

Free Metallophosphines: Extremely Electron-Rich Phosphorus Superbases that are Electronically and Sterically Tunable

Rui Wei, Shaoying Ju, Liu Leo Liu*

[a] Dr. R. Wei; S. Ju; Prof. Dr. L. L. Liu
Department of Chemistry and Shenzhen Grubbs Institute, Southern University of Science and Technology, Shenzhen 518055, China
E-mail: liuleoliu@sustech.edu.cn

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ABSTRACT: A variety of research fields ranging from catalysis to materials science benefit from readily accessible electron-rich ancillary ligands such as phosphines with diverse stereoelectronic properties. We report herein a facile and highly modular access to an intriguing class of free Au-substituted phosphines (AuPhos), namely $(\text{LAu})_n\text{PR}_{3-n}$ (L = singlet carbene ligand; R = H, aryl, alkyl, silyl) ($n = 1-3$). The Tolman electronic parameter (TEP) values coupled with theoretical investigations showcase that Au-substitution can boost the electron-releasing ability of AuPhos, thus leading to an electronically and sterically tunable, extremely electron-rich phosphorus center. The high basicity of AuPhos is attributed to the d-p lone pair π -repulsion arising from interaction between electron-rich d^{10} Au substituents and the lone pair at P. A series of multi-nuclear transition metal complexes (i.e. Rh, Ir, Au, W, Mn) ligated by AuPhos are readily prepared via a straightforward process. Preliminary catalytic results reveal the facilitation of Ir-catalyzed decarbonylation reactions of aldehydes via AuPhos, unveiling their tremendous potential for the development and improvement of transition metal catalysts when electron-rich metal centers are required.

Introduction

The capability of ancillary ligands to tune the reactivity, selectivity, and stability of transition metal (TM) catalysts has generated many breakthroughs in homogeneous catalysis.^[1] Phosphines (PR_3) are one of the most versatile ligands, which are in large part the result of the sensitivity of the electron density and steric environments at the trivalent phosphorus center towards substituent modifications.^[2] Such elaboration of ligand architectures in a predictable manner plays a key role in providing optimum steric protection and stereoelectronic control of the active species.^[2-3] In addition, many other research fields such as organocatalysis,^[4] frustrated Lewis pairs (FLPs),^[5] and nanomaterials^[6] have benefited from readily accessible phosphines having a broad range of steric effects and electronic properties.

While a large variety of phosphines have been documented, expanding the boundary of electron-releasing properties of phosphines remains quite challenging.^[7] The incorporation of π -donor substituents at P has been shown to effectively increase such properties via p-p lone pair π -repulsion (Figure 1a).^[8] It has been demonstrated by Moloy and Petersen that, despite the electron-withdrawing inductive effect of the amino substituents, the potent N-to-P π -repulsion leads to comparable electron-donating ability of tris(N-pyrrolidiny)phosphines **A** and tris(n-

butyl)phosphine.^[9] Proazaphosphatranes **B** described by Verkade et al. are early representatives of rare examples of strong donor phosphines.^[10] In 2017, the Dielmann group described the isolation of imidazolin-2-ylidenaminophosphines (IAPs) **C** with high basicity,^[11] and more recently they reported a tris(tetramethylguanidiny)phosphine.^[12] In 2018, Gessner et al. disclosed a series of ylido-functionalized phosphines (YPhos) **D**^[13] and their superior performance in TM catalysis.^[13a, 14] In 2019, Sundermeyer and co-workers showcased a fascinating class of electron-rich phosphazeny phosphines (PAPs),^[15] one of which (**E**) represents the most electron-rich uncharged phosphorus Brønsted and Lewis base to date. However, the thermodynamically favored conformation of **A-E** adopts a perpendicular arrangement of adjacent lone pairs via rotation of P-E (E = N or C) single bonds (Figure 1a),^[9-13, 15] and this so called “gauche effect”^[16] to some extent impedes boosting the phosphorus basicity.

Of note, the d-p π -interaction has been demonstrated in terminal transition metal phosphide complexes.^[17] For example, the solid-state structure of a complex $[\text{Ru}(\text{PCy}_2)(\eta^5\text{-indenyl})(\text{PPh}_3)]$ displays the Ru-PCy₂ bond length of 2.1589 Å with considerable Ru-P π -bonding, which is 0.113 Å shorter than that of Ru-PPh₃ bond (2.2719 Å).^[18] By contrast, the electronic repulsion of the P lone pair and nonbonding electrons at Ru in $(\text{dmpe})_2\text{Ru}(\text{H})-\text{P}(\text{Me})\text{Ph}$ ($\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$) leads to a much longer Ru-P(Me)Ph bond length (2.513 Å) relative to that seen in $[(\text{dmpe})_2\text{Ru}(\text{H})-(\text{PHMePh})][\text{BPh}_4]$ (2.342 Å).^[19] The Bergman group showed high basicity of late TM amido complexes.^[20] In addition, transition-metal-substituted heavy tetrylenes have been documented by the Power, Tilley and Kato groups.^[21] We thus envisioned that incorporation of extremely electron-rich d^{10} TM substituents at phosphorus would give rise to a repulsive four-electron destabilization that boosts the ground-state energy and makes the P lone pair particularly basic.^[17] This gives access to highly electron-rich phosphines. Such d-p π -repulsion is analogous to the abovementioned p-p π -repulsion (Figures 1a and 1c).^[9-11, 13a, 15] Nonetheless, in this case rotation of the single bonds at P has less perturbation of P-centered basicity due to the presence of five d-type nonbonding lone pairs at a d^{10} TM center with different orientations.

