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Gold Phosphole Complexes as Efficient Catalysts for Alkyne Activation

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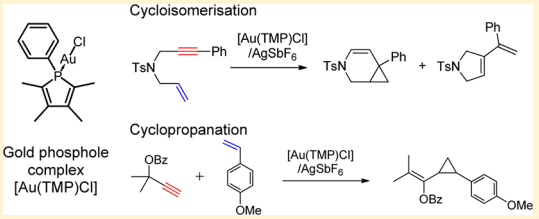
Supporting Information

ABSTRACT: Gold(I) complexes bearing monophosphole ligands were synthesized, and their electronic and steric properties were compared to those of their triphenylphosphine-based counterparts. Cationic phosphole-based gold(I) complexes are active and selective in enyne cycloisomerization and in olefin cyclopropanation, with a good correlation between the ligand σ-donor ability and the catalytic activity. For the most efficient ligand, 1-phenyl-2,3,4,5-tetramethylphosphole (TMP), a highly active, selective, and stable cationic $[Au(TMP)(CH_3CN)]SbF_6$ complex was isolated.



In recent years, homogeneous gold catalysis has received considerable attention in the field of organic synthetic chemistry.[1] Among the broad panel of gold-catalyzed transformations, cycloisomerization of 1,6-enynes has emerged as a powerful tool for the atom-economical preparation of functionalized polycylic structures.[2]

Initially, gold catalysts bearing monodentate phosphine ligands such as triphenylphosphine were used. NHC ligands[3] were then widely used in gold-catalyzed cycloisomerizations,[4] allowing for complementary reactivity.[5] Given the major role played by the ligand in the control of cycloisomerization selectivity,[6] more elaborate ligands were then developed, including biaryl-like phosphines or phosphites,[4c,7] as well as various new carbenes.[8]

Phosphole ligands combine the soft donor character of phosphines with the conformational rigidity associated with the phosphorus heterocyclic skeleton that make them efficient in promoting homogeneous transition-metal catalysis. The most important examples have been reported in olefin hydroformylation catalyzed by Rh complexes bearing simple monophospholes.[9] Very few Au−monophosphole complexes have been described[10] and used in catalysis.[11]

As part of our continuing interest in the design of phosphole-based ligands for application in catalysis[12] and in enyne cycloisomerization,[13] we report herein the synthesis of new gold(I) phosphole complexes which are both active and selective in various alkyne activation reactions, such as enyne cycloisomerization and olefin cyclopropanation.

1-Phenyl-2,3,4,5-tetramethylphosphole (TMP)[14] is particularly attractive among the classical monophosphole ligand series, such as 1-phenyldibenzophosphole (DBP),[15] 1,2,5-triphenylphosphole (TPP),[16] and 1-phenyl-3,4-dimethylphosphole (DMP),[17] because a good σ-donor ability along with a moderate steric hindrance can be expected. However, its potential in catalysis has been underexploited in comparison to the other ligands of the series.[18]

The electronic properties of TMP were first determined and compared to other phosphole ligands of the series and to triphenylphosphine. Following the most widely used Tolman approach,[19] we estimated the electron-donating ability of phosphole ligands by recording the IR frequency of CO in dicarbonyl complexes $[RhCl(L)(CO)_2]$, readily prepared in two steps from $[RhCl(cod)]_2$, as described for N-heterocyclic carbenes.[20] The resulting stretching frequencies of the *cis*- and *trans*-CO moieties in phosphole-based $[RhCl(DBP)(CO)_2]$, $[RhCl(TPP)(CO)_2]$ and $[RhCl(TMP)(CO)_2]$ complexes are summarized in Table 1 and compared with those of the analogous $[RhCl(PPh_3)(CO)_2]$ complex.[21] All the $\nu_{av}(CO)$

Table 1. Determination of Electronic Parameters: IR ν(CO) Stretching Frequencies of $[RhCl(L)(CO)_2]$ Complexes and $^{31}P-^{77}Se$ Coupling Constants for Selenides Prepared from Selected Ligands

