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# Synthesis of Gold(I) Complexes Bearing Verkade's Superbases

Bastien Chatelet,<sup>[a]</sup> Paola Nava,<sup>[a]</sup> Herve Clavier,<sup>\*[a]</sup> and Alexandre Martinez<sup>\*[a]</sup>

**Abstract:** Proazaphosphatranes, also known as Verkade's superbases, have been investigated as ligands for gold(I). If the coordination to the gold center by the phosphorus atom suggests phosphine-like behavior, gold(I)-containing Verkade's superbase complexes could also be prepared from the weak conjugate acid azaphosphatrane by the formation of the corresponding silver complex and subsequent transmetalation to gold, similarly to the synthetic route used for complexes bearing N-heterocyclic carbene ligands (NHCs). A competitive

transmetalation experiment highlighted the higher lability of Verkade's superbases compared with NHCs. Furthermore, combined theoretical and experimental studies showed that they display strong  $\sigma$ -donor ability, better than phosphines and similar to NHCs. Thus, some specific properties of both NHCs and phosphines are combined in Verkade's superbases, thereby providing a new approach to tuning the ligand properties of gold(I) complexes.

## Introduction

Proazaphosphatranes **1** (Figure 1), first described by Verkade and co-workers almost 30 years ago, are known for their strong basic properties.<sup>[1]</sup> Indeed, their unique scaffold, built from the tris(2-aminoethylamine) unit, presents an original aminophosphine moiety leading to very strong non-ionic bases with a  $pK_a$  higher than 32 in acetonitrile,<sup>[2]</sup> much more basic than classical aminophosphines. This improvement in basicity is explained by the high stability of the azatrane structure of their conjugate acids, the protonated azaphosphatranes **2**. Therefore, they have received considerable attention as basic or nucleophilic organocatalysts.<sup>[3]</sup> These phosphorus-based compounds have also been tested as ligands, and this has led to the development of efficient in situ generated palladium-based catalytic systems for cross-coupling reactions.<sup>[4]</sup> Despite these interesting applications, the coordination properties of proazaphosphatranes **1** towards transition metals have scarcely been investigated. Long after the development of their platinum,<sup>[5]</sup> rhenium,<sup>[6]</sup> and mercury complexes,<sup>[6]</sup> further platinum-based complexes were prepared and applied to the hydrosilylation of terminal alkynes.<sup>[7]</sup> More recently, Yang and co-workers synthesized a proazaphosphatrane bearing pyridyl moieties and used this tetradentate ligand to bind a cobalt(II) ion.<sup>[8]</sup> Subsequently, a series of carbonylnickel(0) complexes bearing various proazaphosphatrane ligands were prepared<sup>[9]</sup> to investigate their stereoelectronic parameters according to the work of Tolman.<sup>[10]</sup> It was found that the nature of the R substituents on **1** influences mainly the steric properties, whereas the effect on the electron-donating

strength remains negligible. In comparison with the corresponding trialkylphosphines, proazaphosphatranes **1** are ranked among the sterically most demanding and electron-donating phosphines.<sup>[11]</sup>

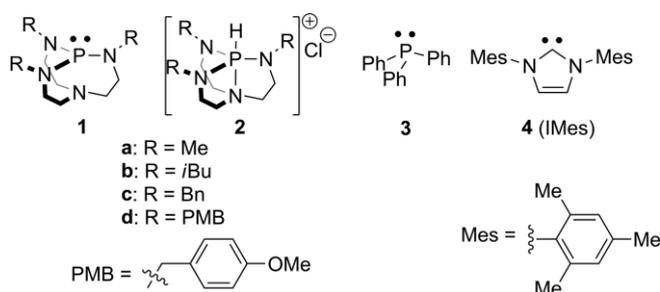


Figure 1. Structures of the ligands and pre-ligands used in this study.