On the other hand, the isolobal analogy of the $[\text{LAu}]^+$ cation and the proton $[\text{H}]^+$ has been well-established.^[22] As $[\text{LAu}]^+$ features a $5d^{10}$ valence electron configuration and the ligand L is highly modular, $(\text{LAu})_n\text{PR}_{3-n}$ ($n = 1-3$) would be potentially phosphorus superbases and can be regarded as electronically and sterically tunable “ $\text{H}_n\text{PR}_{3-n}$ ” via variation of L. While examination of the literature reveals a large number of bridging Au phosphine/phosphide complexes,^[23] there are only

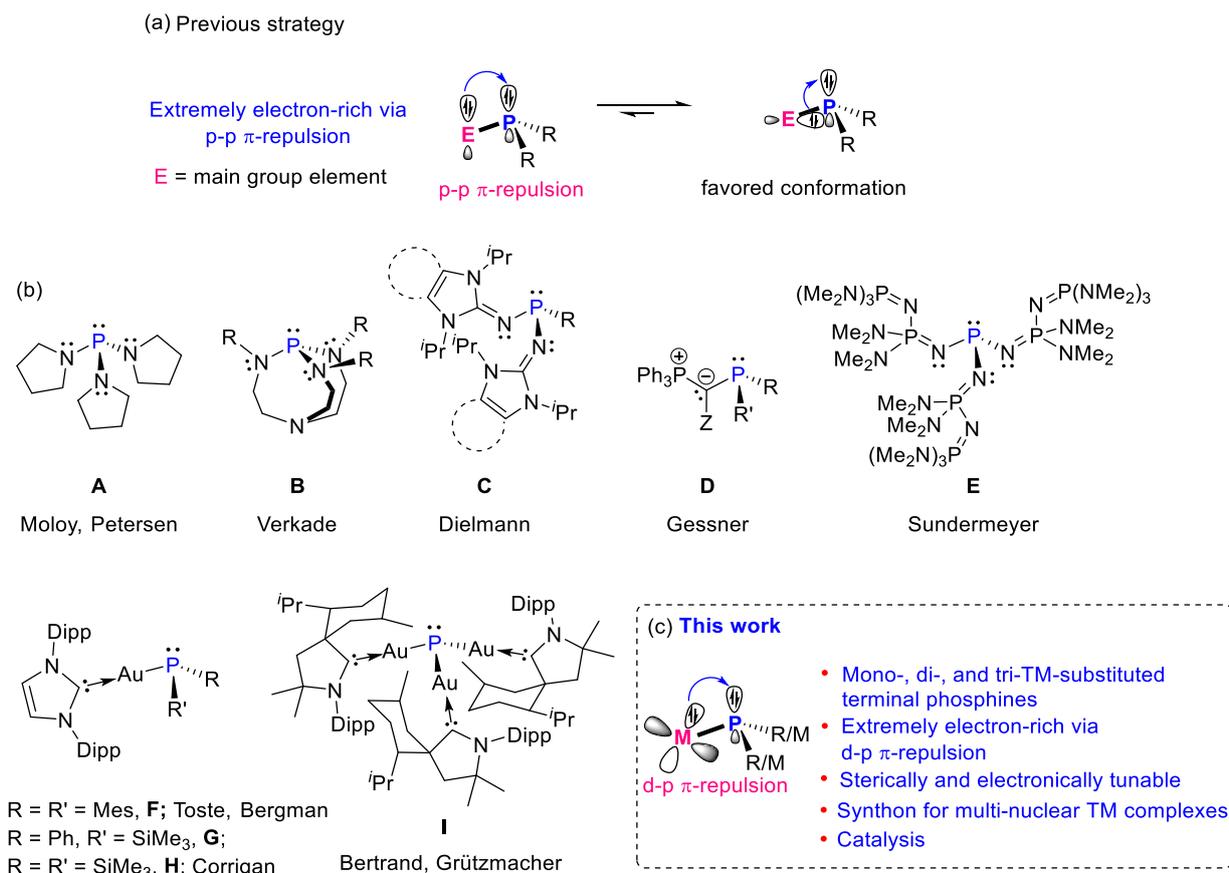


Figure 1. (a) Previous strategy. (b) Representative examples of highly electron-rich phosphines. (c) Present work.

two types of structurally characterized Au terminal phosphines disclosed by the groups of Toste, Bergman, Corrigan, Bertrand, and Grützmacher, namely mono-Au-substituted phosphine **F**,^[24] **G**,^[25] **H**,^[25] and tri-Au-substituted phosphine **I**^[26] (Figure 1a). **F** was synthesized via a deprotonation method,^[24] while **G** and **H** were derived from reactions involving the elimination of trimethylsilyl chloride.^[25] **I** was obtained serendipitously from a THF solution of an Au-PCO complex in low yield (i.e. 22 %).^[26] So far, their electronic properties and reactivities have been virtually unexplored.^[24-26]

In this contribution, we report that indeed Au-functionalization gives an intriguing family of highly electron-rich phosphines (LAu)_nPH_{3-n} (L = singlet carbene ligand; R = H, aryl, alkyl). These Au-substituted phosphines (AuPhos) are readily prepared via salt metathesis or desilylation reactions in high yields. The electronegative nature of gold ($\chi = 2.54$) makes the Au–P bonds in AuPhos highly covalent. The electronic and steric properties of AuPhos is easily tunable, which is crucial for broad applications in homogenous catalysis. This work expands the accessible stereoelectronic properties of phosphines beyond classical boundaries.

Results and Discussion

Design and Synthesis of Mono-AuPhos. To support our abovementioned hypothesis, density functional theory (DFT) investigations were carried out on model species PH₃, (LAu)PH₂,

(LAu)₂PH and (LAu)₃P (L = 1,3-dimethylimidazol-2-ylidene) at the B3LYP-D3(BJ)/def2-SVP level of theory. Figure 2 clearly depicts the crucial roles of [LAu] substituents in increasing HOMO energies of the phosphorus lone pair.^[27] There are significant enhancements of the HOMO energies with respect to [LAu] substitution in the series (LAu)_nPH_{3-n} (n = 0-3). This is indicative of a cumulative d-p π -repulsion effect from successive d¹⁰ [LAu] groups.

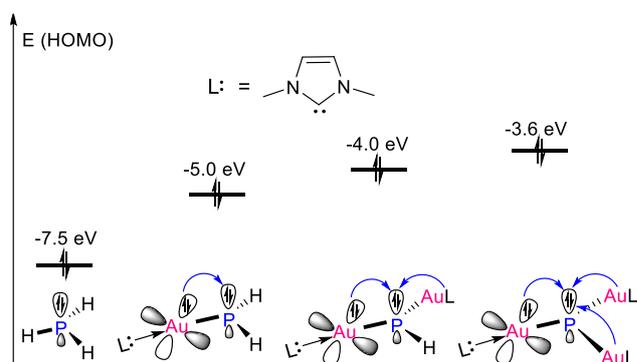


Figure 2. HOMO energies of PH₃ and the model (LAu)_nPH_{3-n} (n = 1, 2, 3).