L	ν(CO) (cm^{-1})	ν_{av}(CO) (cm^{-1})	δ P=Se (ppm)	^1J(P-Se) (Hz)
DBP	2096, 2016	2056	27.64	748
TPP	2097, 2018	2058	35.05	742
DMP	n.d.[a]	n.d.[a]	35.28	730
TMP	2092, 2010	2051	31.18	713
PPh_3	2093, 2012	2053	45.73	708

DBP TPP DMP TMP

[a]tThe synthesis of the [RhCl(cod)(DMP)] intermediate complex failed.

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bands are located in the same region, accounting for similar net donating abilities (including both σ-donor ability and π-acceptor strength[22]) of the phosphole ligands and their PPh_3 counterpart.

To further characterize the electronic properties of the ligands in the phosphole series, evaluation of the σ-donor ability was done by measuring the magnitude of $^1J_{P-Se}$[23] in the ^{77}Se isotopomer of the corresponding phosphole selenides (Table 1).[24] With the smallest value of $^1J_{P-Se}$, TMP appears as the best σ-donor ligand in our monophosphole series while PPh_3 exhibits an intermediate σ-donor ability higher than that of phenyl-substituted phospholes DBP and TPP but lower than that of methyl-substituted phospholes DMP and TMP (Table 1).

From TMP, a new gold(I) complex was prepared under mild conditions using [Au(SMe_2)Cl] as precursor. This complex, isolated as an air- and moisture-stable solid in good yield (79%), was fully characterized by conventional NMR techniques (^{31}P, ^1H, ^{13}C), mass spectrometry, and elemental analysis (see the Supporting Information). The structure of [Au(TMP)Cl] has been established by X-ray diffraction studies (Figure 1).

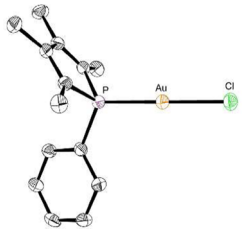


Figure 1. Ortep plot of [Au(TMP)Cl]. Thermal ellipsoids are drawn at the 30% probability level, and the hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au−P = 2.224(1), Au−Cl = 2.285(1); P−Au−Cl = 179.86(5).

Other phosphole complexes of gold(I) chloride were prepared from DBP, DMP, and TPP using the same procedure.[25] These complexes obtained in good yields (76−87%) were fully characterized (the X-ray structure of [Au(TPP)Cl] is described in the Supporting Information) and were isolated as air- and moisture-stable solids, except for [Au(DMP)Cl].

The examination of geometrical parameters within the P−Au−Cl backbone in our chlorogold(I) phosphole complexes is summarized in Table 2. This comparison reveals a typical Au−P bond length in the range of 2.22−2.23 Å and a typical Au−Cl bond length around 2.28 Å in all of the phosphole series as in [Au(PPh_3)Cl]. In all complexes, the Au center shows an almost linear coordination with typical Cl−Au−P angles in the range of 175−180°. Moreover, these structural parameters fall in the range of those for previously reported Au(I) phosphole complexes.[10b,c] Similar Au−Cl bond lengths and linear character were found in NHC-based gold complexes with, as expected, a shorter Au−C bond length within 1.94−2.01 Å.[4a]

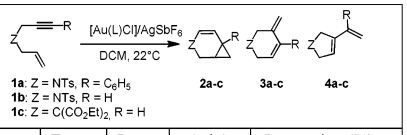
Table 2. Steric Parameters: Selected Bond Lengths (Å) and Angles (deg) and %V_{bur} Values Calculated from X-ray Crystallographic Data of Phosphole or Phosphine Gold(I) Complexes [Au(L)Cl]