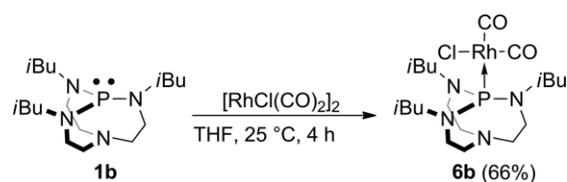
Although proazaphosphatranes **1** present some common features with phosphines, we believe that they also share some properties with N-heterocyclic carbenes (NHCs) such as **4**. In addition to being both efficient organocatalysts and highly basic species,<sup>[12]</sup> they exhibit strong electron-donating properties that do not depend on the nature of the N-substituents.<sup>[13]</sup> Moreover, azaphosphatrane salts **2** may be seen as analogues of imidazolium salts, which are the pre-ligands of NHCs ( $pK_a = 17-25$ ).<sup>[14]</sup> This should make Verkade's superbases interesting alternatives to phosphines and NHC ligands for the stabilization of transition metals. Gold(I) complexes of NHC ligands in the recent past have become very important in the field of bioorganometallic chemistry<sup>[15]</sup> and homogeneous catalysis.<sup>[16]</sup> Herein, we disclose our theoretical and experimental investigations of the coordination properties of proazaphosphatranes with gold(I). First, a modification of the strategy used to prepare phosphine-containing complexes was applied to the synthesis of (proazaphosphatrane)gold(I) complexes, before successfully employing a pathway specific to NHCs involving the formation of silver complexes followed by a transmetalation step.

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## Results and Discussion

We first examined theoretically the electron-donating ability of Verkade's superbases by computing the CO vibrational frequencies for two series of carbonylmetal complexes,  $[\text{Ni}(\text{CO})_3(\text{L})]$  (**5**) and  $[\text{RhCl}(\text{CO})_2(\text{L})]$  (**6**), by means of DFT. Indeed, the CO stretching of these complexes are recognized as an excellent measure of the  $\sigma$ -donating ability of the ligand.<sup>[10,13]</sup> Moreover, a large amount of data is available in the literature for comparison.<sup>[10,13,17]</sup> Calculations employing the TPSS functional and a def2-TZVP basis set and including zero-point energy (ZPE) contributions are discussed.<sup>[18]</sup> Verkade's superbase with *N*-methyl substituents (**1a**) was chosen to reduce the computational cost. For a reasonable comparison, we calculated, at the same computational level, the vibrational frequencies for complexes  $[\text{Ni}(\text{CO})_3(\text{L})]$  (**5**) and  $[\text{RhCl}(\text{CO})_2(\text{L})]$  (**6**) bearing other ligands L, including phosphines, phosphite, or NHC. The calculated carbonyl stretching frequencies show the same trend as the experimental values with a deviation of 10–15  $\text{cm}^{-1}$  (Table 1).<sup>[19]</sup> As expected, among the phosphorus-containing ligands,  $\text{P}(\text{OPh})_3$ -containing complexes display the highest carbonyl stretching frequencies, with the lowest values observed for complexes bearing the  $\text{P}(\text{tBu})_3$  ligand. Verkade's superbase complexes exhibit virtually the same stretching frequencies as those obtained with  $\text{P}(\text{tBu})_3$ ; the values are significantly lower than those calculated with  $\text{PPh}_3$  and slightly higher than those of the NHC system. All these results are in line with data provided by Yang and co-workers and demonstrate the high electron-donating properties of proazaphosphatranes **1** compared with phosphines.<sup>[9]</sup>

To confirm these results, and to gain further experimental insights into the electronic properties of Verkade's superbases, we attempted to prepare a rhodium complex bearing a proazaphosphatranane ligand. The reaction of 1 equiv. of superbase **1b** with 0.5 equiv. of  $[\text{RhCl}(\text{CO})_2]_2$  afforded the expected complex **6b** in 66% yield (Scheme 1). The  $^{31}\text{P}$  NMR spectrum of **6b** shows a doublet at  $\delta = 103.1$  ppm in  $\text{CD}_2\text{Cl}_2$  with a coupling constant  $^1J(^{31}\text{P}-^{103}\text{Rh}) = 89.8$  Hz. The complex turned out to be unstable in solution leading quickly to the protonated azaphosphatranane **2b**. The related FTIR spectrum shows two absorption bands in the carbonyl region at 1990 and 2067  $\text{cm}^{-1}$ , showing a remarkably good agreement with values computed using **1a** as ligand (1984 and 2066  $\text{cm}^{-1}$ ; Table 1 and Figure S16 in the Supporting Information). As mentioned before, these values are comparable to those observed for NHC-containing rhodium complexes and suggest strong electron-donating abilities of superbases, stronger than of most phosphines.