Encouraged by these computational results, we first targeted the synthesis of mono-AuPhos (LAu)PR₂ (L = diamidocarbene (DAC)

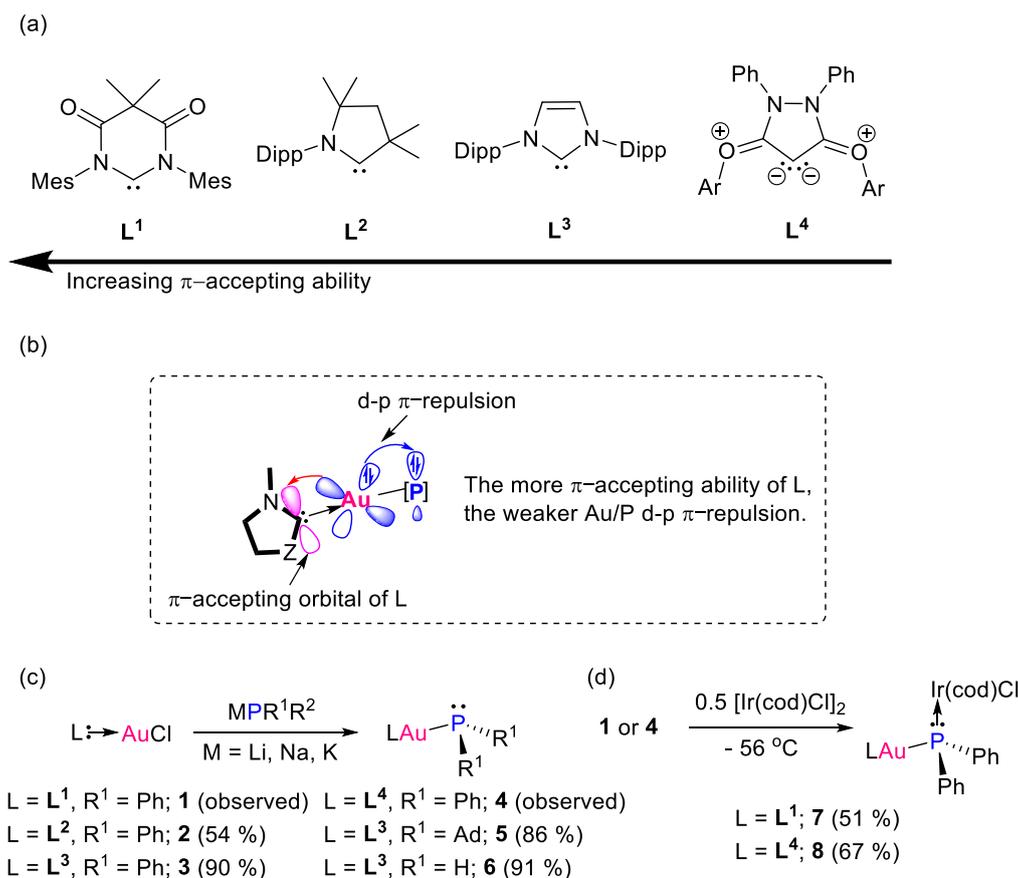


Figure 3. (a) π -Accepting ability of L¹-L⁴. Mes = mesityl; Dipp = 2,6-diisopropylphenyl; Ar = 2,6-dimethylphenyl. (b) A graphical representation of modulation of d-p π -repulsion via variation of L. (c) Synthesis of **1-6**. (d) Trapping of **1** and **4**.

L¹, dimethyl cyclic (alkyl)(amino)carbene (Me₂CAAC) L², N-heterocyclic carbene (NHC) L³, or bent allene L⁴; R = Ph, Ad, or H) (Figures 3a and 3c).^[28] It is well known that L¹-L⁴ exhibit diverse π -acceptor properties (Figure 3a).^[28-29] We speculated the feasible modulation of the degree of Au/P d-p π -repulsion via variation of L (Figure 3b). The more π -accepting ability of L should result in the weaker π -repulsion (& vice versa). This would provide access to electronically and sterically tunable AuPhos. While a salt metathesis strategy was unsuccessful for the preparation of **F** (Figure 1b),^[24] treatment of LAuCl (L = L² or L³) with KPPH₂ in DME or THF at room temperature afforded species **2** (³¹P NMR: 1.7 ppm) or **3** (³¹P NMR: -1.0 ppm) in 54 or 90 % yield, respectively. The ¹³C NMR spectra of **2** and **3** revealed diagnostic doublet resonances (**2**: 260.4 ppm; **3**: 200.2 ppm) with the two-bond P-C couplings (**2**: 37.5 Hz; **3**: 54.6 Hz) attributable to the carbene carbons, indicating the formation of Au-P bonds. The structures of **2** and **3** as mono-AuPhos were unambiguously determined by crystallographic studies (Figures 4a and 4b).^[30] The P center of **2** and **3** adopts a trigonal-pyramidal geometry with the sum of angles equal to 307.7° (**2**) and 315.2° (**3**). Their lone pair of electrons point away from the Au center, imparting residual Lewis basicity at the P donor. As expected, the stronger π -accepting ability of L² results in a shorter Au(1)-C(1) bond length (2.022(12) Å) in **2** compared to that in **3** (2.062(5) Å). The Au(1)-P(1) bond lengths are comparable (**2**: 2.314(3) Å; **3**: 2.3193(13) Å). In a similar vein, dialkyl- and even dihydrogen-substituted analogs **5** (³¹P NMR: 89.9 ppm) and **6** (³¹P NMR: -250.3 ppm) were obtained via the reactions of L³AuCl with LiPAD₂ (Ad = adamantyl) and NaPH₂ in high yields (> 86 %). In the solid state, the geometric parameters of **5** and **6** are comparable to those of **3** (Figures 4c and 4d).

Although we were able to observe the formation of mono-AuPhos **1** (³¹P NMR: 52.4 ppm) and **4** (³¹P NMR: 9.6 ppm) via in-situ ³¹P NMR spectroscopic studies upon mixing LAuCl (L = L¹ or L⁴) with KPPH₂ in THF at low temperature, such species were highly labile in solution (**1**: t_{1/2} = 0.5 h; **4**: t_{1/2} = 0.25 h), thus defying isolation. Nevertheless, chemical trapping experiments of **1** and **4** with [Ir(cod)Cl]₂ at -56 °C allows the isolation of the ensuing iridium complexes **7** (³¹P NMR: 38.7 ppm) and **8** (³¹P NMR: 31.4 ppm) in 76 and 67 % yields, respectively. Further structural authentication of **8** was established by X-ray diffraction (Figure 4e).