L	Au−P	Au−Cl	Cl−Au−P	%V_{bur}
DBP[10a]	2.221(8)	2.282(9)	178.8	48.7
TPP	2.2241(6)	2.282(6)	176.4(2)	50.8
DMP[10a]	2.227(2)	2.288(2)	176.1	n.d.
TMP	2.2241(1)	2.285(4)	179.86(5)	38.3
PPh_3[26]	2.235(3)	2.279(3)	179.6(1)	31.5

Finally, to assess the steric properties of the ligands, their buried volumes (%V_{bur}) were calculated from the X-ray crystallographic data of the [Au(L)Cl] complexes using the web application SambVca developed by Cavallo and co-workers[27] (see the Supporting Information) and were compared to the buried volume of PPh_3[28] (Table 2). As expected, both phenyl-substituted phospholes TPP and DBP exhibit higher %V_{bur} values than the methyl-substituted phosphole TMP and all phosphole ligands were more sterically hindered than the corresponding phosphine PPh_3.

To evaluate the catalytic activity and selectivity of the gold phosphole complexes, we first investigated the cycloisomerization of the N-tethered 1,6-enyne **1a** as a benchmark reaction. The reaction was carried out in dichloromethane at room temperature in the presence of a cationic catalyst generated in situ from 5 mol % of [Au(L)Cl] and 5 mol % of $AgSbF_6$. The results obtained with the different phosphole complexes are shown in Table 3.

Table 3. Gold-Catalyzed Cycloisomerization of 1,6-Enynes[a]



Entry	Enyne	L	t (min)	Conversion (%) Ratio(**2**:**3**:**4**)[b]
1	**1a**	DBP	60	35(100:0:0)
2	**1a**	TPP	60	45(100:0:0)
3	**1a**	PPh_3	60	71(100:0:0)
4	**1a**	DMP	60	< 2
5	**1a**	TMP	60	91(95:0:5)
6	**1b**	TMP	180	99 (0:90:10)
7	**1c**	TMP	10	99 (0:85:15)

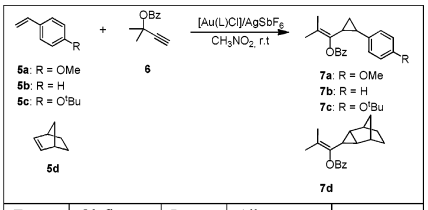
[a]See the Supporting Information for experimental details. [b]Determined by NMR.

All complexes were active in the cycloisomerization of **1a**, after addition of $AgSbF_6$, except for [Au(DMP)Cl], which led to the immediate formation of a black precipitate.[29] The active complexes led to high selectivity (>95%) in the cyclopropane product **2a** (Table 3, entries 1−3 and 5), and TMP appeared as the best ligand of the series in terms of activity in the cycloisomerization of **1a**. Moreover, there is a good correlation between the σ-donor ability of the ligand and the cycloisomerization rate (see the Supporting Information), indicating that the alkyne activation may not be the rate-determining step in the cycloisomerization of the N-tethered enyne **1a**.[5b,30]

In addition, the TMP-based complex proved to be very efficient in the cycloisomerization of enynes bearing terminal alkynes (Table 3, entries 6 and 7). 1,3-dienes **3b,c** were formed as major products from enynes **1b,c**, respectively, as previously reported for phosphine-based gold complexes.[31]

To extend the scope of reactions catalyzed by cationic gold(I) phosphole complexes, we next investigated the cyclopropanation of 4-methoxystyrene (**5a**) using propargyl benzoate (**6**) as the gold(I) carbene precursor (Table 4).[32] The reaction was carried out in nitromethane at room temperature

Table 4. Gold-Catalyzed Cyclopropanation of Olefins



Entry	Olefin	L	Alkyne conversion (isolated yield) (%)	*cis*:*trans* ratio [a]
1	**5a**[b]	DBP	14 (n.d.)	70:20
2	**5a**[b]	TPP	25 (n.d.)	75:25
3	**5a**[b]	DMP	49 (n.d.)	80:20
4	**5a**[b]	TMP	99 (57%)	80:20
5	**5a**[b]	PPh_3	0 (n.d.)	Undesired products
6	**5b**[b]	TMP	99 (71%)	>99:<1
7	**5c**[b]	TMP	99 (72%)	70:30
8	**5d**[c]	TMP	99 (71%)	85:15