Scheme 1. Synthesis of rhodium complex **6b**.

With this preliminary study on the electronic properties in hand, we investigated the ability of proazaphosphatranes to bind gold(I). First we computed the gas-phase dissociation energies of the  $[\text{Au}(\mathbf{1a})]^+$  system and compared it with the values obtained for other  $[(\text{Au})\text{L}]^+$  complexes as a function of the HOMO energies of ligand L [L = phosphine or IMes (**4**); Figure 2]. The trend observed between these two values is due to the nature of the bond between the ligand L and  $\text{Au}^+$ , which is mostly a result of the interaction between the L lone pair and the empty  $\text{Au}^+$  6s orbital. The highest dissociation energy was found for the  $[\text{Au}(\mathbf{1a})]^+$  system, which provides support for the strong  $\sigma$ -donating ability of the superbase.

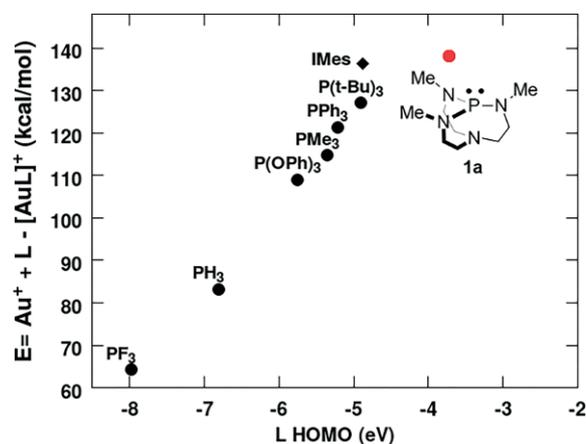


Figure 2. Dissociation energies of the  $[(\text{Au})\text{L}]^+$  complexes (L specified in the plot, TPSS/def2-TZVP level, including ZPE) plotted vs. HOMO energies of L.

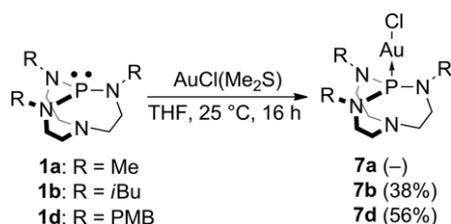
Then (proazaphosphatranane)gold complexes **7** were synthesized by using a procedure extensively employed to prepare (phosphine)gold(I) complexes<sup>[20]</sup> before being transposed to NHCs.<sup>[21]</sup>  $\text{AuCl}(\text{SMe}_2)$  was treated with 1 equiv. of free superbase **1a, b, d** in THF at room temperature for 16 h (Scheme 2). Although **7b** and **7d** could be isolated in moderate yields, no complex formation could be detected with proazaphosphatranane **1a**, and only degradation was observed. The NMR

Table 1. Computed (TPSS/def2-TZVP) CO stretching frequencies for carbonylmetal complexes **5** and **6** with selected ligands.<sup>[a]</sup>

L	$[\text{Ni}(\text{CO})_3(\text{L})]$ ( <b>5</b> )		$[\text{RhCl}(\text{CO})_2(\text{L})]$ ( <b>6</b> )	
	$\nu_{\text{CO A}_1}$ [ $\text{cm}^{-1}$ ]	$\nu_{\text{CO E}}$ [ $\text{cm}^{-1}$ ]	$\nu_{\text{CO cis}}$ [ $\text{cm}^{-1}$ ]	$\nu_{\text{CO trans}}$ [ $\text{cm}^{-1}$ ]
<b>1a</b>	2047 (2057)	1993 (1978)	1984	2066
$\text{PPh}_3$ ( <b>3</b> )	2057 (2069)	2003 (1990)	1998 (2009)	2072 (2087)
$\text{P}(\text{tBu})_3$	2046 (2056)	1989 (1971)	1980	2069
$\text{P}(\text{OPh})_3$	2071 (2085)	2015 (2012)	2013	2083
IMes ( <b>4</b> )	2042 (2051)	1985 (1970)	1982 (1996)	2063 (2081)