It is important to note that, in remarkable contrast to the sensitivity of metal phosphides with ionic M-P bonds,^[31] the high covalent character of the Au-P bonds in AuPhos (vide infra) makes these species highly stable towards alcohols, amines and even water. For example, **3** showed completely inertness with an equal molar portion of EtOH, ¹PrOH, ¹BuOH, Ph₂NH, ¹Pr₂NH and H₂O (Figure S91-S98). The phosphine character of AuPhos was further demonstrated by the FLP reactivity of **5**, BPH₃ and H₂O, which gave **9** and benzene. The former product was characterized by multi-nuclear NMR spectroscopy and X-ray diffraction (Figure 5). **Electronic Properties of Mono-AuPhos.** Corresponding (AuPhos)Rh(acac)(CO) complexes were prepared by reactions of **1-5** with Rh(acac)(CO)₂ (Figure 6). The electronic properties of these mono-AuPhos ligands were established by determination of the CO stretching frequency in these complexes in the solid state (Table 1). Complex **10** exhibits a distinctly higher frequency (ν_{CO} 1943.4 cm⁻¹) with respect to those of **11** (ν_{CO} 1939.4 cm⁻¹), **12** (ν_{CO} 1938.7 cm⁻¹) and **13** (ν_{CO} 1935.8 cm⁻¹), indicative of reduced electron-releasing ability of **1** compared to **2**, **3** and **4**. These data support the notion that decreasing the π -accepting ability of the L

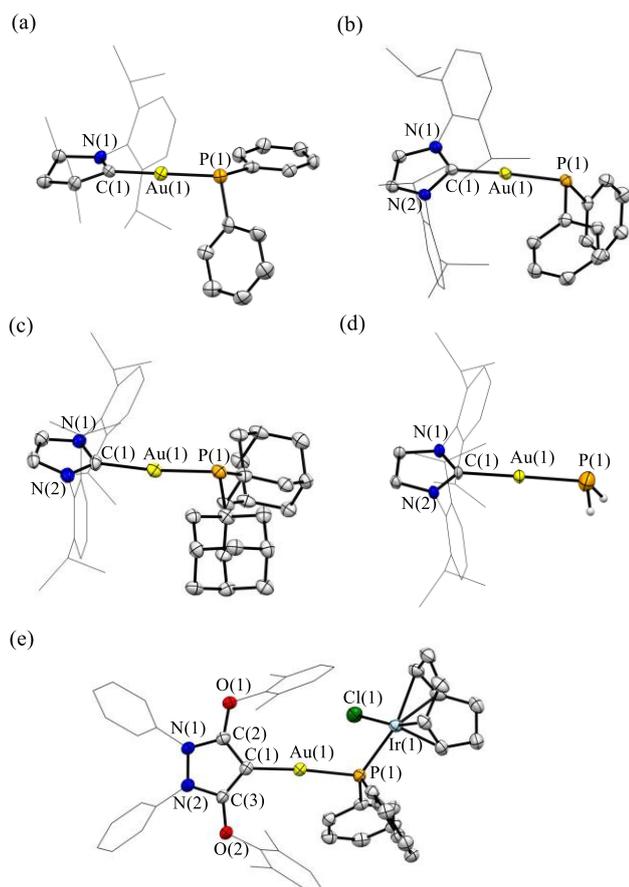


Figure 4. Solid-state structures of **2** (a), **3** (b), **5** (c), **6** (d) and **8** (e). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

leads to a decrease of the ν_{CO} frequency. Moreover, **5** is a stronger electron donor than **3** as demonstrated by the lower frequency of **14** (ν_{CO} 1934.9 cm^{-1}) compared to that of **12** (ν_{CO} 1938.7 cm^{-1}).^[32] The TEP values of **1-5** were subsequently calculated from the relationship between ν_{CO} for (L)Ni(CO)₃ and (L)Rh(acac)(CO) complexes (Table 1).^[7a, 33] Interestingly, monosubstitution of [LAu] shifts the TEP value (PPh₃: 2068.9 cm^{-1})^[2] by 19.6–24.4 cm^{-1} . The TEP values of **1-5** are 2049.3, 2047.1, 2046.7, 2045.0 and 2044.5, respectively. These are comparable to those of mono-imidazolin-2-ylidenamino-phosphines (2039–2053 cm^{-1})^[11] whereas they are lower in comparison to those observed for YPhos **D** (2049–2067 cm^{-1}) (Figure 1a).^[13a] Notably, such TEP values of **1-5** support the conclusion that the donor character of mono-AuPhos is similar to that of the most classical NHCs.^[34] This also implies that di- and tri-substitution of [LAu] may surpass the donor abilities of singlet carbenes.

Theoretical Investigations. To gain more insight into the bonding and electron-rich nature of mono-AuPhos, DFT calculations, natural bond orbital (NBO)^[35] analyses, and energy decomposition analyses with natural orbitals for chemical valence (EDA-NOCV)^[36, 37] calculations were performed. The calculated HOMO energies of **1-4** (**1**: -4.68 eV; **2**: -4.50 eV; **3**: -4.44 eV; **4**: -4.20 eV) suggest that the basicity increases in the order of **1-4**.^[38] Additionally, electrostatic potential (ESP) calculations, which were demonstrated as a quantitative measure of the electronic effect of the phosphine ligands,^[39] show a linear correlation of the calculated value of the ESP at phosphorus of **1-5** (V_{P}) with their TEP values (Table 1 and Figure S85). Inspection of the NBOs of a selected model **3** clearly shows five nonbonding d-electron pairs

at Au, a lone pair of electrons at P, as well as an Au–P σ -bond (Figure 6).

