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ARTICLE

Effective Control of the Electron-donating Ability of Phosphines by using Phosphazenyl and Phosphoniumylidyl Substituents

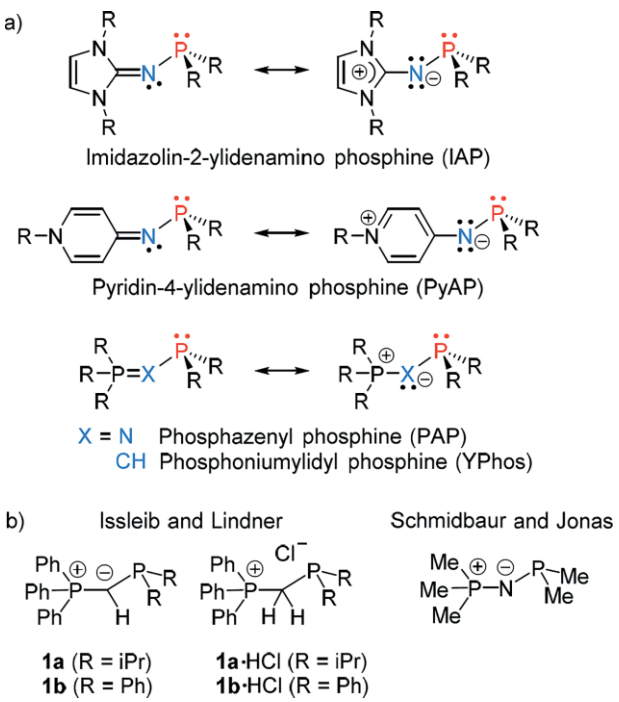
Janina A. Werra,[a] Marius A. Wünsche,[a] Patrick Rathmann,[a] Paul Mehlmann,[a] Pawel Löwe,[a] and Fabian Dielmann*[a]

Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday with our Warmest Congratulations

Abstract. Phosphoniumylidyl and phosphazenyl groups are effective substituents to increase the electron-donating ability of tertiary phosphines. However, the influence of structural variations among those substituents on the electronic properties of the phosphines is little explored. Herein, we show that protonation of the ylidic carbon atom of phosphoniumylidyl phosphines increases the Tolman electronic parameter (TEP) by ΔTEP = 16.0–18.8 cm^{-1}. Furthermore, phosphazenyl phosphines were synthesized with isopropyl groups (NP{*i*Pr}$_3$) and tetramethylguanidino groups (NP{tmg}$_3$) at the phosphonium center. Determination of their TEP values reveals a remarkable low substituent parameter of χ = –18.5 cm^{-1} for the NP(tmg)$_3$ group. In addition, we prepared the corresponding gold(I) complexes and determined their solid-state structures using single-crystal X-ray diffraction studies to analyze the steric profile of the new phosphine ligands.

Introduction

The success of tertiary phosphines as ancillary ligands in coordination chemistry and catalysis is closely related to the outstanding ease to rationally tune their steric and electronic properties via the substituents at the phosphorus atom.[1] This flexibility provides a convenient approach to fine-tuning the performance of known catalysts.[2] In this context, various steric and electronic descriptors of phosphine ligand properties have been proposed,[3] the Tolman electronic parameter being the most commonly used among them.[4] With respect to the accessible electron-donating character, alkylphosphines, particularly tri-*tert*-butylphosphine, have been regarded as the upper limit for more than half a century. Advances to increase the electron-donating power of phosphines include the functionalization with electropositive plumbyl,[5] carboranyl,[6] N-heterocyclic boryl,[7] anionic boratabenzene,[8] or anionic secondary phosphine oxide[9] substituents. Recently, *Carrow* reported a synthesis for tris-adamantylphosphine[10] and showed that the donor strength is in the range of classical N-heterocyclic carbene ligands. We have contributed to this field with the discovery that strong π-donating substituents bound to the phosphorus atom can substantially increase the electron-donating power of phosphines.[11] Following up on early studies on the synthesis of guanidine-functionalized phosphines by *Schmutzler* and *Kuhn*,[12] we used different imidazolin-2-ylidenamino groups to generate phosphines (IAPs) with significantly lower TEP values than those of N-heterocyclic carbenes or abnormal carbenes[13] (Scheme 1a).[11,14]



Scheme 1. (a) Resonance structures of electron-rich phosphines with selected π-donor substituents. (b) Early examples of phosphoniumylidyl and phosphanzenyl phosphines.