[a]Determined by NMR. [b]4 mol equiv of olefin versus alkyne **6**, 20 min. [c]4 mol equiv of olefin versus alkyne **6**, 90 min.

in the presence of a cationic catalyst generated in situ from 2 mol % of [Au(L)Cl] and 2 mol % of $AgSbF_6$ and afforded cyclopropane **7a** as a mixture of *cis* and *trans* diastereoisomers (Table 4, entries 1−4).

TMP appeared here also as the best ligand of the series in terms of activity in the cyclopropanation of **5a**, with the same kind of correlation between the σ-donor ability of the ligand and the alkyne conversion rate as previously observed for the cycloisomerization. Surprisingly, [Au(DMP)Cl] did not decompose upon addition of $AgSbF_6$ in nitromethane and was able to catalyze the cyclopropanation (Table 4, entry 3). The diastereoselectivity of the cyclopropanation of **5a** did not show any significant dependence on the phosphole ligand, in spite of their different steric properties. Notably **6** was fully converted into **7a** with [Au(TMP)Cl] as catalytic precursor (Table 4, entry 4) in 20 min with a 57% isolated yield in cyclopropane, whereas $[Au(PPh_3)Cl]$ led to undesired polymeric products under the same conditions (Table 4, entry 5), indicating that TMP is more selective than its phosphine counterpart. In addition, the TMP-based complex proved to be efficient and selective in the cyclopropanation of various olefins, including styrene (**5b**; Table 4, entry 6), sterically hindered 4-*tert*-butoxystyrene (**5c**; Table 4 entry 7), and even strained bicyclic norbornylene (**5d**; Table 4 entry 8), which usually requires drastic conditions.[33]

From a practical point of view, $[Au(TMP)(NTf_2)]$ was then prepared in good yield (66%), analogously to the air-stable $[Au(PPh_3)(NTf_2)]$ complex developed by Gagosz et al.,[11] to avoid the use of a silver salt as cocatalyst. This new complex was evaluated in the cycloisomerization of enyne **1c**. $[Au(TMP)(NTf_2)]$ is slightly less active than the [Au(TMP)Cl]/$AgSbF_6$ system, as 98% conversion was achieved in 20 min with a 5 mol % catalytic load, leading to 1,3-dienes **3c** and **4c** in a 85/15 ratio. However, $[Au(TMP)(NTf_2)]$ turned out to be much less stable than $[Au(PPh_3)(NTf_2)]$ and [Au(TMP)Cl], since the solid stored under argon turned black within several hours.

Finally, a cationic TMP-Au(I) complex could be isolated and tested in enyne cycloisomerization. $[Au(TMP)(CH_3CN)]SbF_6$ was obtained by chloride abstraction from the corresponding neutral complex with $AgSbF_6$ in acetonitrile[31b] and fully characterized. The X-ray diffraction structure (Figure 2) shows the Au center in an almost linear coordination with Au−P and Au−N bond lengths that are in the same range as in $[AuPPh_3(CH_3CN)]SbF_6$.[34]

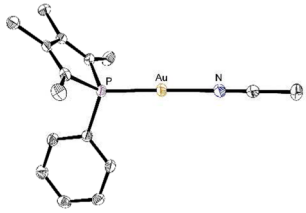


Figure 2. Ortep plot of $[Au(TMP)(CH_3CN)]SbF_6$. Thermal ellipsoids are drawn at the 30% probability level, and the hydrogen atoms and the SbF_6^- anion have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au−P = 2.220(1), Au-N = 2.042(2); P−Au−N = 178.53(6).

