Gold Complexes with ADAP Ligands: The Effect of Bulkiness in Catalytic Carbene Transfer Reactions (ADAP = Alkoxydiaminophosphine)

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Supporting Information Placeholder

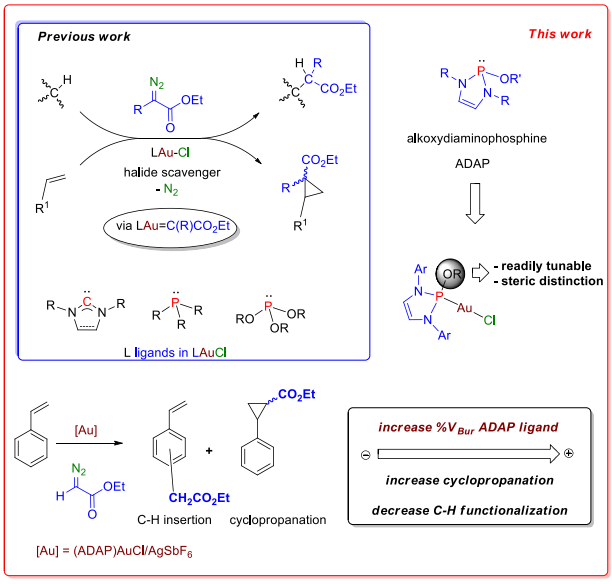
ABSTRACT A family of gold(I) complexes of composition AuCl(ADAP) (ADAP = alkoxydiaminophosphine) has been prepared through a one-pot simple protocol in which the ADAP ligand is in situ prepared before reaction with the Au(I) source. Structural data demonstrate that these ADAP ligands exert a *trans* effect superior to those of phosphine or phosphite ligands. Evaluation of the buried volume (%V_{Bur}) indicates a steric hindrance higher than several NHC-, PR_3 or $P(OR_3)$ ligands, in the context of AuCl(L) complexes. These complexes promote the catalytic transfer of a carbene group from ethyl diazoacetate to alkenes and alkanes. In the case of styrene, both the C_{sp2}-H bonds as well as the C=C bond are functionalized, the relative ratio depending of the catalyst employed, correlating well with the (%V_{Bur}). Data available allow proposing that these compounds display quite similar electronic properties but differ in steric, a variable that can be readily controlled upon modifying the alkoxy group at the ADAP ligand by simply replacing the starting alcohol employed in their synthesis.

INTRODUCTION

After centuries as a dormant metal in terms of chemical reactivity, gold has emerged as one of the most promiscuous elements in the last decades, with particular emphasis in homogeneous catalysis.[1] In its +1 oxidation state, gold complexes are dicoordinated, showing a linear geometry along the L-Au-L' axis.[2] In the context of catalytic uses, the strategy of employing an L ancillary ligand to exert electronic and/or steric control onto the Au(I) center has been extensively employed with either P-donor (phosphine, phosphite) or N-Heterocyclic carbene (NHC) ligands,[1,3] the catalytic reaction taking place at the other coordination position. In a joint collaboration with Nolan, our group discovered[4] the potential of gold as catalyst for the carbene transfer reaction from a diazocompound to saturated or unsaturated fragments.[5] Since then, we and others have employed complexes of type AuXL (L = PR_3, NHC; X = halide) as catalyst precursors for such transformations with notable success (Scheme 1).[6] However, the modification of the composition of those P- or C-donor ligands usually requires considerable synthetic effort, and thus the tuning of the steric and electronic properties at the gold center is not straightforward.

With the idea of expanding the family of Au(I) catalysts, we have moved to a new family of ligands, alkoxydiaminophosphines (ADAP), which contain a five-member cycle with two N atoms directly bonded to the P donor, resembling the skeleton of an NHC ligand. The third substituent at P consists of an alkoxy group, which is readily installed from any alcohol, and provides a certain phosphite-like behavior to the ADAP ligand. We have recently described[7] a family of copper complexes bearing these ligands and showed that their catalytic activity toward several transformations (carbene transfer, CuAAC, nitrene transfer) are similar to that of their NHC ana-

Scheme 1. Gold(I)-catalyzed carbene transfer reactions, now incorporating ADAP ligands.

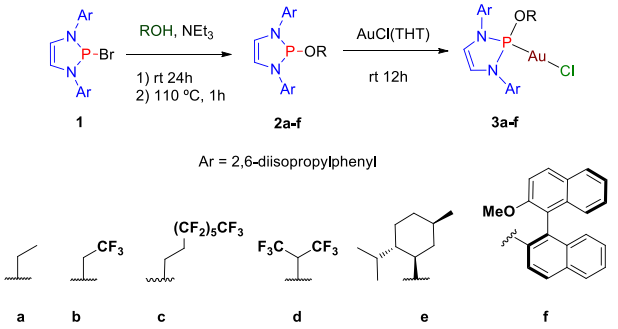


logues. Herein we describe a protocol for the direct syntheses of a new family of gold complexes of formula AuCl(ADAP), where the ligand is prepared in situ before the gold(I) source is added. Their structural characterization provides relevant data regarding a trans effect higher than other NHC or P-donor ligands as well as a noticeable steric effect. These complexes catalyze the functionalization of alkenes and alkanes. Interesting correlations between structural data and the catalytic properties have also been found (Scheme 1).