[a] Experimental values from literature are given in parentheses.<sup>[9,13c,13e,17]</sup>

spectra of these complexes show that they present, on average, a  $C_3$  symmetry in solution. Moreover, they display interesting features: (1)  $^{31}\text{P}$  NMR signals for the phosphorus atom of gold complexes **7b** and **7d** ( $\delta = 108.0$  ppm in  $[\text{D}_6]$ benzene and  $\delta = 107.3$  ppm in  $[\text{D}_8]$ toluene, respectively) are upfield-shifted in comparison with those observed for the corresponding free superbases ( $\delta = 130.9$  ppm and  $\delta = 125.3$  ppm for **1b**<sup>[22]</sup> and **1d**<sup>[23]</sup> respectively) and (2) the benzylic protons of **7d** show a resonance at  $\delta = 4.0$  ppm with an observable coupling constant with phosphorus [ $^3J(^{31}\text{P}-^1\text{H}) = 11.2$  Hz] that is close to the one observed for the corresponding free superbase [ $^3J(^{31}\text{P}-^1\text{H}) = 9.2$  Hz] and much smaller than the coupling constant observed for the corresponding protonated species [ $^3J(^{31}\text{P}-^1\text{H}) = 17.0$  Hz].



Scheme 2. Preparation of complexes **7** from proazaphosphatranes **1**.

Single crystals of complex **7b** suitable for X-ray diffraction study were obtained by slow concentration of a solution of  $[\text{D}_6]$ benzene (Figure 3). The complex shows the expected almost linear coordination of the two ligands at the gold atom with a P–Au–Cl angle of  $177^\circ$  and a pyramidal geometry at the phosphorus atom with N–P–Au angles of  $108^\circ$ . The distance between the nitrogen atom in the apical position and the phosphorus atom is  $3.127 \text{ \AA}$ , a distance comparable to the one observed in proazaphosphatranes,<sup>[24]</sup> which indicates little interaction between this nitrogen atom and the phosphorus atom. The phosphorus–gold bond length of  $2.234 \text{ \AA}$  is comparable to that found in typical (phosphine)gold(I) complexes.<sup>[25]</sup>

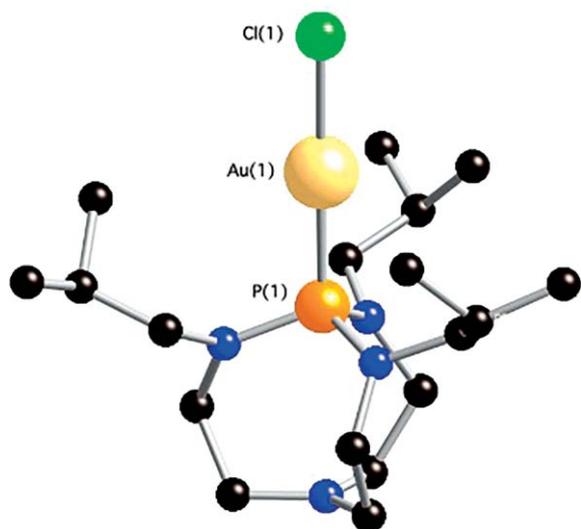


Figure 3. Ball-and-stick representation of **7b** (hydrogen atoms have been omitted for clarity).

The DFT-optimized structure reproduces experimental bond lengths (within  $0.02\text{--}0.03 \text{ \AA}$ ) and confirms the weak interaction

between the phosphorus atom and the apical nitrogen atom; the HOMO orbital is clearly the lone-pair orbital on the nitrogen atom (Figure 4). The X-ray structure data of **7b** allowed us to quantify the steric parameters of ligand **1b** through the calculation of its buried volume ( $\%V_{\text{bur}}$ ).<sup>[26]</sup> With a  $\%V_{\text{bur}}$  value of 45.6 %, which corresponds to a cone angle of  $210^\circ$ ,<sup>[26]</sup> **1b** exhibits a bulk similar to that of  $\text{PMe}_3$ .<sup>[27]</sup> This result is in line with that of Yang and co-workers.<sup>[9]</sup>

