, C. Schwarz, L. T. Scharf, J.-A. Zur, Prof. Dr. V. H. Gessner
Lehrstuhl für Anorganische Chemie II
Fakultät für Chemie und Biochemie
Ruhr-Universität Bochum
Universitätsstrasse 150, 44801 Bochum (Germany)
E-mail: viktoria.gessner@rub.de
T. Scherpf, A. Helbig, Prof. Dr. V. H. Gessner
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201805372.



Scheme 1. Preparation of the YPhos ligands.

and the acidity of the phosphonium salt **A** and ylide **B**, respectively. Although route A is limited to the accessibility of metallated ylides, it is a highly efficient method, delivering the desired phosphines in good to excellent yields. Metallated ylides, such as **1a** or **1b**, with anion-stabilizing substituents can easily be prepared via double deprotonation of the corresponding phosphonium salt, as was previously demonstrated by our group.[18,19] Reaction of **1a** and **1b** with chlorophosphines gives the YPhos ligands **2**–**6** in good to excellent yields of 69–92 %.[20] It should be noted that yldiides can also react with PCl_3 to give the corresponding dichlorophosphines (e.g. Y_SPCl_2) and then transferred to the YPhos ligands by treatment with an organolithium or Grignard reagent (see Supporting Information). Route B and C circumvent the formation and isolation of highly sensitive intermediates. Both methods include the formation of the ylide and its subsequent reaction with a halophosphine. Route B makes use of a sacrificial equivalent of ylide, which acts both as reagent and base and is thus preferable in case of cheap and readily available ylides. In contrast, Route C requires an additional base for deprotonation of the intermediate formed α-phosphino substituted phosphonium salt **C**. It is noteworthy that both, ylide **B** and phosphonium salt **C**, do not necessarily have to be isolated. Instead, generation of the ylide-functionalized phosphines is often accomplished by a one-pot synthesis from the phosphonium salt **A**. The methyl- and silyl-substituted systems **7** and **9** were thus obtained in yields of up to 78 % via a one-step procedure from either commercially available or easily accessible starting materials. The use of dihalophosphines also allows for the synthesis of di(ylide)-functionalized phosphines such as **8**. Overall, the three preparation methods offer facile access to ylide-functionalized phosphines with a wide variety of different substituents Z in the backbone. This allows for tuning of the steric and electronic properties of the phosphine ligands which is necessary for broad applications in homogenous catalysis.

All phosphines were isolated as solid materials and characterized by various methods (Figure 1, Supporting Information). The special electronic and steric properties of the YPhos ligands already become evident in the NMR spectra. Depending on the substituent Z and the phosphorus-bound groups R two rotamers are present in solution due to the hindered rotation about the P2–C1 bond. This confinement results from the steric demand of the substituents and the repulsion between the lone pairs at the phosphorus and the ylide carbon atom leading to a preferred perpendicular arrangement of both lone pairs (Figure 2). Importantly, the two conformers can conveniently be distinguished by $^{31}P\{^1H\}$ NMR spectroscopy (Table 1). For example, Y_SPCy_2 (**4**) shows two sets of doublets in [D_8]THF solution corresponding to the *syn* and *anti*-isomers, in which the phosphorus substituents R either point to the phosphonium (*anti*-Y_SPCy_2: $^2J_{PP} = 41.0$ Hz) or to the sulfonyl substituent (*syn*-Y_SPCy_2: $^2J_{PP} = 165.8$ Hz). The *syn*-conformer is the major component, owing

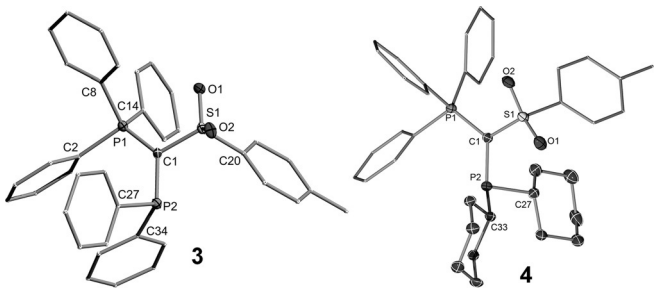


Figure 1. Molecular structures of Y_SPPh_2 (**3**) and Y_SPCy_2 (**4**) in the solid state.[35]