We recently expanded this concept to pyridinylidenamino phosphines (PyAPs) which are accessible in a much shorter synthetic route than IAPs starting from commercially available

* Dr. F. Dielmann
E-Mail: dielmann@uni-muenster.de
[a] Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster
Corrensstrasse 30
48149 Münster, Germany
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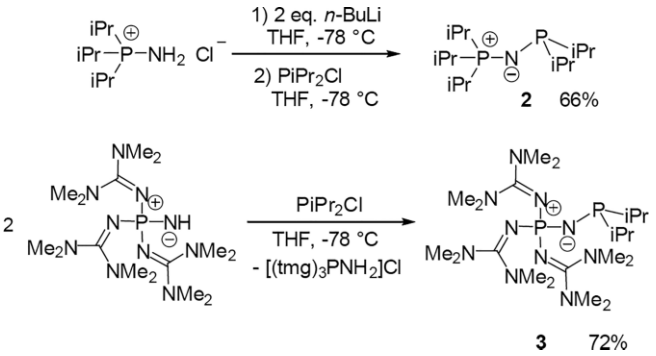
aminopyridines and chlorophosphines (Scheme 1a).[15] The potential of IAPs as strongly donating ligands in catalysis has been demonstrated in Au-catalyzed hydroamination reactions and Pd-catalyzed cross-coupling reactions.[11,16] Moreover, owing to their highly basic character, IAPs became valuable tools in stoichiometric and catalytic phosphine-mediated transformations.[17,18] As a natural continuation of these studies, we became interested to explore the effect of other π-donor substituents such as phosphoniumylidyl and phosphazenyl groups on the electronic properties of phosphines (Scheme 1a). Phosphines with phosphoniumylidyl groups (YPhos) were first prepared in 1966 by *Issleib* and *Lindner* (Scheme 1b).[19] Further contributions to the chemistry of YPhos can be traced back to the groups of *Appel* and *Schmidbaur*.[20] Recently, *Gessner* and co-workers explored the ligand properties of phosphoniumylidyl phosphines and used them in Au-catalyzed hydroamination and Pd-catalyzed cross-coupling reactions.[21,22] However, the donor properties of the first reported YPhos $P(CHPPh_3)Ph_2$ and the effect of protonation at the ylidic carbon atom on the electronic properties of the phosphine P atom remained unexplored.

First reports by *Schmidbaur* and *Jonas* on the synthesis of phosphines with phosphazenyl groups (PAP) date back to 1968 (Scheme 1b).[23] The synthesis and reactivity of PAPs was studied by different groups in the following years.[24] However, the electronic properties of PAPs as a ligand remained unexplored until *Sundermeyer* recently showed that phosphines carrying three tris(dialkylamino)phosphazenyl groups $P(NP\{NR_2\}_3)_3$ are among the strongest neutral superbases and display the lowest TEP values of all phosphine ligands.[25]

Herein we study the influence of structural variations among phosphoniumylidyl and phosphazenyl groups on the electronic properties of the resulting phosphines and compare their substituent effects to those of N-heterocyclic imine substituents.

Results and Discussion

The phosphoniumylidyl phosphines $P(CHPPh_3)iPr_2$ (**1a**), $P(CHPPh_3)Ph_2$ (**1b**), and their corresponding protonated phosphines **1a**·HCl and **1b**·HCl were synthesized according to the reported procedure from *Issleib* and *Lindner*.[19] Phosphazenyl phosphine $P(NPiPr_3)iPr_2$ (**2**) was synthesized following *Schmidbaur's* approach[23] by deprotonation of aminotriisopropylphosphonium chloride with *n*-butyllithium and subsequent treatment with chlorodiisopropyl phosphine, which gave **2** as a colorless oil in 66% yield (Scheme 2). To avoid the formation of coordination compounds with lithium salts,[14] phosphine **3** was synthesized by reacting two equivalents of tris(tetramethylguanidino)phosphazene imine[26] with chlorodiisopropylphosphine (Scheme 2), the second equivalent of imine being used as a base. After extraction with *n*-hexane, the phosphazenyl phosphine **3** was obtained as a white solid in 72% yield. The air and moisture sensitive compounds **2** and **3** both show two characteristic doublets at δ = 68.4 ppm, 33.0 ppm (**2**) and δ = 67.9 ppm, –10.7 ppm (**3**) in the $^{31}P\{^1H\}$ NMR spectra with $^2J_{PP}$ coupling constants of 54 Hz (**2**) and 83 Hz (**3**), respectively.