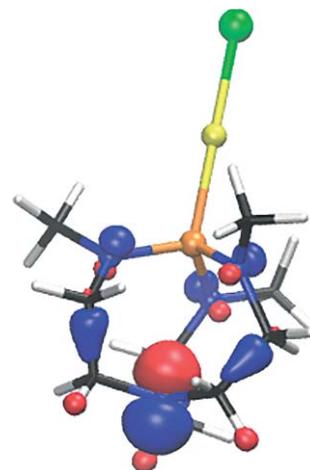
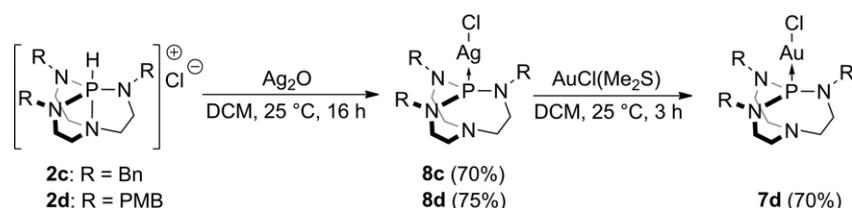


Figure 4. HOMO orbital of complex **7a** (isovalue: 0.07 a.u.).

We found that the preparation of gold(I) complexes **7** needed controlled handling conditions, such as working with dry solvents in the strict absence of oxygen to avoid the protonation or oxidation of superbases **1**, similarly to the most basic phosphines or NHCs. However, in the case of NHCs, it was possible to circumvent the use of free NHCs. Wang and Lin reported that starting from the corresponding imidazolium salts, which are air- and moisture-stable, and treating them with silver oxide, led to the quantitative formation of NHC-containing silver complexes.<sup>[28]</sup> These compounds can then be used as carbene transfer agents to prepare various other (NHC)transition-metal complexes, in particular with gold.<sup>[21]</sup>

Thus, we decided to study whether it would be possible to prepare silver complexes starting from azaphosphatranes **2** and silver oxide followed by transmetalation to gold(I). Calculations were first performed to assess whether the transmetalation is thermodynamically favorable, and a higher dissociation energy [ $\Delta E_{\text{MCl(L)}} = \Delta E_{\text{MCl}} + E_{\text{L}} - E_{\text{MCl(L)}}$ ; M = Au, Ag; L = **1a**] for  $\text{AuCl}(\mathbf{1a})$  than for  $\text{AgCl}(\mathbf{1a})$  was found ( $\Delta E_{\text{Au}} = 68.4$  and  $\Delta E_{\text{Ag}} = 45.7 \text{ kcal mol}^{-1}$ ). Therefore, the reactions of azaphosphatranes **2c** and **2d** with an excess of silver oxide in dichloromethane were performed at room temperature (Scheme 3). Even if the reactions did not reach completion (85 % conversion after 1 d), silver complexes **8c** and **8d** were obtained in yields of 70 and 75 %, respectively; further attempts to improve the conversion by increasing reaction duration, heating, and the addition of molecular sieves were unsuccessful. The  $^{31}\text{P}$  NMR spectra of **8c** and **8d** show signals at  $\delta = 113.5$  and  $112.4$  ppm, respectively, consisting of two sharp well-defined doublets with observable coupling constants  $^1J(^{31}\text{P}-^{109}\text{Ag}) = 1033 \text{ Hz}$  and  $^1J(^{31}\text{P}-^{107}\text{Ag}) = 894 \text{ Hz}$  for **8c**, and  $^1J(^{31}\text{P}-^{109}\text{Ag}) = 1027 \text{ Hz}$  and  $^1J(^{31}\text{P}-^{107}\text{Ag}) =$

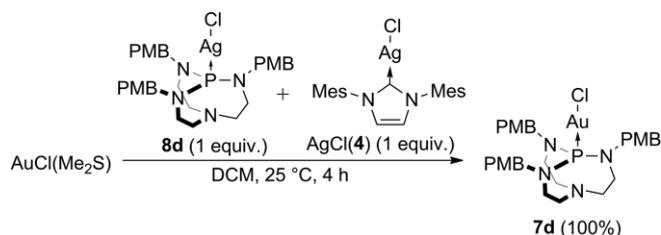


Scheme 3. Synthesis of complexes **7** by formation of silver complexes **8** from azaphosphatranes **2** followed by transmetalation.