Moreover, this new catalyst turned out to be both very stable (several months under argon at room temperature as a white solid) and highly efficient, since the catalytic loading could be decreased to 0.5 mol % without any significant effect on the conversion of the model enyne substrate **1c** (see the Supporting Information).

A 72% conversion was even achieved in 60 min when only 0.05 mol % of catalyst was used (TON = 1440, TOF = 24 min^{-1}). Notably, the selectivity in the 1,3-dienes **3c**/**4c** was maintained at the 85/15 ratio when the catalytic loading was decreased. Echavarren and co-workers reported the formation of **3c** and **4c** in 100% yield and in a 50/50 ratio after 20 min of reaction with 2% $[AuPPh_3(CH_3CN)]SbF_6$ (TON = 50, TOF = 2.5 min^{-1}).[35] Thirty times less catalyst was thus needed to accomplish the same transformation with a better selectivity in the endodiene **3c**.

In conclusion, gold(I) complexes bearing the highly donating and not bulky tetramethylphosphole TMP are very stable compounds and efficient catalysts in 1,6-enyne cycloisomerizations and olefin cyclopropanations, with higher activity than the corresponding phosphine-based complexes. Further studies will be dedicated to structural steric modulations on the phenyl moiety of the TMP ligand to further tune the catalytic activity.[12]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files detailing the preparation of complexes and starting enyne substrates, catalysis protocol, characterization of products formed, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896. (b) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180. (c) Furstner, A. *Chem. Soc. Rev.* **2009**, *38*, 3208. (d) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239. (e) Shen, H. C. *Tetrahedron* **2008**, *64*, 7847. (f) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351. (g) Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266. (h) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5232. (i) Rudolph, M.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2012**, *41*, 2448.

(2) (a) Bruneau, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 2328. (b) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271. (c) Ma, S.; Yu, S.; Gu, Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 200. (d) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410. (e) Jimenez-Nunez, E. S.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326. (f) Michelet, V.; Toullec, P. Y.; Genêt, J.-P. *Angew. Chem., Int. Ed.* **2008**, *47*, 4268. (g) Soriano, E.; Marco-Contelles, J. *Acc. Chem. Res.* **2009**, *42*, 1026.

(3) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612.

(4) (a) de Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411. (b) Marion, N.; Nolan, S. P. *Chem. Soc. Rev.* **2008**, *37*, 1776. (c) Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178. (d) Matsumoto, Y.; Selim, K. B.; Nakanishi, H.; Yamada, K.; Yamamoto, Y.; Tomioka, K. *Tetrahedron Lett.* **2010**, *51*, 404.

(5) (a) López-Carrillo, V.; Huguet, N.; Mosquera, Á.; Echavarren, A. M. *Chem. Eur. J.* **2011**, *17*, 10972. (b) Perez-Galan, P.; Herrero-Gomez, E.; Hog, D. T.; Martin, N. J. A.; Maseras, F.; Echavarren, A. M. *Chem. Sci.* **2011**, *2*, 141.

(6) (a) Benitez, D.; Tkatchouk, E.; Gonzalez, A. Z.; Goddard, W. A., III; Toste, F. D. *Org. Lett.* **2009**, *11*, 4798. (b) Alcarazo, M.; Stork, T.; Anoop, A.; Thiel, W.; Fuerstner, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 2542.

(7) Hashmi, A. S. K.; Loos, A.; Littmann, A.; Braun, I.; Knight, J.; Doherty, S.; Rominger, F. *Adv. Synth. Catal.* **2009**, *351*, 576.

(8) (a) Bartolome, C.; Ramiro, Z.; Garcia-Cuadrado, D.; Perez-Galan, P.; Raducan, M.; Bour, C.; Echavarren, A. M.; Espinet, P. *Organometallics* **2010**, *29*, 951. (b) Bartolome, C.; Ramiro, Z.; Perez-Galan, P.; Bour, C.; Raducan, M.; Echavarren, A. M.; Espinet, P. *Inorg. Chem.* **2008**, *47*, 11391.