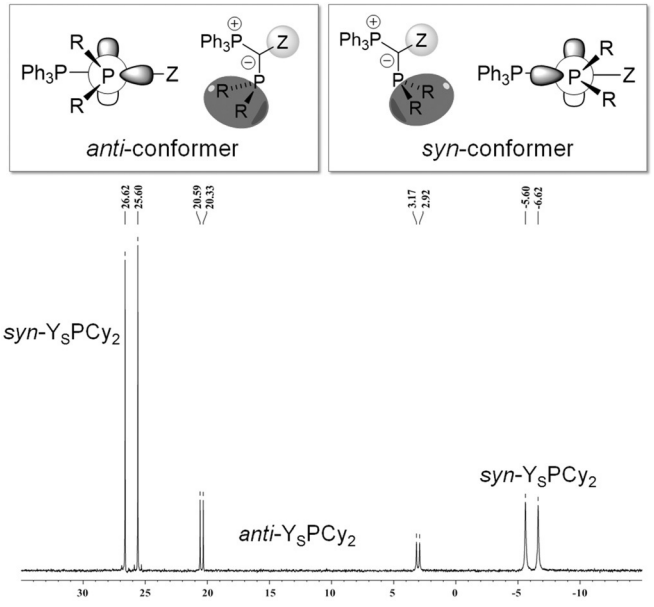


Figure 2. Top: Newman protection of the two possible conformers of the YPhos ligands. Bottom: $^{31}P\{^1H\}$ NMR spectrum of Y_SPCy_2 (**4**) in [D_8]THF.

Table 1: $^{31}P\{^1H\}$ NMR data and ratios of the conformers of the YPhos ligands at room temperature (coupling constants in Hz).

Ligand L	NMR data anti-conformer	NMR data *syn*-conformer	XRD conformer
Y_SPMe_2 (**2**)	–	100%, $^2J_{PP}=146.7$	*syn*
Y_SPPh_2 (**3**)[a]	55%; $^2J_{PP}=37.9$	45%; $^2J_{PP}=169.4$	*anti*
Y_SPCy_2 (**4**)	20%, $^2J_{PP}=41.0$	80%, $^2J_{PP}=165.8$	*syn*
$Y_{CN}PPh_2$ (**5**)	–	100%, $^2J_{PP}=146.8$	*syn*
$Y_{CN}PCy_2$ (**6**)	–	100%, $^2J_{PP}=135.7$	*syn*
$Y_{Me}PCy_2$ (**7**)	–	100%, $^2J_{PP}=177.2$	*syn*
$(Y_{Me})_2PCy$ (**8**)	–	100%, $^2J_{PP}=175.6$	*syn*
$Y_{Si}PCy_2$ (**9**)	40%, $^2J_{PP}=37.3$	60%, $^2J_{PP}=172.7$	*syn*

[a] NMR spectra recorded at −40 °C.

to the smaller repulsion of the cyclohexyl groups with the sulfonyl than with the triphenyl phosphonium moiety. For the smaller ylides with Z = Me and CN the *syn*-conformers are generally the major isomers, while for the bulkier systems (Z = $SiMe_3$) the *anti*-isomer becomes more favored. For the Y_SPPh_2 **3** slow rotation about the P2–C1 bond and thus only broadened signals are observed at room temperature, while a splitting of the signals occurs at −40 °C. In contrast, the signals of Y_sPCy_2 **4** only begin to broaden at 40 °C (see the Supporting Information for NMR spectra). In contrast to the solution, only one conformer (the major conformer in solution) is observed in the solid state. Figure 1 depicts the molecular structures of the two sulfonyl systems **3** and **4**, which exhibit the *anti*- and *syn*-conformer, respectively. Overall, the steric and electronic properties of the phosphines result in rather rigid conformations. Such a restricted flexibility has found to be advantageous in catalysis due to the formation of rigid catalyst structures directing substrates into a specific direction.