890 Hz for **8d**. Both signals are upfield-shifted by 15 and 13 ppm in comparison with those of the corresponding free superbases **1**. The  $^1\text{H}$  NMR spectra of complexes **8c** and **8d** show a single resonance for benzylic protons with chemical shifts upfield-shifted by 0.2 ppm with observable coupling constants  $^3J(^{31}\text{P}-^1\text{H}) = 11.49$  Hz for **8c** and  $^3J(^{31}\text{P}-^1\text{H}) = 11.74$  Hz for **8d**, which suggest a pyramidal geometry at the phosphorus atom as in the gold complexes.

Complex **8d** was then treated with  $\text{AuCl}(\text{SMe}_2)$  in dichloromethane under aerobic conditions (Scheme 3). After 3 h,  $^{31}\text{P}$  NMR monitoring showed the complete disappearance of the two doublets of the silver complex and the appearance of a singlet corresponding to the gold complex **7d**, which was easily isolated in 70 % yield. This clearly demonstrates the usefulness of this synthetic route as well as the analogy between NHCs and Verkade's superbases.

Finally, we compared the ability of a (proazaphosphatranes)-silver complex and an (NHC)silver complex to undergo transmetalation with gold. Thus, a competition experiment between the (NHC)silver complex  $[\text{AgCl}(\mathbf{4})]$  and the (proazaphosphatranes)silver complex **8d** with  $\text{AuCl}(\text{SMe}_2)$  was performed in DCM at room temperature (Scheme 4). It turned out that after 4 h, complex **8d** had been completely converted into the gold complex **7d**, which suggests an enhanced lability of the phosphorus–silver bond compared with the carbon–silver bond in the silver–carbene complex. This is consistent with the lower calculated dissociation energy of the phosphorus–silver bond in **8d** compared with the carbon–silver bond in  $[\text{AgCl}(\mathbf{4})]$  (45.7 and 54.3 kcal mol $^{-1}$ , respectively).



Scheme 4. Competition experiment of transmetalation between a proazaphosphatranes and NHC ligand.

## Conclusions

Proazaphosphatranes complexes of gold(I) have been prepared for the first time and fully characterized. Coordination of the phosphorus atom to the metal atom suggests phosphine-like behavior, but these metal complexes can be directly prepared from the free superbases or by transmetalation of silver com-

plexes of protonated azaphosphatranes. These two different synthetic pathways to (superbase)metal complexes highlight the similarity between Verkade's superbases and carbene complexes. Thus, it appears that Verkade's superbases share some dual behavior of both phosphines and carbenes, making them a unique class of ligands for gold(I) and paving the way to their use in organometallic catalysis. In particular, their structures and steric hindrance can be easily tuned, providing potentially highly bulky ligands for gold(I). Such complexes could present high turnover numbers, for instance, in intramolecular hydroalkoxylation and enyne or furanyne cyclization reactions, as recently reported by Hashmi and co-workers for bulky (phosphite)gold(I) complexes.<sup>[29]</sup>

## Experimental Section

**General:** All reagents were obtained from commercial sources and used as received. Superbases **1a** and **1b** were purchased from Aldrich; **1d**, **2c**, and **2d** were synthesized according to a procedure described elsewhere.<sup>[4e,23]</sup> Solvents (THF, DCM, toluene, and Et $_2$ O) were purified and dried by using a Braun solvent purification system (MB-SPS-800) or dried by standard procedures prior to use.<sup>[30]</sup> Reactions were carried out under argon using classic Schlenk techniques because of the high sensitivity of Verkade's superbases towards water and O $_2$ . IR spectra were recorded with an FT-IR Bruker Alpha Platinum ATR spectrometer.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra were recorded at ambient temperature with Bruker Avance III 300 or 400 spectrometers operating at 300 and 400 MHz, respectively, for  $^1\text{H}$ , 75.5 and 100.6 MHz, respectively, for  $^{13}\text{C}$ , and 121.5 and 162.0 MHz, respectively, for  $^{31}\text{P}$ . The  $^{13}\text{C}$  signals were observed with  $^1\text{H}$  decoupling. Solvent residual signals were used as internal standards.<sup>[31]</sup> Chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) are given in ppm and Hz, respectively. The multiplicities are indicated as follows: s: singlet; d: doublet; t: triplet; q: quartet; sept: septet; m: multiplet; dd: doublet of doublets; dt: doublet of triplets; dm: doublet of multiplets, etc.). HRMS was performed at the "Spectropôle" of Aix-Marseille Université with a SYNAPT G2 HDMS (Waters) or QStar Elite (Applied Biosystems SGIEX) spectrometer equipped with an atmospheric pressure ionization (API) source. Mass spectra were obtained with a time-of-flight (TOF) analyzer.<sup>[32]</sup> For the competition experiment, analyses were performed in ESI mode with a Bruker Alpha Platinum ATR spectrometer. X-ray diffraction data were collected with a Bruker–Nonius KappaCCD diffractometer using Mo- $K_\alpha$  radiation (0.71073 Å) at 293(2) K. Data reduction was performed by using the HKL-2000 software package. The structure was resolved by using SIR92<sup>[33]</sup> by direct methods and refined by using SHELXL-97.<sup>[34]</sup> CCDC 1547329 (for **7b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**[RhCl(CO) $_2$ (**1b**)] (**6b**):** A solution of free superbase **1b** (175 mg, 0.510 mmol) in THF (10 mL) was added dropwise to a solution of