(9) (a) Hayashi, T.; Tanaka, M.; Ogata, I. *J. Mol. Catal.* **1979**, *6*, 1. (b) Neibecker, D.; Réau, R. *J. Mol. Catal.* **1989**, *53*, 219. (c) Neibecker, D.; Réau, R. *J. Mol. Catal.* **1989**, *57*, 153. (d) Neibecker, D.; Réau, R. *Angew. Chem., Int. Ed.* **1989**, *28*, 500. (e) Keglevich, G.; Kégl, T.; Chuluunbaatar, T.; Dajka, B.; Mátyus, P.; Balogh, B.; Kollár, L. *J. Mol. Catal. A: Chem.* **2003**, *200*, 131. (f) Odinets, I.; Körtvelyesi, T.; Kégl, T.; Kollar, L.; Keglevich, G. *Transition Met. Chem.* **2007**, *32*, 299.

(10) (a) Attar, S.; Bearden, W. H.; Alcock, N. W.; Alyea, E. C.; Nelson, J. H. *Inorg. Chem.* **1990**, *29*, 425. (b) Fave, C.; Cho, T.-Y.; Hissler, M.; Chen, C.-W.; Luh, T.-Y.; Wu, C.-C.; Réau, R. *J. Am. Chem. Soc.* **2003**, *125*, 9254. (c) Dienes, Y.; Eggenstein, M.; Neumann, T.; Englert, U.; Baumgartner, T. *Dalton Trans.* **2006**, 1424. (d) Escalle, A. l.; Mora, G.; Gagosz, F.; Mézailles, N.; Le Goff, X. F.; Jean, Y.; Le Floch, P. *Inorg. Chem.* **2009**, *48*, 8415. (e) Matano, Y.; Miyajima, T.; Imahori, H.; Kimura, Y. *J. Org. Chem.* **2007**, *72*, 6200.

(11) Mézailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133.

(12) (a) Mourgues, S.; Serra, D.; Lamy, F.; Vincendeau, S.; Daran, J.-C.; Manoury, E.; Gouygou, M. *Eur. J. Inorg. Chem.* **2003**, 2820. (b) Guadalupe Lopez Cortes, J.; Ramon, O.; Vincendeau, S.; Serra, D.; Lamy, F.; Daran, J.-C.; Manoury, E.; Gouygou, M. *Eur. J. Inorg. Chem.* **2006**, 5148. (c) Nguyen, D. H.; Bayardon, J.; Salomon-Bertrand, C.; Jugé, S.; Kalck, P.; Daran, J.-C.; Urrutigoïty, M.; Gouygou, M. *Organometallics* **2012**, *31*, 857.

(13) (a) Costes, P.; Weckesser, J.; Dechy-Cabaret, O.; Urrutigoïty, M.; Kalck, P. *Appl. Organomet. Chem.* **2008**, *22*, 211. (b) Fuente-Hernandez, A.; Costes, P.; Kalck, P.; Ruiz-García, J. A.; Jáuregui-Haza, U.; Urrutigoïty, M.; Dechy-Cabaret, O. *Cat. Comm.* **2010**, *12*, 142. (c) Fuente-Hernandez, A.; Costes, P.; Kalck, P.; Jáuregui-Haza, U.; Dechy-Cabaret, O.; Urrutigoïty, M. *Appl. Organomet. Chem.* **2011**, *25*, 815.

(14) (a) Fagan, P. J.; Nugent, W. A. *Org. Synth.* **1992**, *70*, 272. (b) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.

(15) Affandi, S.; Green, R. L.; Hsieh, B. T.; Holt, M. S.; Nelson, J. H.; Alyea, E. C. *Synth. React. Inorg. Met.-Org. Chem.* **1987**, *17*, 307.

(16) Campbell, I. G. M.; Cookson, R. C.; Hocking, M. B.; Hugues, A. N. *J. Chem. Soc.* **1965**, 2184.