Scheme 2. Synthesis of phosphanzenyl phosphines **2** and **3**. (tmg = *N*,*N*,*N*′,*N*′-tetramethylguanidino).

Single-crystal X-ray diffraction (XRD) studies of **1a**·HCl and **1b**·HCl (Figure 1) confirm the proposed structure by *Issleib* and *Lindner*[19] with the additional proton attached to the ylidic carbon atom. For both compounds hydrogen bonding interactions are observed between one of the acidic methylene protons and the chloride counteranion with H···Cl distances of 2.694 Å (**1a**·HCl) and 2.746 Å (**1b**·HCl). The P1–C1–P2 angels of **1a**·HCl (111.4°) and **1b**·HCl (115.5°) are slightly larger than expected for an ideal tetrahedral arrangement of 109.5°. The P2–C1 bonds (**1a**·HCl: 1.798 Å, **1b**·HCl: 1.791 Å) are in the typical range of phosphonium P–C bonds ($[Ph_3PCH_3]^+$: 1.783 Å),[27] and the P1–C1 bond lengths (**1a**·HCl: 1.877 Å, **1b**·HCl: 1.867 Å) are of similar magnitude to those in PCy_3 (1.866 Å).[28]

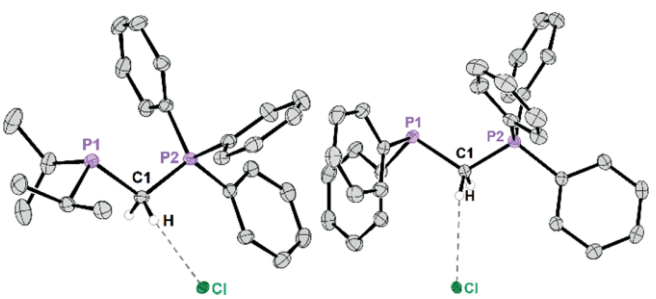
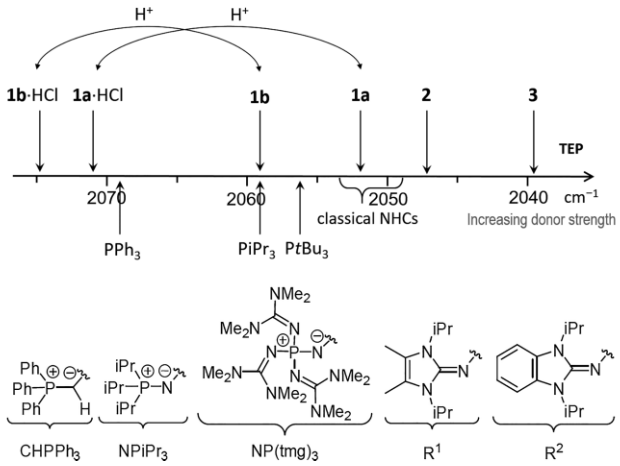


Figure 1. Molecular structures of **1a**·HCl (left) and **1b**·HCl (right). Only the hydrogen atoms of the PCH_2P unit are depicted; thermal ellipsoids are set at 50% probability. Solvent molecules are not displayed. Selected bond lengths /Å and angles /°: **1a**·HCl: P1–C1 1.877(2), P2–C1 1.798(2), P1–C1–P2 111.42(12). **1b**·HCl: P1–C1 1.867(2), P2–C1 1.791(2), P1–C1–P2 115.52(9).

To analyze the influence of the individual π-donor substituents on the donor strength of the phosphines, we prepared the corresponding nickel(0) complexes $[Ni(CO)_3(L)]$ (L = phosphine ligand) from the reaction of the phosphines with nickel(0) tetracarbonyl. The frequency of the A_1 CO stretching mode of these complexes, referred to as Tolman electronic parameter (TEP),[4] is a method to gauge the overall electron-donating ability of ligands (Table 1). *Tolman* also defined a single substituent parameter χ_i [$\sum_{i=1}^{3}\chi_i$ = TEP – 2056.1 cm^{-1}],[4] which reflects the individual contributions of a substituent R^i to the overall donor strength of a phosphine $PR^1R^2R^3$. Since

these contributions are largely additive, it in turn enables the prediction of TEP values of unknown phosphines. However, the substituents parameters can differ significantly depending on the nature of the remaining substituents.[29] Hence, for a better comparison of the π-donor substituents, we calculated the χ values using the TEP values of phosphines with two additional isopropyl groups [χ(*i*Pr) = 1.0] at the phosphorus atom (Table 2).