[RhCl(CO)<sub>2</sub>]<sub>2</sub> (100 mg, 0.254 mmol) in THF (10 mL). The reaction mixture was stirred at 25 °C for 4 h. The THF was evaporated, and pentane was added. The yellow solid that precipitated was filtered off and washed with pentane (yield 75 mg, 66 %). IR (neat):  $\tilde{\nu}_{\text{CO}} = 2067.9, 1990.0 \text{ cm}^{-1}$ . <sup>31</sup>P NMR ([D<sub>8</sub>]THF, 121.5 MHz):  $\delta = 103.1$  [d, <sup>1</sup>J(<sup>31</sup>P-<sup>103</sup>Rh) = 89.8 Hz] ppm.

**[AuCl(1b)] (7b):** (Dimethyl sulfide)gold(I) chloride (146 mg, 0.500 mmol) was added to a solution of **1b** (170 mg, 0.500 mmol) in THF (2 mL). The resulting solution was kept in the dark and stirred at room temperature overnight. The volatiles were then removed in vacuo. Toluene was then added, and the solution was filtered. The mother liquor was concentrated and dried under vacuum to afford a light-yellow solid (110 mg, 38 %). <sup>1</sup>H NMR ([D<sub>6</sub>]benzene, 300 MHz):  $\delta = 2.84\text{--}2.67$  (m, 6 H, NCH<sub>2</sub>CH<sub>2</sub>N), 2.43–2.28 (m, 6 H, NCH<sub>2</sub>CH<sub>2</sub>N), 2.28–2.17 [m, 6 H, NCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>], 1.99–1.81 [sept, *J* = 6.60 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.02–0.86 [d, *J* = 6.60 Hz, 18 H, (CH<sub>3</sub>)<sub>2</sub>] ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]benzene, 75 MHz):  $\delta = 55.3$  (d, *J* = 15.9 Hz), 49.5 (d, *J* = 1.65 Hz), 45.5 (s), 27.7 (d, *J* = 3.3 Hz), 20.5 (s) ppm. <sup>31</sup>P NMR ([D<sub>6</sub>]benzene, 121.5 MHz):  $\delta = 108.0$  ppm. HRMS (ESI): calcd. for C<sub>18</sub>H<sub>39</sub>AuClN<sub>4</sub>PNa<sup>+</sup> [M + Na]<sup>+</sup> 597.2159; found 597.2162.

**[AuCl(1d)] (7d):** A preparation method similar to that used for compound **7b** starting from **1d** (100 mg, 0.187 mmol) gave a light-yellow solid (80 mg, 56 %). <sup>1</sup>H NMR ([D<sub>6</sub>]benzene, 300 MHz):  $\delta = 7.20$  (d, *J* = 8.44 Hz, 6 H), 6.79 (d, *J* = 8.53 Hz, 6 H), 4.20 (d, *J* = 11.37 Hz, 6 H), 3.69 (s, 9 H, OMe), 2.78–2.58 (m, 12 H) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]benzene, 75 MHz):  $\delta = 159.4, 130.2, 129.9, 114.1, 54.8, 49.6, 49.2, 45.2$  ppm. <sup>31</sup>P NMR ([D<sub>6</sub>]benzene, 121.5 MHz):  $\delta = 107.4$  ppm. HRMS (ESI): calcd. for C<sub>30</sub>H<sub>39</sub>N<sub>4</sub>O<sub>3</sub>PAuClNa<sup>+</sup> [M + Na]<sup>+</sup> 789.2006; found 789.2015.