RESULTS AND DISCUSSION

Synthesis and characterization of the AuCl(ADAP) complexes. Following our recent protocol for related copper complexes,[7] we have prepared a series of six gold complexes bearing alkoxydiaminophosphine (ADAP) ligands. The bromo derivative **1** (1,3-bis[2,6-bis(1-methylethyl)phenyl]-2-bromo-2,3-dihydro-1H-1,3,2-diazaphospholene, Scheme 2) was reacted with the desired ROH in toluene with added NEt_3 generating ADAP ligands **2a-2f** before AuCl(THT) (THT = tetrahydrothiophene) was incorporated to the reaction mixture. After workup, complexes of composition AuCl(ADAP) (**3a-3f**, Scheme 2) were isolated in 75-95% yields, based on initial **1**, all but **3e** providing crystalline materials suitable for X-ray characterization. The isolation of most ADAP ligands is elusive[7] due to fast hydrolysis. This procedure generates a clean solution of **2a-2f** as inferred from $^{31}P\{^1H\}$ NMR studies, which are subsequently treated with AuCl(THT). The ligation of ADAP to gold can be monitored by that technique, showing the smooth disappearance of the resonances of ligands **2** and the appearance of those of complexes **3**.

Scheme 2. One-pot synthesis of ADAP ligands 2a-2f and their corresponding Au(I) derivatives 3a-3f.



Spectroscopic and analytical data for complexes **3a-3f** agreed with the formulation AuCl(ADAP) (see Experimental). Since the already described copper[7] analogues showed a dinuclear structure in the solid state in some cases, supported by two bridging Cl ligands, we have determined the solid-state structure[8] of the new gold complexes **3a-3d** and **3f** to ascertain the molecularity of the new complexes. Figure 1 displays such structures, which show their mononuclear nature, as well as the typical linear coordination of the two ligands around the gold center. The relevant Au-P1 and Au-Cl distances, as well as the P-Au-Cl angles are given in Table 1. Despite

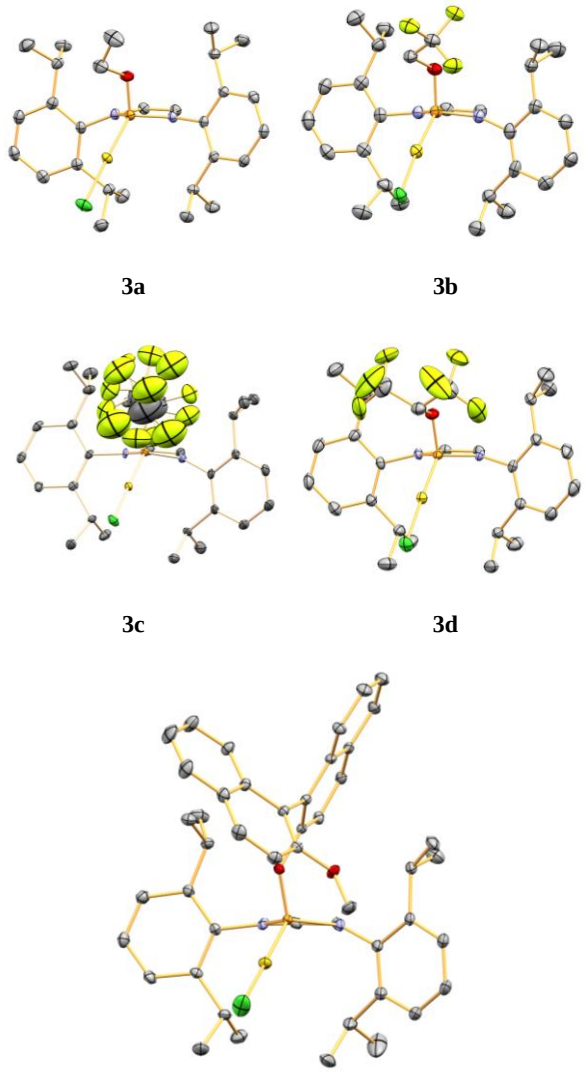


Figure 1. Molecular structures of complexes **3a-3d** and **3f**. Hydrogen atoms have been omitted for clarity.

Table 1. Main distances (Å) and angles (°) for complexes 3a-3d and 3f.

Complex	d(Au-P)	d(Au-Cl)	P-Au-Cl angle
3a	2.2114(6)	2.2853(8)	176.23(3)
3b	2.2062(8)	2.2846(8)	175.49(3)
3c	2.2083(15)	2.2700(16)	177.68(6)
3d	2.2136(13)	2.2834(13)	177.34(5)
3f	2.2070(8)	2.3007(9)	177.56(4)

the differences in the R group of the alkoxy fragment, the three magnitudes are found within a narrow range of values. Thus, both P-Au and Au-Cl distances seem unaf-

fected by that R group, despite being as distinct as ethyl or binaphthyl.

Table 2 displays the values for the Au-L and Au-Cl distances and the L-Au-Cl angles for representative AuCl(L) complexes bearing ADAP, NHC, phosphine or phosphite ligands. The main difference is provided by the IPr-containing complex,[9] with a significantly shorter L-Au distance, explained as the result of the nearly inexistent π-backbonding contribution, at variance with the ligands containing P-donors. The average distance for the P-Au distance in AuCl(ADAP) complexes is 2.209 Å, slightly shorter than the phosphine (PCy_3, PPh_3)[10] derivatives, and similar to that of the phosphite ($P(OAr)_3$) analogue.[11] The Au-Cl distance (average) for ADAP complexes is longer than any other of those complexes, a feature which supports the proposal that these ADAP ligands induce a *trans* effect higher than IPr, PCy_3, PPh_3 or ($P(OAr)_3$).