Table 1. TEP values of phosphines **1a**, **1b**, **1a**·HCl, **1b**·HCl, **2**, **3** and selected phosphines for comparison. Values were obtained in CH_2Cl_2.



Phosphine (L)	TEP /cm^{-1}
$P(OMe)_3$	2079.5 [a]
$[P(CH_2PPh_3)Ph_2]Cl$ (**1b**·HCl)	2075.0
$[P(R^1H)iPr_2]OTf$	2070.4 [a]
$[P(CH_2PPh_3)iPr_2]Cl$ (**1a**·HCl)	2070.7
PPh_3	2068.9 [a]
$P(CHPPh_3)Ph_2$ (**1b**)	2059.0
$PiPr_3$	2059.2 [a]
$P(R^2)iPr_2$	2053.6 [a]
$P(CHPPh_3)iPr_2$ (**1a**)	2051.9
$P(R^1)iPr_2$	2047.5 [a]
$P(NPiPr_3)iPr_2$ (**2**)	2047.1
$P(R^2)_3$	2044.3 [a]
$P(NP\{tmg\}_3)iPr_2$ (**3**)	2039.6 (2037.1) [b]
$P(R^1)_3$	2029.7 [a]

a) Values taken from *Tolman* et al.[4] and *Dielmann* et al.[11,14,18,32]. b) Value obtained using the solid compound.

The TEP values of phosphoniumylidyl phosphines **1a** (2051.9 cm^{-1}) and **1b** (2059.0 cm^{-1}) are in the range of alkylphosphines[4] and N-heterocyclic carbenes (NHCs),[30] respectively. With an χ of –6.2 cm^{-1} the contribution of the $CHPPh_3$ substituent to the donor strength of the phosphine is in the range of that of benzimidazonlin-2-ylidenamino groups (R^2).[14,18] The comparison with phosphoniumylidyl phosphines developed by *Gessner* and co-workers reveals similar substituent parameters if the ylidic H atom is replaced by a methyl group, while the introduction of cyanide or tosyl groups at this position results in significantly less negative χ values (Table 2).[22] The most significant effect on the χ value is observed upon protonation of the ylidic carbon atom, which transforms the neutral phosphoniumylidyl group into a cationic substituent comprising a substituent parameter (χ = 12.6 cm^{-1}) in the range of the C_6F_5 group[4] (χ = 11.2 cm^{-1}) but less positive than *Alcarazo*'s cationic cyclopropenium substituents (χ = 18.2 cm^{-1}).[31]

Table 2. Substituent parameters χ of phosphoniumylidyl, phosphazenyl and selected other substituents for comparison. Values were calculated from $PiPr_2R$.

Substituent (R)	χ /cm^{-1}
$CH_2PPh_3^+$	12.6
OMe	7.7 [a]
Ph	4.3 [a]
$C(CN)PPh_3$	1.5 [b]
*i*Pr	–1.0 [a]
$C(SO_2Tol)PPh_3$	–1.2 [b]
R^2	–4.5 [c]
$CHPPh_3$	–6.2
$C(CH_3)PPh_3$	–6.2 [b]
R^1	–10.6 [c]
$NPiPr_3$	–11.0
$NP(NMe_2)_3$	–11.2 [a]
$NP(tmg)_3$	–18.5 (–21.0) [d]

a) Calculated from PR_3.[4,25] b) Calculated from PCy_2R. The corresponding TEP value was calculated from the relationship between ν_{CO} for $[Ni(CO)_3(L)]$ and $[Rh(acac)(CO)(L)]$.[22] c) Calculated from literature TEP values.[11,18] d) Calculated from the TEP value of the solid compound.