The electronic properties of the YPhos ligands were assessed by determination of the CO stretching frequency in the Rh(acac)(CO)L complexes in CH_2Cl_2 solution. The corresponding TEP values were then calculated from the relationship between ν_{CO} for $Ni(CO)_3(L)$ and Rh(acac)(CO)-(L) complexes (Table 2).[21,22] For example, Y_SPPh_2 (**3**) shows a TEP value of 2066.5 cm^{-1} and Y_SPCy_2 (**4**) a TEP value of 2055.1 cm^{-1}, which are both significantly lower than the value of PPh_3 ($\Delta\nu = 2.6\ cm^{-1}$) and PCy_3 ($\Delta\nu = 3.0\ cm^{-1}$), respectively. This comparison allows the determination of the χ_i value[23] for the ylide substituent in the systems **2**, **3**, and **4**, which amounts in average to $\chi_i = -0.7$. Thus, the sulfonyl-substituted ylide Y_S is more electron releasing than a *t*Bu group and in the range of an adamantyl group.[14] In comparison to Y_S, the cyano-functionalized ylide is slightly less electron-donating, while the methyl-substituted system is even more electron-donating ($\chi_i = -6.8$). $Y_{Me}PCy_2$ (**7**) possesses a TEP value of 2050.1 cm^{-1}, which is even smaller than that reported for PAd_3 and comparable to the *N*-heterocyclic carbene IMes.[14,22] The silyl-system $Y_{Si}PCy_2$ (**9**) further surpasses this donor-capacity featuring a TEP value of 2048.9 cm^{-1} ($\chi_I = -7.4$).

To determine and predict the electronic properties of our YPhos ligands we calculated the electrostatic potential (ESP) at the phosphorus atom, which was reported to be a good measure for the donor strength, also being independent of conformational changes.[24] In general, the value of the ESP at phosphorus V_P becomes more negative with decreasing TEP and increasing donor strength. Correlation of the calculated V_P values of a series of simple phosphines and YPhos ligands with their experimentally determined TEP values gave a linear relationship (see Supporting Information), which confirmed the high donor strength of the new phosphines and allowed the calculation of TEP values for unknown systems (Table 2). For example, a remarkably low TEP value of 2044.6 was calculated for the di(ylide)-substituted phosphine **8**, with which we failed to obtain reliable experimental data.

Table 2: The structural and spectroscopic properties of the different phosphine ligands.

Ligand L	ν_{CO}(Rh)[a] [cm^{-1}]	TEP[b] [cm^{-1}]	TEP_{calcd}[c] [cm^{-1}]	$\%V_{bur}$[d]
PPh_3	1978.0	2069.1	2066.9	29.9[e]
PCy_3	1958.7	2058.1	2057.3	–
PAd_3[e]	1948.3	2052.1	–	40.5
IMes[f]	1958	2050.7	–	31.2
Y_SPMe_2 (**2**)	1961.6	2059.7	2061.0	46.2
Y_SPPh_2 (**3**)	1973.4	2066.5	2066.2	49.6
Y_SPCy_2 (**4**)	1953.5	2055.1	2057.7	54.3
$Y_{CN}PPh_2$ (**5**)	1973.8	2066.7	2064.4	44.3
$Y_{CN}PCy_2$ (**6**)	1958.3	2057.8	2058.2	45.4
$Y_{Me}PCy_2$ (**7**)	1944.8	2050.1	2051.7	48.2
$(Y_{Me})_2PCy$ (**8**)	–	–	2044.6	55.1
$Y_{Si}PCy_2$ (**9**)	1942.7	2048.9	2053.7	45.1[g]

[a] ν_{CO} in Rh(acac)(CO)L in CH_2Cl_2, see Ref. [1]. [b] Calculated from the relationship between ν_{CO} for $Ni(CO)_3(L)$ and Rh(acac)(CO)(L).[14] [c] See Supporting Information for details. [d] Calculated with the SambVca 2.0 program for the LAuCl complexes with a P–M distance of 2.28 Å including H atoms.[25] [e] Ref. [14]. [f] Ref. [22,5] [g] Ref. [26].