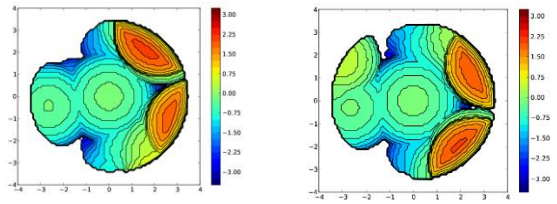
Table 2. Comparison of relevant structural data for several AuCl(L) complexes (L = ADAP, NHC, PR_3, $P(OR_3)$.

Complex	d(Au-L)	d(Au-Cl)	L-Au-Cl angle
AuCl(ADAP)[a]	2.209	2.284	176.86
AuCl(IPr)	1.942	2.269	177.0
$AuCl(PCy_3)$	2.242	2.279	177.0
$AuCl(PPh_3)$	2.235	2.279	179.63
$AuCl[(ArO)_3P]$[b]	2.198	2.260	176.52

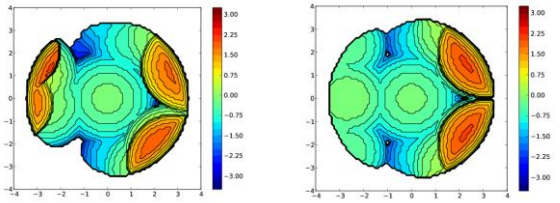
[a]Average of values in Table 1. [b]Ar = 2-isopropyl-5-methylphenyl

Estimation of the steric hindrance of ADAP ligands: calculation of $\%V_{Bur}$. The structural characterization of five AuCl(ADAP) complexes has allowed the estimation of the buried volumes ($\%V_{Bur}$) for the **2a-2d** and **2f** ADAP ligands.[12] The topographic steric maps are shown in Figure 2. The buried volume values range from 45.1 for the ethyl-containing **3a** to 50.0 for the bulkier binaphthyl derivative **3f**. The trend follows the increasing in the volume of the R group attached to the O atom in the alkoxy group, the remaining five-member ring very likely providing the same steric hindrance along the series. In the previous section structural data have served to proposing that these ADAP ligands induce a trans effect higher than other NHC or P-donor ligands. With the $\%V_{Bur}$ values, we can now evaluate their steric pressure related to other AuCl(L) complexes. Figure 2 contains the reported values for several L ligands in such those complexes.[13] Those bearing PPh_3, PCy_3, P^tBu_3, P(o-Tol)$_3$ and IPr ligand display $\%V_{Bur}$ values lower than those calculated for the ADAP ligands reported herein. Only the very bulky $PMes_3$ (Mes = 2,4,6-trimethylphenyl) shows a buried volume (50.5) higher than any of the ADAP ligands **2**, albeit very close to the binaphthyl derivative **2f** (50.0).

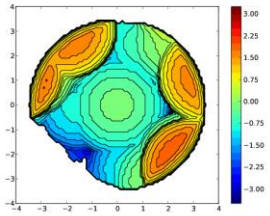
Catalytic activity of complexes 3a-3f in carbene transfer reaction to hydrocarbons. Previous work from our laboratory demonstrated the potential of some (NHC)AuCl complexes for the catalytic transfer of the $CHCO_2Et$ group from ethyl diazoacetate (N_2=$CHCO_2Et$, EDA) to arenes, olefins or alkanes, among others.[4,6,14] In order to check the capabilities of the AuCl(ADAP) complexes toward that end, we first carried out a series of



$\%V_{Bur}$ (**3a**) = 45.1 $\%V_{Bur}$ (**3b**) = 46.5



$\%V_{Bur}$ (**3c**) = 48.1 $\%V_{Bur}$ (**3d**) = 48.5



$\%V_{Bur}$ (**3f**) = 50.0

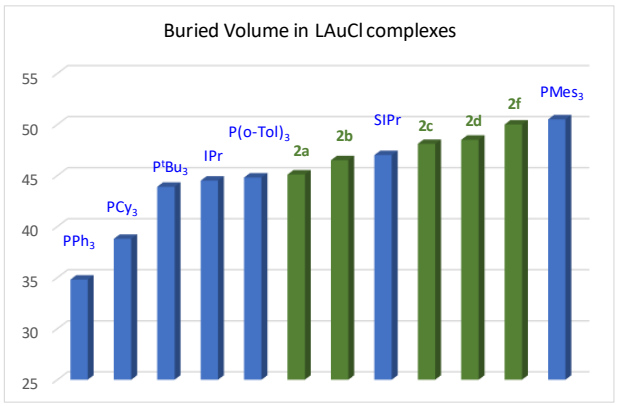
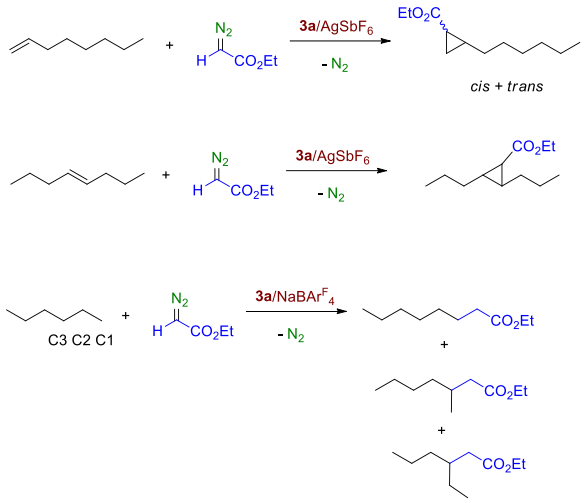