Upon protonation, the TEP values of phosphines **1a** and **1b** shift by ΔTEP = 16.0 cm^{-1} and ΔTEP = 18.8 cm^{-1} to higher wave numbers, respectively (see the Supporting Information for the XRD study of $[Ni(CO)_3$(**1b**·HCl)]). Similar proton responsive properties have been observed for imidazolin-2-ylidenamino phosphines, which allow for switching the phosphine's donor strength within a larger range (ΔTEP up to 43.4 cm^{-1}).[32]

Sundermeyer and co-workers recently showed that phosphazenyl groups are most effective in increasing the electron-donating ability and the basicity of phosphines.[25] From the TEP value of $P(NP\{NMe_2\}_3)_3$ (2022.4 cm^{-1}) a substituent parameter of χ = –11.2 cm^{-1} can be derived. Surprisingly, the TEP value of **2** (2047.1 cm^{-1}) suggests a similar substituent parameter for the $NP(iPr)_3$ group (χ = –11.0 cm^{-1}). This similarity agrees with the similar basicities of proton sponges equipped with those substituents [with $NP(iPr)_3$: pK_α(THF) = 21.9, with $NP(NMe_2)_3$: pK_α(THF) = 22.6].[33]

In phosphine **3**, strongly π-donating tetramethylguanidino (tmg) groups are attached to the phosphonium center resulting in a χ value of –18.5 cm^{-1} for the $NP(tmg)_3$ substituent. This homologization concept leads to a further delocalization of the positive charge into the guanidine groups and has been introduced by *Schwesinger* to increase the basicity of phosphazene nitrogen superbases.[26,34] Although phosphine **3** carries only one π-donor group at the P atom, the TEP value of **3** (2039.5 cm^{-1}) is significantly lower than those of the IAP $P(R^2)_3$ (see Table 1) and has comparable donor abilities to abnormal NHCs[35] and cyclic alkyl amino carbenes.[36] Given the additivity of the substituent effects, TEP values of 2020.1 cm^{-1} and 2000.6 cm^{-1} can be estimated for the hypothetical phosphines $P\{NP(tmg)_3\}_2iPr$ and $P\{NP(tmg)_3\}_3$, respectively. Note that the determination of the donor strength

of **3** using a solid sample of [Ni(CO)$_3$(**3**)] gives an even lower TEP value of 2037.1 cm^{-1}. It has been observed that the interaction of the basic nitrogen atoms adjacent to the phosphorus atom with acidic CH protons such as those in dichloromethane can increase the TEP value.[15,32]

In order to compare the stability of the phosphines towards oxidation with molecular oxygen, phosphines **1a** and **3** were exposed to an oxygen atmosphere at room temperature. ^{31}P NMR analysis of the reaction mixture showed partial decomposition (30 %) of **1a** and complete decomposition of **3** after nine hours (see the Supporting Information). These preliminary results indicate a higher stability of the YPhos **1a** towards oxygen compared to PAP **3**, which agrees with the higher basicity of the latter.

To explore the coordination behavior of the electron-rich phosphines **1a**, **1b**, **2** and **3**, we prepared the corresponding Au^{I} complexes [AuCl(L)] (**4a**, **4b**, **5**, **6**) from the reaction of [AuCl(tht)] with the respective phosphines. After removing the volatiles under reduced pressure the complexes were obtained as colorless solids in quantitative yields.

The ^{31}P NMR signals of phosphines **1–3** and their corresponding complexes **4–6** are listed in Table 3. Regarding the YPhos compounds, the P^{III} signals are significantly shifted to higher frequencies upon coordination, while the chemical shift of the P^{V} are largely unaffected. For the PAPs, only minor changes were observed among the ^{31}P NMR chemical shifts upon coordination. However, the $^{2}J_{PP}$ coupling constants of all investigated phosphines decrease significantly upon coordination to the gold(I) chloride fragment. These results are consistent with previous observations.[20,21,37,38]

Table 3. ^{31}P NMR shifts and $^{2}J_{PP}$ coupling constants of phosphines **1a**, **1b**, **2** and **3**, and the corresponding gold complexes **4a**, **4b**, **5** and **6**.