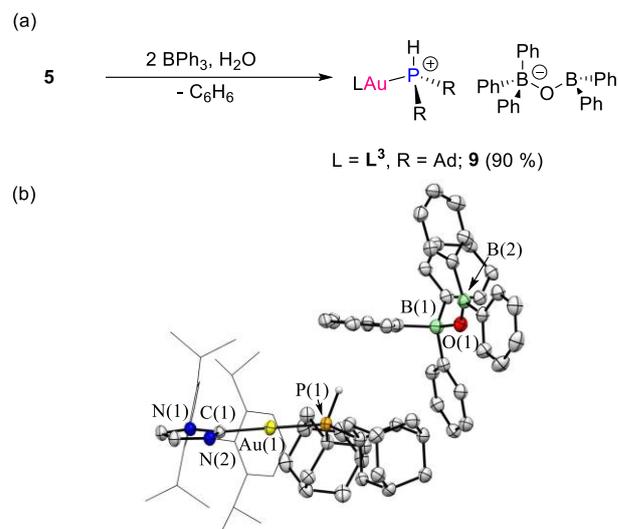


Figure 5. (a) Synthesis and solid-state structure of **9**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

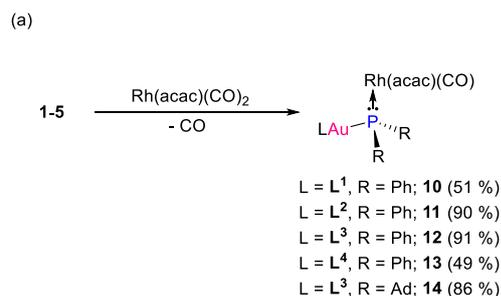


Figure 6. (a) Synthesis of **10-14**. Solid-state structures of **12** (b) and **14** (c). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

As Pauli repulsion energies obtained from EDA-NOCV calculations can account for the unfavorable interaction of overlapping filled orbitals between fragments, we employed such energies to estimate the d-p π -repulsion.^[36] We found that the π -accepting ability of L can considerably effect the Pauli repulsion energy between [LAu⁺] and [PPh₂⁺] fragments in **1-4**. Such energies of **1**, **2**, **3** and **4** are calculated to be 191.2, 212.3, 218.4 and 221.1 kcal/mol, respectively (Figures S86–S89), in line with

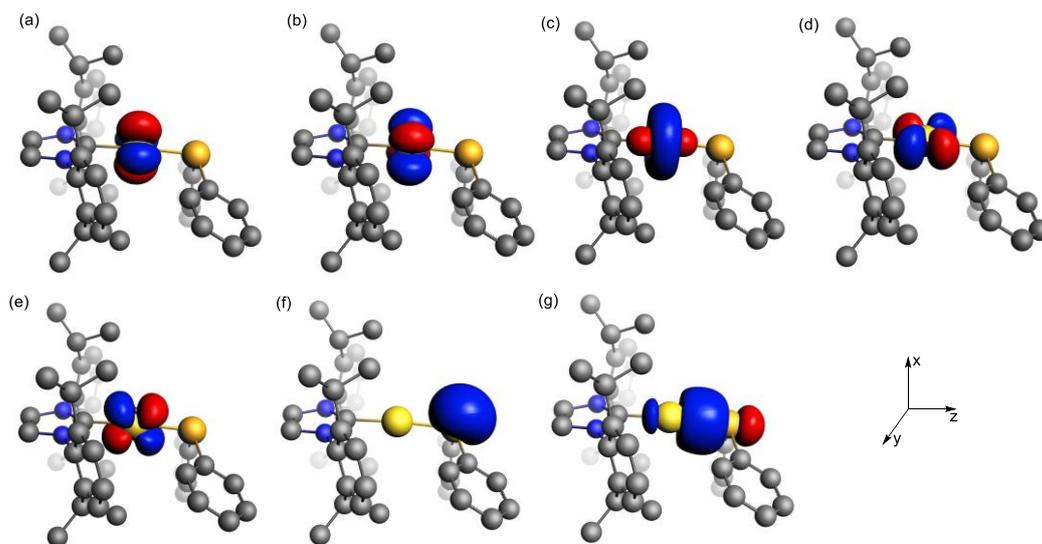


Figure 7. Selected NBOs of **3**. Lone pair = LP. (a) Au LP ($d_{x^2-y^2}$). (b) Au LP (d_{xy}). (c) Au LP (d_{z^2}). (d) Au LP (d_{yz}). (e) Au LP (d_{xz}). (f) P LP. (g) Au–P σ -bond.

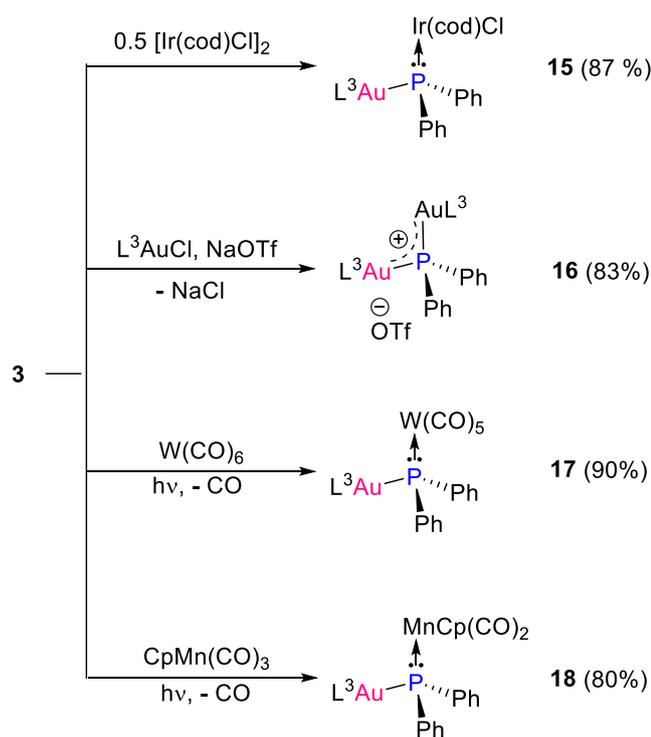


Figure 8. Synthesis of **15-18**.

the trend of the observed TEP values. Taken as a whole, the Au-substitution is proven to enhance the electron-releasing character of AuPhos via d-p π -repulsion. Variation of the L readily modulates the strength of the repulsion.

The quantum theory of atoms in molecules (QTAIM)^[40] analysis of **3** reveals that the electron density $\rho(r)$ at the bond critical point (BCP) of Au–P bond is 0.10 a.u., while the energy density $H(r)$ is -0.04 a.u., which indicate the covalent character of the P–Au bond. This is consistent with the localized orbital locator (LOL)^[41] analysis that demonstrates the region between the P and Au

atoms with concentrated kinetic energy density, similar to those observed for the P–C and Au–C bonds (Figure S90).