(17) Breque, A.; Mathey, F.; Savignac, P. *Synthesis* **1981**, 983.

(18) Only TMP-based diphosphole ligands were reported by Doherty for copolymerization reactions: (a) Doherty, S.; Eastham, G. R.; Tooze, R. P.; Scanlan, T. H.; Williams, D.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **1999**, *18*, 3558. (b) Doherty, S.; Robins, E. G.; Knight, J. G.; Newman, C. R.; Rhodes, B.; Champkin, P. A.; Clegg, W. *J. Organomet. Chem.* **2001**, *640*, 182.

(19) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(20) Fürstner, A.; Alcarazo, M.; Krause, H.; Lehmann, C. W. *J. Am. Chem. Soc.* **2007**, *129*, 12676.

(21) Sato, T.; Hirose, Y.; Yoshioka, D.; Oi, S. *Organometallics* **2012**, *31*, 6995.

(22) Kühl, O. *Coord. Chem. Rev.* **2005**, *249*, 693.

(23) The magnitude of the $^{31}P-^{77}Se$ coupling constant provides a measure of σ-basicity of the parent P ligand through an inverse relationship between σ-basicity and the value of $^{1}J_{P-Se}$: (a) Allen, D. W.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* **1982**, 51. (b) Socol, S. M.; Verkade, J. G. *Inorg. Chem.* **1984**, *23*, 3487. (c) Barnard, T. S.; Mason, M. R. *Organometallics* **2001**, *20*, 206.

(24) Selenides were prepared quantitatively by simply reacting the corresponding phosphole ligand with elemental selenium in $CDCl_3$ at room temperature.

(25) DMP and DBP complexes have already been synthesized[10a] using $HAuCl_4{\cdot}H_2O$. The TPP complex was already synthesized[11] using $[Au(SMe_2)Cl]$. All of these complexes were only partially characterized.

(26) Baenziger, N. C.; Bennett, W. E.; Soborofe, D. M. *Acta Crystallogr., Sect. B* **1976**, *32*, 962.

(27) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. *Eur. J. Inorg. Chem.* **2009**, 1759.

(28) Clavier, H.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 841.

(29) A control experiment mixing only $[Au(DMP)Cl]$ and $AgSbF_6$ showed the formation of several phosphorus species whose ^{31}P chemical shifts do not match those of the expected catalytically active cationic species (see the Supporting Information).

(30) (a) Wang, W.; Hammond, G. B.; Xu, B. *J. Am. Chem. Soc.* **2012**, *134*, 5697. (b) Benitez, D.; Shapiro, N. D.; Tkatchouk, E.; Wang, Y.; Goddard, W. A., III; Toste, F. D. *Nat. Chem.* **2009**, *1*, 482.

(31) (a) Nieto-Oberhuber, C.; Muñoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2402. (b) Nieto-Oberhuber, C.; Munoz, M. P.; Lopez, S.; Jimenez-Nunez, E.; Nevado, C.; Herrero-Gomez, E.; Raducan, M.; Echavarren, A. M. *Chem. Eur. J.* **2006**, *12*, 1677.

(32) (a) Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002. (b) Sperger, C. A.; Tungen, J. E.; Fiksdahl, A. *Eur. J. Org. Chem.* **2011**, 3719. (c) Strand, R. B.; Helgerud, T.; Solvang, T.; Dolva, A.; Sperger, C. A.; Fiksdahl, A. *Tetrahedron: Asymmetry* **2012**, *23*, 1350.

(33) Tenaglia, A.; Marc, S. *J. Org. Chem.* **2006**, *71*, 3569.

(34) Herrero-Gómez, E.; Nieto-Oberhuber, C.; López, S.; Benet-Buchholz, J.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 5455.

(35) Cabello, N.; Jiménez-Núñez, E.; Buñuel, E.; Cárdenas, D. J.; Echavarren, A. M. *Eur. J. Org. Chem.* **2007**, 4217.