To measure the steric demand of the YPhos ligands, the buried volume ($\%V_{bur}$) was calculated[25] using the geometries from the molecular structures of the LAuCl complexes (Table 2 and Supporting Information). The steric protection is considerably higher than that of other phosphines. As such, $\%V_{bur}$ of Y_SPPh_2 is calculated to be 49.6, and is thus even higher than the value calculated for PAd_3 and most of the commonly used NHCs, but in the range of Buchwald ligands.[5] Importantly, the steric demand can be tuned by the ylide-substituent Z. Bulky Z moieties result in a larger P-C-Z and smaller P-C-P angle forcing the phosphine substituents closer to the metal. This can be seen from the series of ligands $Y_{CN}PCy_2$ (**6**), $Y_{Me}PCy_2$ (**7**), and Y_SPCy_2 (**4**), in which the Z substituent and with that $\%V_{bur}$ increases from 45.4% to 54.3%. It is noteworthy that the ligands show a *syn*-arrangement in all complexes, with the phosphonium moiety being on the same side as the AuCl fragment (Figure 3).[26] This *syn*-preference contrasts with the structures of the free phosphines and can be explained by attractive π-interactions between gold and one of the phenyl groups of the phosphonium moiety. Such an interaction between an aryl group and a metal center presumably stabilizes low-coordinate metal centers thus being beneficial for the catalytic performance.[8,27]

The observed electronic and steric properties of the YPhos ligands promise an excellent aptitude to support active

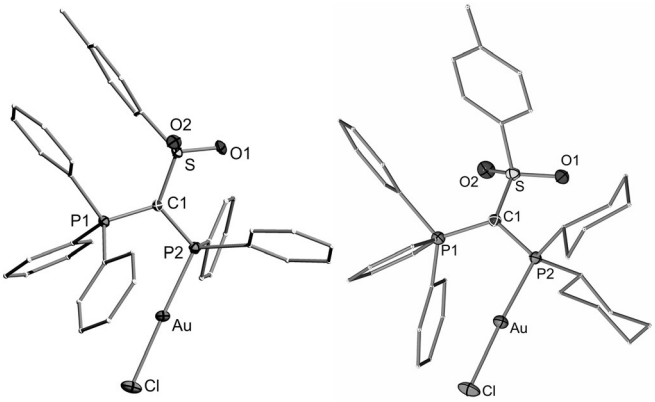


Figure 3. Molecular structures of the AuCl complexes of **3** (left) and **4** (right).[35]

transition metal catalysts, particularly in reactions where strong electron-donating ligands and steric protection of low-coordinated species are required. To verify this hypothesis, we turned our attention towards gold catalysis, since here bulky phosphine ligands have proven to possess superior activity than NHC analogues.[28] We chose the Au^I-catalyzed hydroamination of phenyl acetylene with aniline as test reaction.[29,30] In a typical reaction, the reagents were stirred at a given reaction temperature with catalytic amounts of the gold complex LAuCl and $NaBAr^F_4$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$) for halide abstraction. We focused on mild reaction temperatures, since most Au catalysts require harsh reaction conditions, thus limiting their synthetic scope. At low temperatures, complexes with simple phosphines (PCy_3 or PPh_3) only provide low conversions due to catalyst degradation. At first, 1 mol% of the gold complex of Y_SPPh_2 was applied in a 1:1 neat mixture of amine and alkyne at room temperature, which resulted in a highly exothermic reaction and the boiling of the reaction mixture. This suggested high reaction rates and a highly active catalyst, which should thus also operate at lower loadings than usually applied in gold catalysis. To study the activity in a more controlled manner the catalyst loading was decreased. Using 0.1 mol% at 50°C led to complete conversion within 12 h. On preparative scale, 82% product were isolated after 5 h. Under the same conditions, PPh_3 only allowed the formation of approximately 30% product. Control experiments using either only LAuCl or $NaBAr^F_4$ showed no activity. To further study the activity of the phosphine ligands kinetic studies were performed at 50°C with low catalyst loadings (Figure 4). The catalysts are highly active in the beginning of the reaction. For example, 70% conversion was already obtained after 2 h reaction time with 0.1 mol% Y_SPPh_2. This performance is comparable to the structurally optimized Buchwald-type phosphines, which are the most active gold catalysts for hydroamination reactions.[31] Owing to the high costs of gold, low catalyst loadings are particularly important for applications. However, only few catalysts exist that allow for turnover numbers (TON) higher than 5000 in hydroamination of alkynes with primary amines.[32] Hence, we turned our attention towards the methyl and cyclohexyl systems, Y_SPMe_2 and Y_SPCy_2, which showed higher electron-donating properties. As expected, the Y_SPCy_2 ligand turned out to be superior, while Y_SPMe_2 and Y_SPPh_2 are equal in activity (Table 3; entry 4, 6, and 9). With 0.1 mol% Y_SPCy_2·AuCl at 50°C full conversion (>95%) was already reached within 3 h reaction time. A further decrease in the catalyst loading to 0.05 mol% required longer reaction times but still provided 94% yield in 24 h. With 0.01 mol% a TON of 8000 could be reached over 2 days, also demonstrating the long-term stability of the catalytic system. At 80°C even TONs of 14400 were obtained within 48 h. Hence, the Y_SPCy_2 based catalyst outperforms—despite its facile synthesis—most of the reported gold catalysts for hydroamination reactions without requiring additional additives or elaborate