With AuPhos available, we made attempts to experimentally measure their pK_{BH^+} via NMR titration.^[42] The conjugate acid $[\text{L}^3\text{AuP}(\text{HPh})_2][\text{BF}_4]$ of **3** was prepared by treating L^3AuCl with $\text{HPPH}_2/\text{AgBF}_4$. However, this method was problematic: the combination of **3** and $[\text{L}^3\text{AuP}(\text{HPh})_2][\text{BF}_4]$ led to an instantaneous demetallation reaction, yielding $[(\text{L}^3\text{Au})_2\text{P}(\text{HPh})_2][\text{BF}_4]$ (23.8 ppm), HPPH_2 (-40.5 ppm) and $\text{L}^3\text{AuP}(\text{HPh})_2$ (-1.0 ppm). Nevertheless, DFT calculations, which were shown in satisfying agreement with the experimental pK_{BH^+} ,^[11, 15] suggest AuPhos **1-5** are highly basic with the pK_{BH^+} having values of 25.5, 29.3, 29.1, 35.6 and 38.3, respectively (Table 1). For comparison, the calculated pK_{BH^+} values of P^tBu_3 (16.1) are consistent with the experimental observations (17.0).

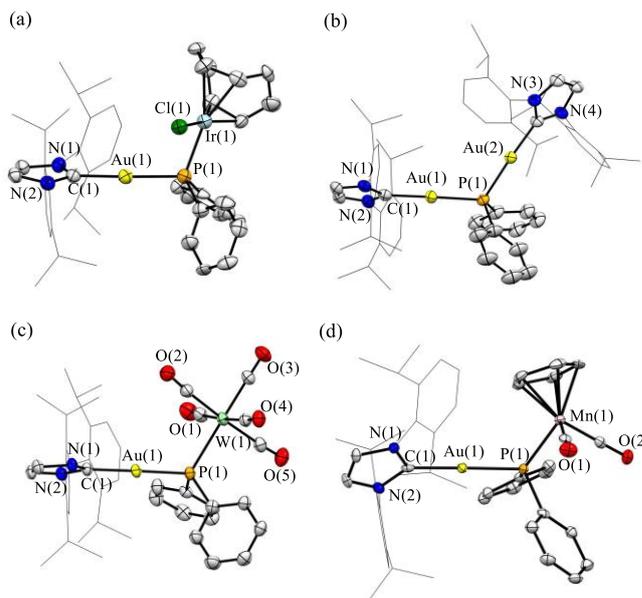


Figure 9. Solid-state structures of **15** (a), **16** (b), **17** (c) and **18** (d). Hydrogen atoms and the OTf anion are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

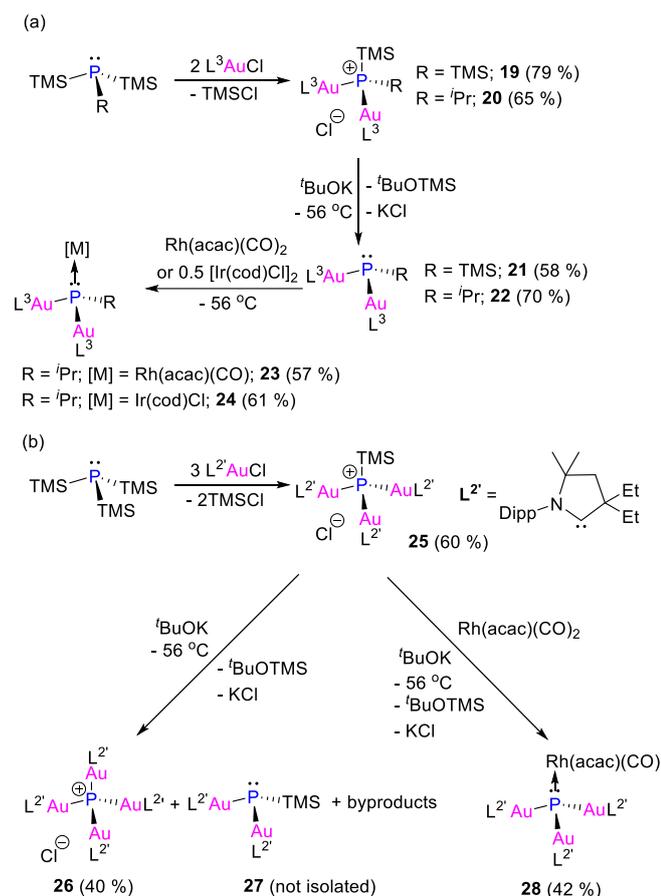


Figure 10. (a) Synthesis of di-AuPhos **20** and **21** and complex **22**. (b) Generation and trapping of tri-AuPhos leading to **24-27**.

The steric demand of the AuPhos ligand was estimated using the buried volume (% V_{bur})^[43] from the optimized geometries of the corresponding (AuPhos)AuCl complexes (Table 1). Depending on the steric bulk of L, % V_{bur} varies from 27.1 to 43.7 %. The % V_{bur} of **5** is even larger than the value calculated for PAd₃ (40.5 %).^[7a] Of critical importance, sterically encumbering ligands are beneficial for a large number of TM-catalyzed reactions,^[44] implying potentially high catalytic performance of AuPhos.

Coordination Chemistry of Mono-AuPhos. Dinuclear metal complexes have found numerous applications in catalysis.^[45] Indeed, these mono-AuPhos are powerful synthons for hetero- and homo-dinuclear complexes (Figure 7). **3** readily reacted with [Ir(cod)Cl]₂ or L³AuCl/NaOTf at room temperature to give a neutral Au/Ir complex **15** (³¹P NMR: 29.0 ppm) or a cationic diauro complex **16** (³¹P NMR: 23.8 ppm) in high yield (> 83 %), respectively. While **3** was completely inert with W(CO)₆ without irradiation, upon exposing to UV lamp (254 nm) an Au/W complex **17** (³¹P NMR: -12.6 ppm) was isolated in 90 %. Similarly, an Au/Mn complex **18** (³¹P NMR: 76.9 ppm) was formed through the photo-induced reaction with CpMn(CO)₃. The solid-state molecular structures of **15-18** were determined by X-ray diffractometry (Figure 9). The facile preparation of **15-18** paves a new way to hetero-dinuclear Au phosphide complexes that are rare and otherwise tricky to prepare.^[46]