**[AgCl(1c)] (8c):** A mixture of silver(I) oxide (193 mg, 0.832 mmol) and **2c** (200 mg, 0.416 mmol) in dichloromethane (5 mL) was stirred overnight. The mixture was filtered through a short pad of Celite®, and the filtrate was concentrated to afford a brown solid (170 mg, 70 %). Some protonated azaphosphatane still remained after purification (10 %, estimated by <sup>1</sup>H NMR spectroscopy). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta = 7.39\text{--}7.16$  (m, 15 H), 4.30 (d, *J* = 11.83 Hz, 6 H), 2.83–2.62 (m, 12 H) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz):  $\delta = 138.3, 128.7, 128.0, 127.5, 51.0, 50.2, 45.7$  ppm. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.5 MHz):  $\delta = 113.4$  [d, <sup>1</sup>J(<sup>31</sup>P-<sup>109</sup>Ag) = 1027.7 Hz], 113.4 [d, <sup>1</sup>J(<sup>31</sup>P-<sup>107</sup>Ag) = 890.1 Hz] ppm. HRMS (ESI): calcd. for C<sub>27</sub>H<sub>33</sub>N<sub>4</sub>PAgClNa<sup>+</sup> [M]<sup>+</sup> 609.1075; found 609.1072.

**[AgCl(1d)] (8d):** The same procedure as for **8c** was applied starting from **2d** (100 mg). Yield 89 mg, 75 % of a brown solid. Some protonated azaphosphatane still remained after purification (10 %, estimated by <sup>1</sup>H NMR spectroscopy). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz):  $\delta = 7.20$  (d, *J* = 8.53 Hz, 6 H), 6.79 (d, *J* = 8.53 Hz, 6 H), 4.19 (d, *J* = 11.37 Hz, 6 H), 3.69 (s, 9 H, OMe), 2.78–2.62 (m, 12 H) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz):  $\delta = 159.2, 130.4, 129.4, 114.0, 55.3, 50.8, 50.3, 45.5$  ppm. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 121.5 MHz):  $\delta = 112.4$  [d, <sup>1</sup>J(<sup>31</sup>P-<sup>109</sup>Ag) = 1027.7 Hz], 112.4 [d, <sup>1</sup>J(<sup>31</sup>P-<sup>107</sup>Ag) = 890.1 Hz] ppm. HRMS (ESI): calcd. for C<sub>30</sub>H<sub>39</sub>N<sub>4</sub>O<sub>3</sub>PAgCl<sup>+</sup> [M]<sup>+</sup> 677.1572; found 677.1577.

**Transmetalation:** A mixture of silver(I) oxide (81 mg, 0.350 mmol) and **2d** (100 mg, 0.175 mmol) in dichloromethane (5 mL) was stirred overnight. (Dimethyl sulfide)gold(I) chloride (52 mg, 0.175 mmol) was then added to the reaction mixture, which was stirred for 3 h. The reaction mixture was filtered through a pad of Celite®, and the solvent was evaporated to yield **7d** (93 mg, 70 %). The <sup>1</sup>H and <sup>31</sup>P NMR and mass spectra of the light-yellow solid are identical to the ones obtained by direct synthesis.

**Competition Experiment:** A mixture of **8d** (73 mg, 0.109 mmol), [AgCl(**4**)] (50 mg, 0.109 mmol) and AuCl(SMe<sub>2</sub>) (32 mg, 0.109 mmol)

were mixed in dry dichloromethane (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 4 h. The solvent was then removed under vacuum. The crude reaction mixture was analyzed by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy and mass spectrometry. Only the formation of **7d** was observed.

**Computational Treatment:** Calculations were performed at the TPSS level<sup>[18a]</sup> by using a relativistic effective core potential for gold<sup>[15c]</sup> and the def2-TZVP basis set.<sup>[18b]</sup> The resolution of identity technique was employed.<sup>[35]</sup> The calculated energies contain zero-point energy (ZPE) contributions. The TURBOMOLE program package was used throughout this work.<sup>[18d]</sup>

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