Figure 2. Top: topographic maps and buried volumes for ADAP ligands in complexes **3a-3d** and **3f**. Bottom: Comparison of $\%V_{Bur}$ for several L ligands in complexes AuCl(L).

experiments using 1-octene, 4-*trans*-octene and n-hexane, with ethyl diazoacetate as the carbene source. Scheme 3 displays the results of this screening performed with

complex **3a** and a halide scavenger, as representative catalyst. Terminal and internal octenes gave the corresponding cyclopropanes, as the result of the catalytic transfer of the $CHCO_2Et$ unit from EDA via gold-carbene intermediates.[15] For the terminal olefin, a 60:40 ratio of the *cis* and *trans* diastereomers was found (yields have not been optimized), whereas the internal olefin only gave the corresponding *trans* cyclopropane, as the result of a stereorententive transfer of the carbene unit. This is in agreement with the well-known concerted nature of such process,[5]

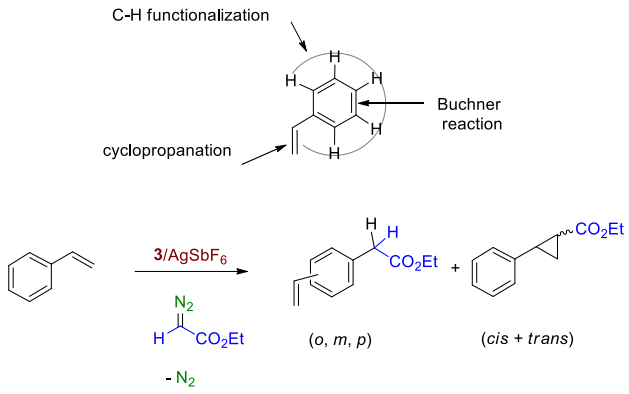
Scheme 3. Alkene and alkane functionalization by carbene insertion from ethyl diazoacetate catalyzed by 3a.



n-Hexane has also been tested as substrate, aiming at the more challenging C_{sp^3}-H bond functionalization by carbene insertion.[16] Albeit at low yield (30 % based in initial EDA), products derived from the insertion of the carbene group into the three different C-H bonds of hexane were obtained (Scheme 3). The distribution of products favored that derived from modification at C2, followed by C1 and C3. It is worth mentioning that, to our knowledge, this is the first example of the functionalization of alkane C-H bonds with gold catalysts not containing NHC ligands: P-donors have been employed in Au-mediated carbene transfer but only aromatic C-H bonds have been achieved to date.

The use of styrene implies an increase in the number of possible transformations (Scheme 4). This is a substrate which may undergo the incorporation of the carbene unit onto the olefinic C=C bond, leading to cyclopropanes. However, the aromatic ring is not exempted of participating, and may incorporate the carbene into a C=C bond (Buchner reaction) or into a C-H bond. In previous work from our laboratory we found that with (NHC)Au-based catalyst mixtures of products derived from cyclopropanation and C-H functionalization were obtained, the Buchner reaction being deactivated.[4,15] With **3a**/$AgSbF_6$ as the catalyst, we observed a similar behavior: 46% of the products derived from styrene corresponded to those derived from C-H modification (three isomers: *o*, *m*, *p*) and 54% to cyclopropanes (two isomers *cis* and *trans*), with an overall yield of 90% (EDA-based). Table 3

Scheme 4. Styrene functionalization by incorporation of a carbene group from a diazocompound. Top: potential reaction sites. Bottom: use of complexes 3 as catalysts.



shows the outcome with the other five AuCl(ADAP) complexes. Regarding the distribution of products, i. e., C-H functionalization vs olefin cyclopropanation, a variation from 46:54 with **3a** to 27:73 with **3f** is observed, parallel to the increasing of the steric pressure around the gold center as inferred from the $\%V_{Bur}$ values. There is also a slight variation in the isomer ratio within each type of products. Thus, the formation of the ortho isomer seems to decrease in favor of the para isomer when moving from **3a** to **3f**, in line with the augment in the amount of the *cis* isomer of the cyclopropane.

Table 3. Catalytic functionalization of styrene with ethyl diazoacetate using 3a-3f + $AgSbF_6$ as catalyst.[a]

Complex	C-H Func. (%)[b] (*o*:*m*:*p*)	Cyclopropanes (%)[b] (*cis*:*trans*)
3a	46 (48:27:25)	54 (50:50)
3b	41 (44:24:32)	59 (51:49)
3c	40 (46:26:28)	60 (52:48)
3d	30 (30:30:40)	70 (52:48)
3e	31 (34:29:37)	69 (57:43)
3f	27 (35:26:39)	73 (62:38)

[a]See Experimental [b] Distribution of products.