Synthesis of Di- and Tri-AuPhos. Attempts on synthesis of di-AuPhos were undertaken. We chose a desilylation route with the corresponding silylphosphonium salt as a precursor (Figure 10a). These species **19** and **20** were easily prepared via the reaction of

RPTMS₂ (R = TMS, ⁱPr) and L³AuCl. Treatment of **19** or **20** with ^tBuOK in THF at -56 °C immediately generated a yellow solution, in which after workup di-AuPhos **21** (³¹P NMR: -203.3 ppm) or **22** (³¹P NMR: -11.5 ppm) were isolated as yellow powders in 58 or 70 % yield, respectively. While characterization of **21** by multinuclear NMR spectroscopic methods and high-resolution mass spectrometry was achieved, it slowly decomposed even at low temperature in solution (e.g. THF and benzene) within hours to give an unidentified complex mixture, precluding the formation of single crystals. On the other hand, slow evaporation of a concentrated Et₂O solution of **22** at -30 °C produced X-ray quality pale-yellow single crystals. Although the systematic disorder of **22** in the solid state does not allow for an accurate discussion of bond lengths and angles, the structure of a free di-AuPhos was unambiguously authenticated (Figure 11a). Notably, **21** and **22** are the first examples of a group 11 free dimetallaphosphine.

The calculated pK_{BH^+} of **21** (41.8) and **22** (41.9) are much higher than those of mono-AuPhos **1-5** (25.5-38.3) (Table 1), indicating the di-Au-substitution increases the pK_{BH^+} by several orders of magnitude. The calculated V_P values of **21** (-44.7) and **22** (-52.4) suggest their high donor ability. Additionally, flanking two bulky L³ ligands, **21** and **22** exhibit large % V_{bur} values (**21**: 41.0 %; **22**: 48.5 %).

Such di-AuPhos proved to be versatile synthons for tri-nuclear TM complexes. The combination of **22** with Rh(acac)(CO)₂ or [Ir(cod)Cl]₂ in THF at -56 °C gave rise to the ensuing complex **23** or **24** in 57 % or 61 % yield, respectively. In the solid state of **23**, the bond length of P(1)-Rh(1) lies within the range of the typical single bond (Figure 11b). The Au(1)-Rh(1) (3.6282(8) Å) and Au(2)-Rh(1) (3.8560(7) Å) separations are much longer than the Pyykkö standard value for an Au-Rh single bond (2.49 Å).^[47] Remarkably, infrared spectroscopic investigations of **23** gave a considerably low CO stretching frequency of 1902.4 cm⁻¹ and its TEP value is calculated to be 2025.9 cm⁻¹ (Table 1), demonstrating the presence of an extremely electron-rich phosphorus center. Significant to note is that this TEP is lower than most of the known trivalent phosphines (i.e. **A-D**, Figure 1a)^[9-11, 13] whereas higher relative to those observed for a handful of examples of PAPs (e.g. **E**: 2014.5 cm⁻¹).^[15] Unfortunately, efforts to prepare LRh(acac)(CO) complex (L = **21**) were unsuccessful, precluding the measure of its TEP value.

Table 1. The spectroscopic/structural properties and DFT results of the different phosphine ligands.

| | TEP (cm ⁻¹) | V_P ^[b] | GB ^[c] | pK_{BH^+} ^[d] | % V_{bur} ^[f] |
|---------------------------------------|-------------------------|----------------------|-------------------|-----------------------------------|-----------------------------------|
| PPh ₃ | 2068.9 ^[2] | -23.4 | 230.2 | 7.6 ^[e] | 30.0 |
| P(^t Bu) ₃ | 2056.1 ^[2] | -27.9 | 240.7 | 16.1 (17.0) ^[e] | 37.4 |
| 1 | 2049.3 | -35.4 | 254.7 | 25.5 | 39.1 |
| 2 | 2047.1 | -39.5 | 259.6 | 29.3 | 27.1 |
| 3 | 2046.7 | -40.1 | 259.6 | 29.1 | 41.2 |
| 4 | 2045.0 | -42.1 | 268.1 | 35.6 | 40.8 |
| 5 | 2044.5 | -44.0 | 272.0 | 38.3 | 43.7 |
| 21 | N.A. ^[a] | -44.7 | 276.9 | 41.8 | 41.0 |
| 22 | 2025.9 | -52.4 | 276.8 | 41.9 | 48.5 |
| (L ² Au) ₃ P | 2025.4 | -58.5 | 282.5 | 45.8 | 50.0 |

[a] Efforts to prepare LRh(acac)(CO) complex (L = **21**) were unsuccessful.

[b] ESP calculations were conducted at the B3LYP-D3BJ/def2-SVP level of theory

[c] Gas phase basicity (GB) (kcal/mol) were calculated at the PW6B95-D3BJ/TPSS-D3BJ/def2-TZVP level of theory.

[d] pK_{BH}⁺ values were referenced to [HPPH₃]⁺ [pK_a(CH₃CN) = 7.6] at the PW6B95-D3BJ/TPSS-D3BJ/def2-TZVP level of theory using SDD solvation model (CH₃CN).

[e] Experimental value.

[f] Buried volume values were obtained from the optimized structures of (AuPhos)AuCl complexes at the B3LYP-D3BJ/def2-SVP level of theory.

We adopted a similar strategy to generate tri-AuPhos (Figure 10b). However, desilylation of a triaurosilylphosphonium salt **25** in THF at -56 °C in 30 min produced species **26** (³¹P NMR: -160.3 ppm) and **27** (³¹P NMR: -215.3 ppm) rather than the desired free tri-AuPhos (L²Au)₃P. Attempts to observe (L²Au)₃P failed as the demetallation reaction occurred exceedingly fast. The formulation of **26** as [(L²Au)₄P][Cl] was further confirmed by single crystal X-ray diffraction (Figure 11c). **26** represents the first example of a tetra-aurophosphonium salt albeit the structure features of [P(AuPH₃)₄]⁺ were thoroughly investigated by quantum chemical calculations.^[48] Unlike its arsenic analog [(LAu)₄As][Cl] (L = Ph₃P) featuring the geometry of a distorted square,^[49] the solid-state structure of **26** displays a distorted tetrahedron geometry.^[48a] The presence of aurophilic attraction was evident as the shortest Au(1)–Au(3) distance is 3.4445(9) Å.^[50] The longest Au(1)–Au(2) distance is 3.9990(6) Å.