Compound	δ(P^{III}) /ppm	δ(P^{V}) /ppm	$^{2}J_{PP}$ /Hz
1a	–2.7	22.4	132
1b	–18.4	23.5	149
4a	37.6	21.8	45
4b	15.2	23.7	64
2	68.4	33.0	54
3	67.9	–10.7	83
5	71.3	38.4	5
6	65.4	–14.1	5

The solid-state structures of **4a**, **4b**, **5** and **6** were established using XRD studies (Figure 2). The Au–Cl bonds in *trans* position to the phosphines (**4a**: Au–Cl 2.2939 Å, **4b**: Au–Cl 2.3067 Å, **5**: Au–Cl 2.3112 Å, **6**: Au–Cl 2.3302 Å) are significantly elongated with increasing donor character of the phosphines. The P–C–P angles of the phosphines in **4a** (126.4°) and **4b** (124.3°) are larger than those of the free protonated phosphines **1a**·HCl (111.4°) and **1b**·HCl (115.5°). The protonation of the ylidic carbon in **1a**,**b** also effects the P–C1 bond lengths. For example, the P1–C1 bond (1.877 Å) and P2–C1 bond (1.798 Å) in **1a**·HCl are elongated compared to those in **4a** (P1–C1: 1.737 Å, P2–C1: 1.696 Å). From the solid-state structures of complexes **4a**, **4b**, **5** and **6** the percent buried volume (% V_{bur}) of the phosphines was calculated (Table 4). The values calculated for **1a** (45.1 %) and **1b** (44.1 %) are comparable to PMes$_3$ (45.0 %).[39] The investigated phosphazenyl phosphines **2** (37.3 %) and **3** (42.9 %) show a lower steric demand than the carbon analogues. This presumably derives from the larger P–N–P angles of **2** and **3** in relation to P–C–P angles of **1a** and **1b**. The obtained % V_{bur} of **2** and **3** are similar to values of alkylphosphines as P*t*Bu$_3$ or P(*o*-tol)$_3$ (Table 4).[39]

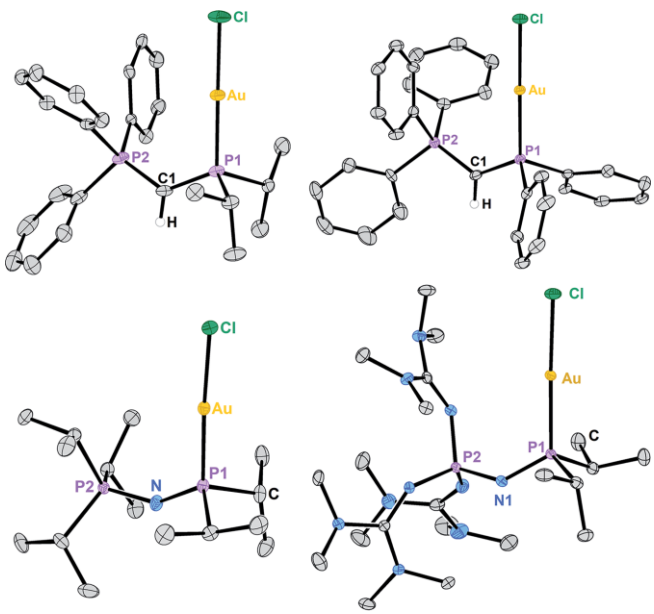


Figure 2. Molecular structures of **4a** (top, left), **4b** (top, right), **5** (bottom, left) and **6** (bottom, right). Only the hydrogen atoms of the PCHP unit are depicted; thermal ellipsoids are set at 50 % probability. Disorders and solvent molecules are not displayed. Selected bond lengths /Å and angles/°: **4a**: Au–Cl 2.2939(6), Au–P1 2.2407(6), P1–C1 1.737(2), P2–C1 1.696(2), P1–Au–Cl 178.01 (2), P2–C1–P1 126.43(14). **4b**: Au–Cl 2.3067(8), Au–P1 2.2438(8), P1–C1 1.719(3), P2–C1 1.700(3), P1–Au–Cl 179.25(3), P2–C14–P1 124.3(2). **5**: Au–Cl 2.3112(4), Au–P1 2.2446(4), P1–N 1.6089(14), P2–N 1.5682(14), P1–Au–Cl 176.64(2), P2–N–P1 144.97(10). **6**: Au–Cl 2.3302(6), Au–P1 2.2489(6), P1–N1 1.609(2), P2–N1 1.585(2), P1–Au–Cl 178.00(2), P2–N1–P1 131.33(13).

Table 4. Percent buried volume (% V_{bur}) for P–M length at 2.28 Å of **1a**, **1b**, **2** and **3** and selected phosphines for comparison. The values were calculated from the complexes **4a**, **4b**, **5**, **6** using the SambVca 2.1 web application [39] (r = 3.5 Å, bond radii are scaled to 1.17 Å).