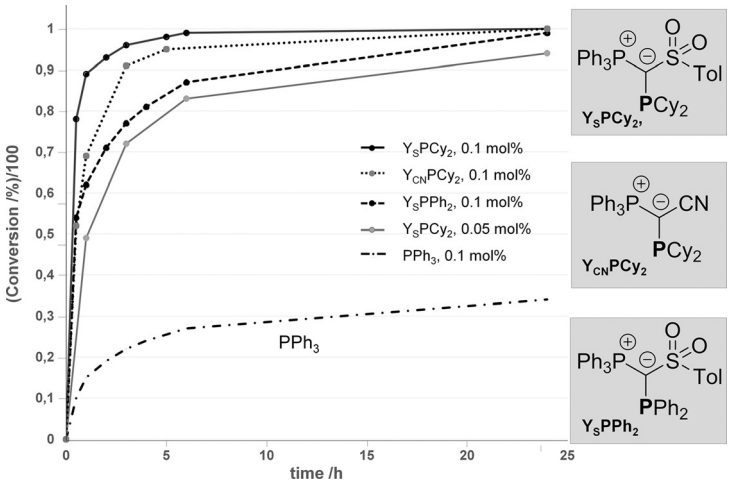
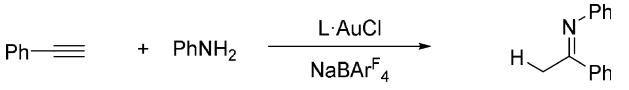


Figure 4. Catalytic activity of the LAuCl with selected YPhos ligands; conditions: 0.1 mol% cat., 0.1 mol% $NaBAr^F_4$, 50°C, unless otherwise stated.

Table 3: Gold(I)-catalyzed hydroamination of phenylacetylene with aniline and ylide-functionalized phosphines.



Entry	L in Cat. LAuCl	Cat [Mol%]	*t* [h]	*T* [°C]	Yield [%][a]
1	Y_SPPh_2	0.1	1	50	52
2	Y_SPPh_2	0.1	5	50	82 isolated
3	Y_SPPh_2	0.1	12	50	99
4	Y_SPPh_2	0.05	24	50	69
5	Y_SPMe_2	0.1	24	50	96
6	Y_SPMe_2	0.05	24	50	71
7	Y_SPCy_2	0.1	1	50	83
8	Y_SPCy_2	0.1	3	50	96
9	Y_SPCy_2	0.05	6	50	83
10	Y_SPCy_2	0.05	24	50	94
11	Y_SPCy_2	0.01	24	50	62
12	Y_SPCy_2	0.01	48	50	80
13	Y_SPCy_2	0.005	24	80	63
14	Y_SPCy_2	0.005	48	80	72

[a] NMR yields determined by direct integration of the peak for the alkyne starting material with respect to the peak for the imine product.

ligand design. Notably, the catalytic system is highly stable also towards water or exposure to air.[33]