To establish the donor behavior of tri-AuPhos, low-temperature chemical trapping experiments in the presence of Rh(acac)(CO)₂ were conducted (Figure 10b). Gratifyingly, the formation of the Rh complex **28** was shown by a doublet ³¹P NMR resonance at -137.1 ppm (*J*_{P–Rh} = 93.7 Hz). X-ray diffractometry further confirmed the connectivity of **28** (Figure 11d). The TEP value of (L²Au)₃P (2025.4 cm⁻¹) is only slightly lower compared with that of **22** (2025.9 cm⁻¹), which is likely due to the π-accepting nature of L² over L³. It is important to note that the preparation of **25** is unique as the similar reaction of PTMS₃ with L³AuCl in a molar ratio of 1:3 only gave **19**, along with unchanged L³AuCl. The lack of suitable synthetic routes towards [(LAu)₃PTMS][Cl] (L = L¹, L³, L⁴) limits the exploration of other tri-AuPhos. More efficient methods leading to free tri-AuPhos are therefore needed in the future study.

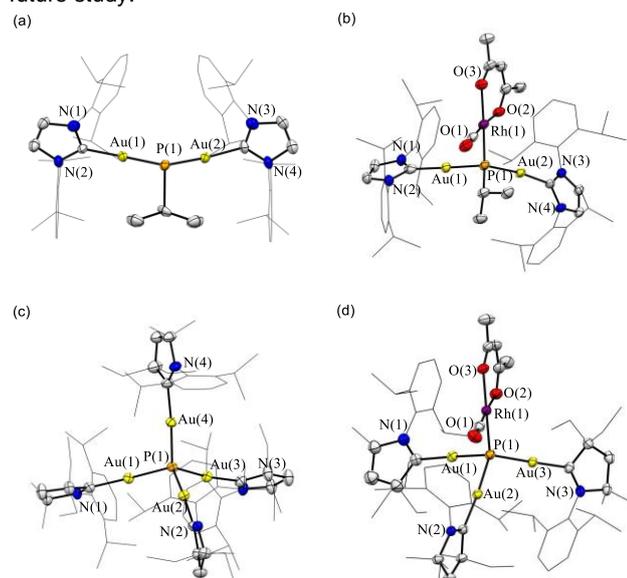


Figure 11. Solid-state structures of **22** (a), **23** (b), **26** (c), and **28** (d). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

Table 2. Ir-catalyzed decarbonylation reaction of 2-naphthaldehyde.^a

| Entry | Ligand | T [h] | NMR Yield [%] |
|-------|-----------------------|-------|---------------|
| 1 | no | 12 | 0 |
| 2 | PPh ₃ | 2 | 4 |
| 3 | PPh ₃ | 12 | 14 |
| 4 | PCy ₃ | 2 | 5 |
| 5 | PCy ₃ | 12 | 17 |
| 6 | PCy ₃ | 24 | 27 |
| 7 | 3 | 2 | 24 |
| 8 | 3 | 12 | 46 |
| 9 | 5 | 2 | 48 |
| 10 | 5 | 12 | 71 |
| 11 | 5 | 24 | 85 |
| 12 | 5 ^b | 12 | 0 |

[a] Conditions: 2-naphthaldehyde (0.25 mmol), [Ir(cod)Cl]₂ (2 mol %), ligand (4 mol %), in a mixed solvent consisting of THF (5 mL) and C₆D₆ (1 mL), 75 °C, Ar.

[b] In the absence of [Ir(cod)Cl]₂.

Catalysis. Numerous TM-catalyzed transformations that require electron-rich metal centers will benefit from the electron-donating phosphines. Among them, the use of electron-releasing phosphine ligands have been shown to facilitate Ir-catalyzed decarbonylation reactions of aldehydes.^[51] This prompted us to explore such catalytic reactions with our AuPhos (Table 2). The combination of commercially available [Ir(cod)Cl]₂ (2 mol %) and PPh₃ or PCy₃ (4 mol %) only sluggishly promoted the decarbonylation of 2-naphthaldehyde in refluxing THF/C₆D₆ (v:v = 5:1) (i.e. 75 °C) (Entries 2-6). Gratifyingly, employing AuPhos **3** or **5** provided much higher catalytic activity (Entries 7-11), giving the product naphthalene in yields of up to 85 % within 24 h (Entry 11). In the absence of either [Ir(cod)Cl]₂ or ligand, no conversion was observed (Entries 1 and 12). These results combined, demonstrates the remarkable potential of AuPhos in the development of TM catalysis.

Conclusion

To conclude, we have systematically explored a family of AuPhos, including mono-, di- and tri-AuPhos. These species are readily synthesized via either a salt metathesis reaction or a desilylation reaction. The electron-rich nature of AuPhos is attributed to the d-p lone pair repulsion, which can be easily modulated by modifying the π-accepting ability of the L at Au. This makes AuPhos extremely electron-rich phosphorus superbases that are electronically and sterically tunable. Importantly, this concept could be extended to other systems with tunable electronic properties. AuPhos have also shown as potent synthons for multi-nuclear TM complexes. Preliminary attempts on catalysis reveal that AuPhos can improve the outcome of Ir-catalyzed decarbonylation reactions of aldehydes, showcasing their huge potential for the development and improvement of TM catalysis when electron-rich metal centers are required. The application of AuPhos in the production of other catalytically active species, the

deeper evaluation of these new TM complexes, and the extension of AuPhos as catalysts are the subjects of ongoing work.

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Conflict of Interest

The authors declare no conflict of interest.

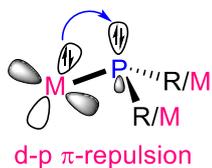
Keywords: Phosphine; Metal substituents; Multi-nuclear complexes; Electron-rich; Catalysis

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Entry for the Table of Contents



- Mono-, di-, and tri-AuPhos
- Extremely electron-rich via d-p π -repulsion
- Sterically and electronically tunable
- Synthon for multi-nuclear TM complexes
- Catalysis

An intriguing class of free Au-substituted phosphines (AuPhos) featuring an electronically and sterically tunable, extremely electron-rich phosphorus center has been described. These AuPhos are potent synthons for multi-nuclear transition metal complexes and have tremendous potential for transition metal catalysis when electron-rich metal centers are required.

Institute and/or researcher Twitter usernames: @LLL_lab_SUSTech @SUSTechSZ