Phosphine (L)	% V_{bur}
PCy$_3$	33.4 [a]
P(NP*i*Pr$_3$)*i*Pr$_2$ (**2**)	37.3
P*t*Bu$_3$	38.1 [a]
P(*o*-tol)$_3$	41.4 [a]
P(NP(tmg)$_3$)*i*Pr$_2$ (**3**)	42.9
P(CHPPh$_3$)Ph$_2$ (**1b**)	44.1
PMes$_3$	45.0 [a]
P(CHPPh$_3$)*i*Pr$_2$ (**1a**)	45.1

a) Values taken from *Nolan* et al.[40]

Conclusions

In summary, the influence of structural variations among phosphoniumylidyl and phosphazenyl groups on the stereoelectronic properties of the resulting phosphines was studied

upon synthesis and characterization of two phosphoniumylidyl phosphines (**1a**, **1b**), two phosphazenyl phosphines (**2**, **3**) and their corresponding gold(I) complexes. Structural analyses of the new phosphines indicate that the phosphoniumylidyl groups generate more bulky phosphines than the phosphazenyl groups due to the larger P–N–P angle of the latter. The determination of the TEP values reveals that the electron-donating ability of phosphines is generally increased more efficiently by phosphazenyl than by phosphoniumylidyl substituents [$\chi(NPiPr_3) = -11.0\ cm^{-1}$, $\chi(CHPPh_3) = -6.2\ cm^{-1}$]. This contribution can be significantly amplified by attaching π-donating tetramethylguanidino substituents at the phosphonium center [$\chi(NP(tmg)_3) = -18.5\ cm^{-1}$], as demonstrated by the remarkably low TEP value of **3** (2039.5 cm^{-1}) with only one phosphazenyl substituent. Additionally, we have shown that protonation of the ylidic carbon atom of phosphoniumylidyl phosphines increases their TEP values by $\Delta TEP = 18.8\ cm^{-1}$ (**1a**) and $\Delta TEP = 16.0\ cm^{-1}$ (**1b**). Given this considerable influence on the phosphine's donor properties, this finding may inspire the design of the next generation proton-switchable catalysts.

Experimental Section

The synthesis of the phosphazenyl phosphines is described below. For further information on the synthesis of the phosphoniumylidyl phosphines, nickel(0) and gold(l) complexes please see the Supporting Information.

Phosphine 2: At –78 °C a solution of *n*-butyllithium in *n*-hexane (4.50 mmol, 2.8 mL, 1.6 M) was added dropwise to a suspension of triisopropylphosphoniumamine chloride (2.25 mmol, 476 mg) in THF. After allowing the reaction mixture to warm up to room temperature and stirring for 3 h it was cooled to –78 °C again. A chlorodiisopropylphosphine solution (2.25 mmol, 9.0 mL, 0.25 M) in toluene was added dropwise and the mixture was allowed to warm up to room temperature slowly overnight. All volatiles were removed in vacuo and the residue was extracted with *n*-hexane (2 × 40 mL). The solvent was removed in vacuo to give the product as a colorless oil (66% yield, 1.51 mmol, 439 mg). **^{1}H NMR** (400 MHz, C_6D_6): δ (ppm) = 1.85 [m, 3 H, P(C*H*$(CH_3)_2)_3$], 1.66 [sept, $^3J_{HH}$ = 7.1 Hz, 2 H, P(C*H*$(CH_3)_2)_2$], 1.24 [dd, $^3J_{PH}$ = 10.0, $^3J_{HH}$ = 7.1 Hz, 6 H, P(CH(CH_3)$_2$)$_2$],1.18 [dd, $^3J_{PH}$ = 14.0, $^3J_{HH}$ = 7.1 Hz, 6 H, P(CH(CH_3)$_2$)$_2$], 1.06 [dd, $^3J_{PH}$ = 14.0, $^3J_{HH}$ = 7.1 Hz, 18 H, P(CH(CH_3)$_2$)$_3$]. **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6): δ (ppm) = 29.9 [dd, $^1J_{PC}$ = 17, $^3J_{PC}$ = 8 Hz, P(*C*H$(CH_3)_2)_2$], 26.9 [dd, $^1J_{PC}$ = 60, $^3J_{PC}$ = 1 Hz, P(*C*H$(CH_3)_2)_3$], 19.8 [d, $^1J_{PC}$ = 21 Hz, P(*C*H$(CH_3)_2)_2$], 18.2 [d, $^2J_{PC}$ = 10 Hz, P(CH(*C*H_3)$_2$)$_2$], 17.6 [d, $^2J_{PC}$ = 6 Hz, P(CH(*C*H_3)$_2$)$_3$]. **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ (ppm) = 68.4 [d, $^2J_{PP}$ = 54 Hz, P(CH$(CH_3)_2)_2$], 33.0 [d, $^2J_{PP}$ = 54 Hz, P(CH$(CH_3)_2)_3$]. **^{31}P NMR** (162 MHz, C_6D_6): δ (ppm) = 68.4 [m, P(CH$(CH_3)_2)_2$], 33.0 [m, P(CH$(CH_3)_2)_3$]. **HR-MS** (**ESI**): *m/z* calculated for $[C_{15}H_{36}NP_2]^+$ $[M + H]^+$: 292.23230, found: 292.23117.