We have plotted the ratio of products for both reactions, i. e. cyclopropanation and C-H functionalization, relative to the $\%V_{Bur}$ values obtained for the gold complexes **3a**-**3d**

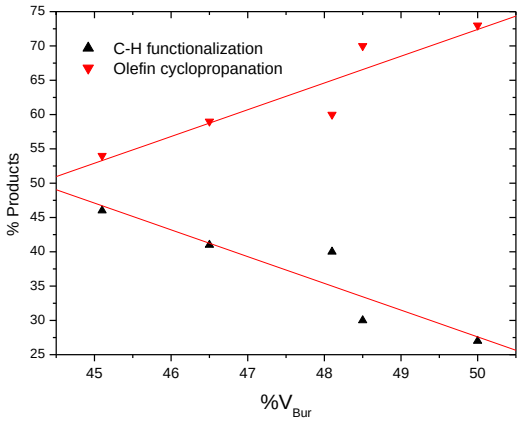
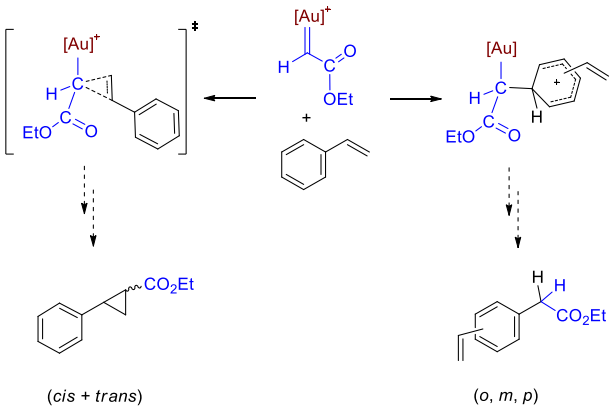


Figure 3. Correlation between the $\%V_{Bur}$ in complexes **3** and the selectivity cyclopropanation/C-H functionalization in the reaction of styrene and EDA catalyzed by **3**/$AgSbF_6$.

and **3f** (**3e** could not be crystallized with enough quality for X-ray studies). Figure 3 shows such plot, where a correlation is clearly observed. The increase in the steric pressure of the ADAP ligands onto the gold center favors the cyclopropanation products instead of the C-H functionalization ones.

To explain the above results we must relay on previous mechanistic work with AuCl(IPr) precatalysts.[15] Based on that, the reaction of complexes **3**, in the presence of halide scavengers, with ethyl diazoacetate provides an electrophilic gold-carbene intermediate which reacts with arene ring forming Wheland-like intermediates (Scheme 5) as the first step toward the C-H functionalization product. It seems reasonable assuming that the approach of the styrene substrate with the C-H bonds oriented toward the carbene carbon atom is less favored than that of the styrene olefinic bond when increasing the steric bulk of the ADAP ligand, as it is experimentally observed. This reasoning also applies to the increase of the functionalization of the *para* position and that of the *cis* isomer of cyclopropane.

Scheme 5. The two competitive pathways for the interaction of styrene with the gold-carbene intermediate.



CONCLUSIONS

A new family of gold(I) complexes AuCl(ADAP) bearing alkoxydiaminophosphine ligands (ADAP) have been synthetized and characterized, including structural studies from which steric hindrance have been determined using the $\%V_{Bur}$ magnitude. These compounds promote the catalytic transfer of carbene $CHCO_2Et$ groups from ethyl diazoacetate to olefins, alkanes and styrene. The latter substrate undergoes competitive transformations in which the carbene group is transferred to the aromatic C-H bond or to the olefinic C=C bond. The relative ratio of these two products depends of the catalyst employed, a correlation between the $\%V_{Bur}$ value and such ratio has been found. This family of complexes seems displaying similar electronic properties and significantly different steric properties, imposed by the alkoxy group, thus providing a valuable tool for the control of such variable in numerous systems already reported for Au(I) catalysts.

EXPERIMENTAL SECTION

General methods. Preparations and manipulation of metal complexes were carried out under a nitrogen atmosphere by using standard Schlenk techniques or under nitrogen atmosphere in an MBraun glovebox. Alcohols were purchased from Aldrich. The 1,3-bis(2,6-diisopropylphenyl)-2-bromo-2,3-dihydro-1H-1,3,2-diazaphosphole ligand, was prepared according to literature methods.[17] Solvents were distilled and degassed before use. NMR spectra were recorded on Agilent 400 MR or Agilent 500 DD2. ^1H and ^{13}C NMR shifts were measured relative to deuterated solvents peaks but are reported relative to tetramethylsilane. Elemental analyses were performed on a PerkinElmer Series II CHNS/O Analyzer 2400. Crystal structure determinations were carried out using a BRUKER D8 FIXED-CHI diffractometer equipped with an Oxford Cryosystem low-temperature device.

Synthesis of AuCl(ADAP) complexes. The in situ generation of the ADAP ligands[7] was carried out by treatment of toluene solutions of **1** (1 mmol) with the corresponding alcohol and NEt_3. After filtration, a clean solution (by $^{31}P\{^1H\}$ of the ADAP ligand was obtained. Complex AuCl(THT) (THT = tetrahydrothiophene) was added (1 mmol) and the mixture stirred for 12 h at room temperature. Upon filtration, the volatiles were removed at reduced pressure and the residue washed with hexane, affording complexes **3a**-**3f** as off-white or beige solids. The compounds can be crystallized from dichloromethane:hexane mixtures (6:4), after cooling at -30 °C (yields. 75-95%, combined crops).