To evaluate the substrate scope further amines and alkynes were tested in hydroamination reactions using Y_SPCy_2·AuCl in low catalyst loadings (Figure 5). A series of different amines could successfully be transferred into the corresponding imines in high yields, thus confirming the activity of the catalytic system and its functional group tolerance. Electron-rich and electron-poor primary aryl amines as well as secondary amines reacted effectively with phenylacetylene to the corresponding imines (and enamine, respectively). Also, aliphatic as well as internal alkynes easily underwent hydroamination with aniline. All reactions were performed without any solvent thus further demonstrating the efficiency of the catalyst described and the sustainability of the reaction protocol. Besides the hydroamination of alkynes the YPhos ligands were also applied in further transformations. Fortunately, Y_SPCy_2·AuCl was also active in the intramolecular cyclization of 4-pentynoic acid **10** to lactone **11** as well as the hydration of phenyl acetylene to acetophenone. More impressively, also the intermolecular [2+2] cycloaddition of phenylacetylene and α-methylstyrene to **13** was found to be catalyzed by Y_SPCy_2·AuCl. This reaction was reported by Echavarren and López-Carrillo in 2010, who obtained the best results with the Buchwald ligand *t*Bu-XPhos, which performed superior to NHC complexes.[34] While they observed 81% yield with 3 mol% of catalyst, Y_SPCy_2 accomplishes 78% yield with 0.5 mol% catalyst loading. Overall, these examples underline the excellent performance of our YPhos ligands in gold catalysis.

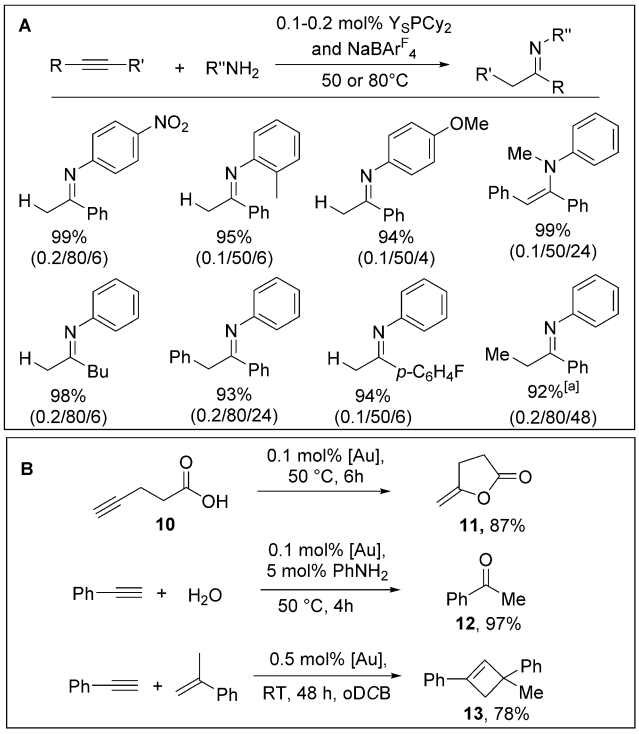


Figure 5. A) Hydroamination of different alkynes with different amines; numbers in brackets are (mol% catalyst/reaction temperature [°C]/time [h]). [a] 1:1 mixture of both regioisomers. B) Further Au-catalyzed reactions with Y_SPCy_2 (^{1}H NMR yields; [Au] = Y_SPCy_2·AuCl, $NaBAr^F_4$).

In conclusion, we reported the synthesis of ylide-functionalized phosphines and their use as strong donor ligands. The ligands are easily accessible from cheap and commercially available starting materials and allow for a facile variation of the steric and electronic properties. Spectroscopic studies confirm the high electron-releasing properties, surpassing classical phosphine and even NHC ligands. Together with the large buried volume, these new phosphine ligands are beneficial to stabilize low coordinate transition metal compounds often being the active species in catalysis. Consistently, the YPhos ligands were found to support highly active gold(I) catalysts such as for the hydroamination or hydration of alkynes under mild reaction conditions. Owing to the multifarious variation possibilities to tune their steric and electronic properties, the YPhos ligands are ideal ligands for further catalytic applications. Current studies concern the utility of the ligands in large-scale processes and coupling reactions.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

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