Phosphine 3: A standard solution of P*i*Pr_2Cl (0.68 mmol, 1.0 mL, 0.68 M) in toluene was added dropwise to a solution of $(tmg)_3$PNH (1.37 mmol, 530 mg) in THF at –78 °C. The reaction mixture was allowed to warm up to room temperature slowly and the solvent was removed in vacuo. After extraction with *n*-hexane (2 × 10 mL) the solvent was removed under reduced pressure and the product was obtained as a colorless solid (72% yield, 0.49 mmol, 247 mg). **^{1}H NMR** (500 MHz, C_6D_6): δ (ppm) = 2.76 [s, 36 H, N(CH_3)$_2$], 1.84 [heptd, $^3J_{HH}$ = 6.9, $^2J_{PH}$ = 1.6 Hz, 2 H, C*H*$(CH_3)_2$], 1.49 [dd, $^3J_{PH}$ = 9.3, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(CH_3)$_2$], 1.44 [dd, $^3J_{PH}$ = 13.9, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(CH_3)$_2$]. **^{1}H{^{31}P} NMR** (400 MHz, C_6D_6): δ (ppm) = 2.76 [s, 36 H, N(CH_3)$_2$], 1.84 [hept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*$(CH_3)_2$], 1.49 [d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(CH_3)$_2$], 1.44 [d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(CH_3)$_2$]. **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ (ppm) = 157.2 [s, N*C*(N$(CH_3)_2)_2$], 40.3 [d, $^4J_{CP}$ = 2 Hz, NC(N(*C*H_3)$_2$)$_2$], 29.7 [dd, $^1J_{CP}$ = 18, $^3J_{CP}$ = 12 Hz, *C*H$(CH_3)_2$], 20.3 [d, $^2J_{CP}$ = 22 Hz, CH(*C*H_3)$_2$], 18.9 [d, $^2J_{CP}$ = 10 Hz, CH(*C*H_3)$_2$]. **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ (ppm) = 67.9 [d, $^2J_{PP}$ = 83 Hz, *i*Pr_2*P*NP(tmg)$_3$], –10.7 [d, $^2J_{PP}$ = 83 Hz, *i*Pr_2PN*P*(tmg)$_3$]. **^{31}P NMR** (162 MHz, C_6D_6): δ (ppm) = 67.9 [m, *i*Pr_2*P*NP(tmg)$_3$], –10.7 [d, $^2J_{PP}$ = 83 Hz, *i*Pr_2PN*P*(tmg)$_3$]. **HR-MS** (**ESI**): *m/z* calculated for $[C_{21}H_{51}N_{10}P_2]^+$ $[M + H]^+$: 505.37383, found: 505.36992. The matching isotope pattern was found.

Supporting Information (see footnote on the first page of this article): The supporting information contains the experimental procedures and the characterization data of all new compounds, including their NMR spectra and crystallographic data.

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Keywords: Ligand design; Phosphines; Gold; Single substituent parameter; Phosphazenyl; Phosphoniumylidyl

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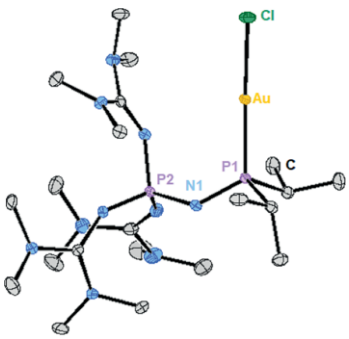

χ (NP{tmg}$_3$) = -18.5 cm^{-1}