Complex 3a: 95% yield (713 mg, 0.95 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.12 (d, 6H, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$), 1.21 (d, 6H, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$), 1.22 (t, 3H, *J* = 7.2 Hz, OCH$_2$C*H*$_3$), 1.28 (d, 6H, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$), 1.47 (d, 6H, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$), 3.33 (m, 2H, C*H*(CH$_3$)$_2$), 3.52 (m, 2H, C*H*(CH$_3$)$_2$), 4.07 (m, 2H, OC*H*$_2$CH$_3$), 6.03 (dd, 2H, J_{H-P} = 12.7 Hz, C*H*N), 7.22 (d, 4H, C*H*$_{Ar}$), 7.37 (m, 2H, C*H*$_{Ar}$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 16.2 (s, OCH$_2$*C*H$_3$), 23.3 (s, CH(*C*H$_3$)$_2$), 23.4 (s, CH(*C*H$_3$)$_2$), 26.1 (s, CH(*C*H$_3$)$_2$), 26.3 (s, CH(*C*H$_3$)$_2$), 27.8 (s, *C*H(CH$_3$)$_2$), 29.4 (s, *C*H(CH$_3$)$_2$), 64.6 (d, J_{C-P} = 6.5 Hz, POCH$_2$CH$_3$), 118.2 (*C*HN), 124.1, 124.7, 129.5, 129.6, 132.9, 133.1 (*C*$_{Ar}$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 104.30 (s). Anal. Calcd. for $C_{28}H_{41}AuClN_2OP$: C 49.09, H 6.03, N 4.09. Found C 48.99, H 6.10, 4.09 N.

Complex 3b: 86% yield (694 mg, 0.86 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.90 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.03 (d, *J* = 6.7 Hz, 6H, CH(C*H*$_3$)$_2$), 1.09 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.65 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 3.33 (q, J_{H-F} = 8.3 Hz, 2H, C*H*$_2$CF$_3$), 3.36 (hept, *J* = 6.7 Hz, 2H, C*H*(CH$_3$)$_2$), 3.48 (hept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 5.64 (d, J_{H-P} = 13.1 Hz, 2H, C*H*N), 6.89-7.16 (m, 6H, CH*Ar*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 22.5 (s, CH(*C*H$_3$)$_2$), 23.0 (s, 2C, CH(*C*H$_3$)$_2$), 26.1 (s, 2C, CH(*C*H$_3$)$_2$), 26.3 (s, 2C, CH(*C*H$_3$)$_2$), 27.9 (s, 2C, *C*H(CH$_3$)$_2$), 29.6 (s, 2C, *C*H(CH$_3$)$_2$), 63.2 (s, 1C, *C*H$_2$CF$_3$), 118.6 (d, J_{C-P} = 4.2 Hz, 2C, *C*HN), 124.2, 124.3, 124.7, 125.3, 128.1, 128.9, 129.9, 130.0, 132.5, 132.6 (*C*$_{Ar}$), 148.44 (dd, J_{C-F} = 2.7 Hz, 1C, CH$_2$*C*F$_3$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 110.0; ^{19}F NMR (400 MHz, $CDCl_3$) δ -73.4 (t, CH$_2$C*F*$_3$, J_{H-F} = 8.3 Hz). Anal. Calcd. for $C_{28}H_{38}AuClF_3N_2OP$: C 45.51, H 5.18, N 3.79. Found C 46.49, H 5.20, N 3.66.

Complex 3c: 75% yield (752 mg, 0.75 mmol); ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 1.15 (d, 6H, *J* = 6.8 Hz, (CH(C*H*$_3$)$_2$), 1.22 (d, 6H, *J* = 6.8 Hz, (CH(C*H*$_3$)$_2$), 1.31 (d, 6H, *J* = 6.9 Hz, (CH(C*H*$_3$)$_2$), 1.47 (d, 6H, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$), 2.46 (m, 2H, J = 7.1, J_{H-F} = 10.0 Hz, C*H*$_2$CF$_2$), 3.34 (sept, 2H, *J* = 6.9 Hz, C*H*(CH$_3$)$_2$), 3.50 (sept, 2H, *J* = 6.8 Hz, C*H*(CH$_3$)$_2$), 4.35 (m, 2H, *J* = 7.1 Hz, OC*H*$_2$), 6.15 (d, 2H, J_{H-P} = 12.9 Hz, C*H*N), 7.26-7.47 (m, 6H, C*H*$_{Ar}$); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) δ = 22.9 (s, 2C, CH(*C*H$_3$)$_2$), 23.0 (s, 2C, CH(*C*H$_3$)$_2$), 25.9 (s, 2C, CH(*C*H$_3$)$_2$), 26.0 (s, 2C, CH(*C*H$_3$)$_2$), 27.9 (s, 2C, *C*H(CH$_3$)$_2$), 29.4 (s, 2C, *C*H(CH$_3$)$_2$), 32.0 (dq, 1C, *C*H$_2$CF$_2$), 59.8 (m, 1C, OCH$_2$), 118.6 (d, J_{C-P} = 4.6 Hz, 2C, *C*HN), 124.2, 124.3, 129.6, 129.7, 132.7, 132.8 (C$_{Ar}$), 148.6 (dd, *C*-F); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ = 107.06 (s); ^{19}F NMR (400 MHz, CD_2Cl_2) δ = -79.2 (t, 2F, J_{H-F} = 10.0, CH$_2$C*F*$_2$), -111.8 (t, 2F, -C*F*$_2$-), -120.2 (t, 2F, -C*F*$_2$-), -121.2 (t, 2F, -C*F*$_2$-), -121.8 (t, 2F, -C*F*$_2$-), -124.4 (m, 3F, -C*F*$_3$). Anal. Calcd. for $C_{34}H_{40}AuClF_{13}N_2OP$: C 40.71, H 4.02, N 2.79; found C 40.66, H 3.90, N 2.78.

Complex 3d: 80% yield (700 mg, 0.8 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.11 (d, 6H, *J* = 6.5 Hz, CH(C*H*$_3$)$_2$), 1.19 (d, 6H, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.31 (d, 6H, *J* = 6,5 Hz, CH(C*H*$_3$)$_2$), 1.51 (d, 6H, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$), 3.31 (sept, 2H, *J* = 6.5 Hz, C*H*(CH$_3$)$_2$), 3.41 (sept, 2H, *J* = 6.9 Hz, C*H*(CH$_3$)$_2$), 5.61 (m, 1H, J_{H-F} = 8.8 Hz, C*H*(CF$_3$)$_2$, 6.20 (d, 2H, J_{H-P} = 13.2 Hz, C*H*N), 7.25-7-39 (m, 6H, C*H*$_{Ar}$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 22.6 (s, CH(*C*H$_3$)$_2$), 23.0 (s, CH(*C*H$_3$)$_2$), 26.0 (s, CH(*C*H$_3$)$_2$), 26.2 (s, CH(*C*H$_3$)$_2$), 28.4 (s, *C*H(CH$_3$)$_2$), 30.0 (s, *C*H(CH$_3$)$_2$), 67.9 (s, *C*H(CF$_3$)$_2$, 120.0 (d, $J_{P.C}$ = 5.5 Hz, *C*HN), 124.2, 130.0 (*C*$_{Ar}$), 124.7, 130.0, 132 (*C*) ,147.8 (d, J_{C-F} = 2.6 Hz, CH(*C*F$_3$)$_2$), 148.6 (d, J_{C-F} = 2.6 Hz, CH(*C*F$_3$)$_2$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 122.85; ^{19}F NMR (400 MHz, $CDCl_3$) δ = -72.5 (dd, J_{F-H} = 5.3 Hz, J_{F-P} = 1.8 Hz). Anal. Calcd. for $C_{29}H_{37}AuClF_6N_2OP$: C 43.16, H 4.62, N 3.47; found C 43.09, H 4.58, N 3.36.

Complex 3e: 88% yield (691 mg, 0.88 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.39 (d, 3H, *J* = 6.5 Hz, (CH(C*H*$_3$)$_2$)$_{ment}$), 0.46 (d, 3H, *J* = 6.5 Hz, (CH(C*H*$_3$)$_2$)$_{ment}$), 0.55 (m, 1H, (C*H*CCH$_3$)$_{ment}$) 0.72 (d, 3H, *J* = 6.7 Hz, (CH$_2$(C*H*$_3$)$_{ment}$), 0.78 (m, 2H, (C*H*$_2$CH$_2$)$_{ment}$), 0.90 (m, 1H, C*H*(CH$_3$)$_2$), 0.91 (m, 2H, (CH$_2$C*H*$_2$)$_{ment}$, 1.13 (d, 3H, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.17 (d, 3H, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.21 (d, 3H, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.23 (d, 3H, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.25 (m, 1H, CH(C*H*$_3$)$_{ment}$), 1.29 (d, 3H, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.33 (d, 3H, *J* = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.44 (d, 3H, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.51 (d, 3H, *J* = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.91 (m, 2H, OCHC*H*$_{2ment}$), 2.99 (sept, 1H, *J* = 6.7 Hz, C*H*(CH$_3$)$_2$), 3.44 (sept, 1H, *J* = 6.7 Hz, C*H*(CH$_3$)$_2$), 3.73 (sept, 1H, *J* = 6.7 Hz, C*H*(CH$_3$)$_2$), 3.97 (sept, 1H, *J* = 6.7 Hz, C*H*(CH$_3$)$_2$), 4.56 (m, 1H, (C*H*-O)$_{ment}$), 6.08 (dd, 2H, J_{H-P} =13.3 Hz, C*H*N), 7.11-7-45 (m, 6H, C*H*$_{Ar}$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 16.2 (s, (CH(*C*H$_3$)$_2$)$_{ment}$), 21.4 (s, CH(*C*H$_3$)$_2$)$_{ment}$, 21.7 (s, (CH$_2$(*C*H$_3$)$_{ment}$), 21.9 (s, CH(*C*H$_3$)$_2$), 22.4 (s, CH(CH$_3$)$_2$), 22.7 (s, CH(*C*H$_3$)$_2$), 23.7 (s, CH(*C*H$_3$)$_2$), 24.1 (s, CH(*C*H$_3$)$_2$), 24.4 (s, CH(*C*H$_3$)$_2$), 26.4 (s, CH(*C*H$_3$)$_2$), 26.6 (s, CH(*C*H$_3$)$_2$), 27.9 (s, *C*H(CH$_3$)$_2$), 28.1 (s, *C*H(CH$_3$)$_2$), 29.1 (s, *C*H(CH$_3$)$_2$), 29.8 (s, *C*H(CH$_3$)$_2$), 78.8 (d, J_{C-P} = 14.2, *C*HOP), 117.3 (s, *C*HN), 120.6 (s, *C*HN), 123.4, 124.1, 124.4, 128,5, 135.5, 135.7, 146.8, 148.1, 148.3, 148.8, 149.3 (*C*$_{Ar}$); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 122.81 (s). Attempts to obtain samples with analytical purity within the ±0.4% range failed. The following corresponds to an average of three different samples. Anal. Calcd. for $C_{36}H_{55}AuClN_2OP$: C 54.37, H 6.97, N 3.52; found C 55.00, H 7.63, 3.87 N.

Complex 3f: 90% yield (844 mg, 0.9 mmol); ^{1}H NMR (400 MHz, C_6D_6) δ = 0.3 (d, 3H, *J* = 6.4 Hz, CH(C*H*$_3$)$_2$), 0.61 (d, 3H, *J* = 6.4 Hz, CH(C*H*$_3$)$_2$), 0.87 (d, 3H, *J* = 6.4 Hz, CH$_2$(C*H*$_3$)$_2$, 0.91 (d, 3H, *J* = 6.4 Hz, CH(C*H*$_3$)$_2$), 1.05 (d, 3H, *J* = 6.4 Hz, CH(C*H*$_3$)$_2$), 1.07 (d, 3H, *J* = 7.1 Hz, CH(C*H*$_3$)$_2$), 1.56 (d, 3H, *J* = 7.1 Hz, CH(C*H*$_3$)$_2$), 1.68 (d, 3H, *J* = 7.1 Hz, CH(C*H*$_3$)$_2$), 3.12 (s, 3H, C*H*$_3$-Ph), 3.05 (sept, 1H, *J* = 6.4 Hz, C*H*(CH$_3$)$_2$), 3.19 (sept, 1H, *J* = 6.4 Hz, C*H*(CH$_3$)$_2$), 3.64 (sept, 1H, *J* = 6.4 Hz, C*H*(CH$_3$)$_2$), 3.89 (sept, 1H, *J* = 7.1 Hz, C*H*(CH$_3$)$_2$), 5.82 (dd, 2H, J_{H-P} =12.2 Hz, C*H*N), 6.70-7.59 (m, 18H, C*H*$_{Ar}$); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ = 21.4 (s, CH$_2$(*C*H$_3$), 22.2 (s, CH$_2$(*C*H$_3$), 22.8 (s, CH$_2$(*C*H$_3$), 23.1 (s, CH$_2$(*C*H$_3$), 25.6 (s, CH$_2$(*C*H$_3$), 26.2 (s, CH$_2$(*C*H$_3$), 26.3 (s, CH$_2$(*C*H$_3$), 26.7 (s, CH$_2$(*C*H$_3$), 27.8 (s, *C*H(CH$_3$)$_2$), 28.0 (s, *C*H(CH$_3$)$_2$), 29.6 (s, *C*H(CH$_3$)$_2$), 29.3 (s, *C*H(CH$_3$)$_2$), 55.2 (s, *C*H$_3$-Ph), 118.8 (d, *C*HN, J_{C-P} =3.3 Hz), 119.3 (d, *C*HN, J_{C-P} =2.1 Hz), 121.5, 123.1, 124.2, 124.5, 124.7, 124.8, 125.1, 125.3, 126.2, 126.3, 128.1, 129.1, 129.3, 130.0, 130.1, 132.7, 133.7, 133.9, 134.5, 136.0 (*C*$_{Ar}$); ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ = 104.32 (s). Attempts to obtain samples with analytical purity within the ±0.4% range failed. The following corresponds to an average of two different samples. Anal. Calcd. for

$C_{47}H_{51}AuClN_2O_2P$: C 60.10, H 5.47, N 2.98; found C 60.87, H 5.92, N 3.05.

General Catalytic Experiment. *(a) Octenes*. The precatalyst **3a** (0.0125 mmol) and $AgSbF_6$ (0.0125 mmol) were dissolved in 3 mL of dichloromethane and stirred for 15 min. The olefin (2.5 mmol) was added before a solution of EDA (0.25 mmol) in 6 mL of dichloromethane was added for 12 h with the aid of a syringe pump. After that time, volatiles were removed and the products isolated by column chromatography.
(b) n-Hexane. An equimolar mixture of complex **3a** and $AgSbF_6$ (0.025 mmol) was dissolved in 10 mL of n-hexane and 4 mL of dichloromethane. After 15 min of stirring, EDA (0.5 mmol) dissolved in n-hexane (10 mL) was added for 12 h via syringe pump. Yields were determined using calibration curves following already reported protocols from our lab.[18]
(c) Styrene. The catalyst precursor **3a**-**3f** and $AgSbF_6$ (0.0125 mmol each) were dissolved in a mixture of 1 mL of styrene and 2 mL of dichloromethane. Ethyl diazoacetate (0.25 mmol) was added pure, in one portion, and the reaction mixture was stirred for 3 h. After completion and removal of volatiles, the composition of the reaction mixtures was determined by ^{1}H NMR ($CDCl_3$) and GC.

Supporting Information. NMR data for new compounds, $\%V_{Bur}$ determination and quantification of catalytic experiments.

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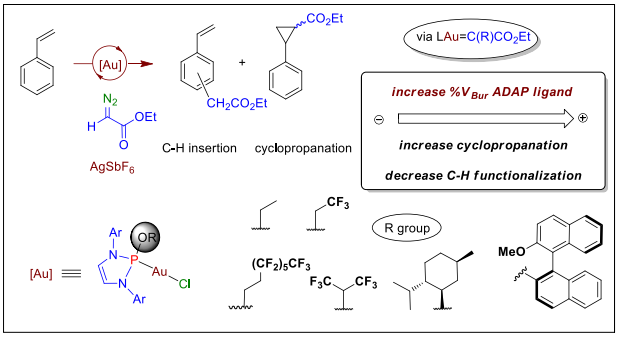
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cyclopropanation
via LAu=C(R)CO2Et
increase %VBur ADAP ligand
increase cyclopropanation
decrease C-H functionalization
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