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Gold(I) Complexes of KITPHOS Monophosphines: Efficient Cycloisomerisation Catalysts

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Dedicated to Prof. H.-U. Reissig to the occasion of his 60th birthday.

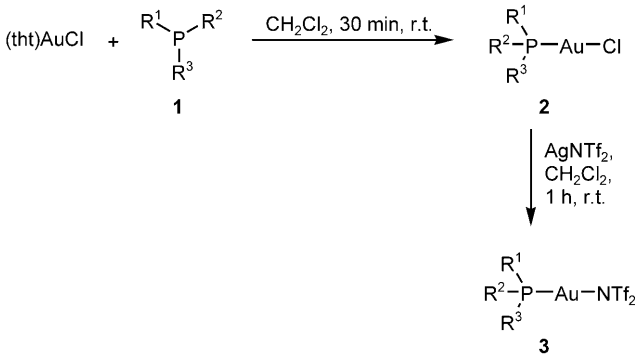
Abstract: Gold(I)-triflimide ($AuNTf_2$)complexes of H-KITPHOS and *o*-MeO-KITPHOS have been prepared and shown to be efficient catalysts for a range of intramolecular cyclisations to afford phenols, acylindenes, alkylidene oxazoles, tetrahydropyrans and lactones, in the majority of cases these catalysts are superior to those previously reported.

Keywords: alkynes; cyclization; gold; heterocycles; homogeneous catalysis; KITPHOS

Fine-tuning of reactivity and selectivity has been an important goal in homogeneous gold catalysis in recent years.[1,2] For instance, in the case of gold(III) a significant improvement in catalyst performance has been achieved by changing from gold(III) halides to catalysts based on anionic N,O ligands.[3] In contrast phosphines[4] and N-heterocyclic carbenes are proving to be the ligands of choice for gold(I)-based catalysts.[5] Chloride-bridged dinuclear gold(I) complexes have recently been shown to be efficient catalysts for the cyclisation of ω-alkynylfurans while their mononuclear counterparts failed to provide acceptable results and that the dimer based on the bulky trimesitylphosphine, $PMes_3$, was markedly more active than its triphenylphosphine counterpart.[6]

Gold(I) phosphine-based catalysts are most commonly prepared by substitution of the weakly coordinated tht (tht = tetrahydrothiophene) or Me_2S in (tht)AuCl or (Me_2S)AuCl, respectively, with an appropriate phosphine to afford **2**, which is typically converted into the active catalyst *in situ* by removal of the chloride with a silver salt of a non-coordinating counterion. However, rather than generating the catalyst *in situ* we have found it more reproducible, convenient and time efficient to prepare complexes of the type $[LAu(NTf_2)]$ (**3**) which do not need to be activated for catalysis and are stable with respect to long-term storage. These complexes were prepared by modification of a procedure first developed by Gagosz et al.[7] which involves abstraction of the chloride from **2** by silver triflimide to afford **3** which can be isolated and characterised using conventional spectroscopic and analytical techniques (Scheme 1).

Recently, Doherty et al. have reported the synthesis of a new class of electron-rich biaryl-like monophosphine KITPHOS (Figure 1), which forms highly efficient catalysts for Buchwald–Hartwig aminations and Suzuki–Miyaura cross couplings.[8] The similarity be-



Scheme 1. Synthesis of gold-catalysts **3**.

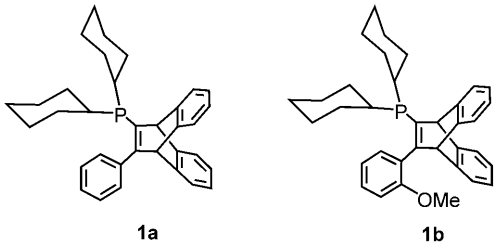
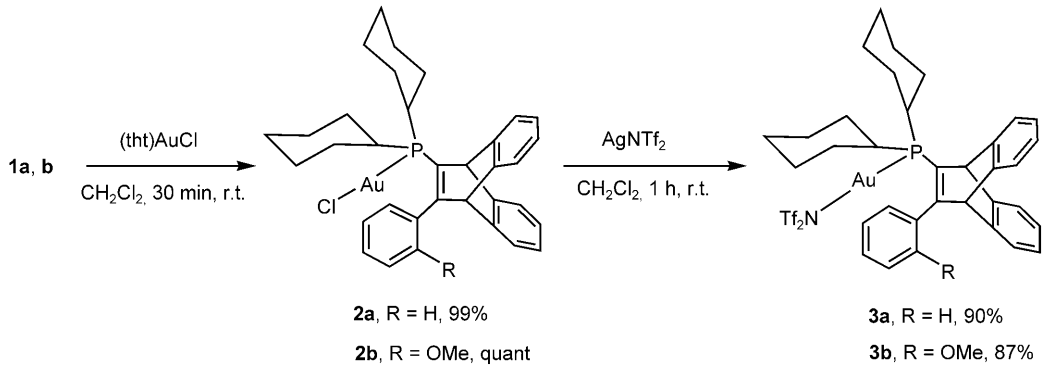


Figure 1. H-KITPHOS (**1a**) and *o*-MeO-KITPHOS (**1b**).



Scheme 2. Synthesis of gold-complexes **3a** and **3b**.

tween KITPHOS and Buchwald's biaryl monophosphines, combined with the fact that the latter have proven to be very successful ligands for a vast array of gold-catalysed transformations[9] prompted us to synthesise gold complexes of these KITPHOS monophosphines and investigate their applications in a selection of gold-catalysed cycloisomerisations.

Gold(I) complexes **3a** and **3b** were prepared in excellent yield in an operationally straight-forward two-step procedure according to Scheme 2. In the first step (tht)AuCl was reacted with the appropriate KITPHOS monophosphine in dichloromethane to afford **2a** and **2b**, both of which have been characterised by spectroscopic and analytical methods. In the second step, **3a** and **3b** were generated in 90 and 87% yield, respectively, by stirring a dichloromethane solution of the corresponding chloride complex with 1 equivalent of $AgNTf_2$ at room temperature for 1 h.

As these are the first examples of gold(I) complexes of KITPHOS monophosphines the identities of **3a** and **3b** have been unequivocally established by single-crystal X-ray crystallography; the structures of both are shown in Figure 2.[10]

Figure 2 reveals that the gold atoms in **3a** and **3b** both adopt a near linear geometry, coordinated by the phosphorus atom of **1a** and **1b**, respectively, and the nitrogen atom of the triflimide. Typical bond lengths for **3a** are Au1–N1 = 2.114(4) Å and Au1–P1 =

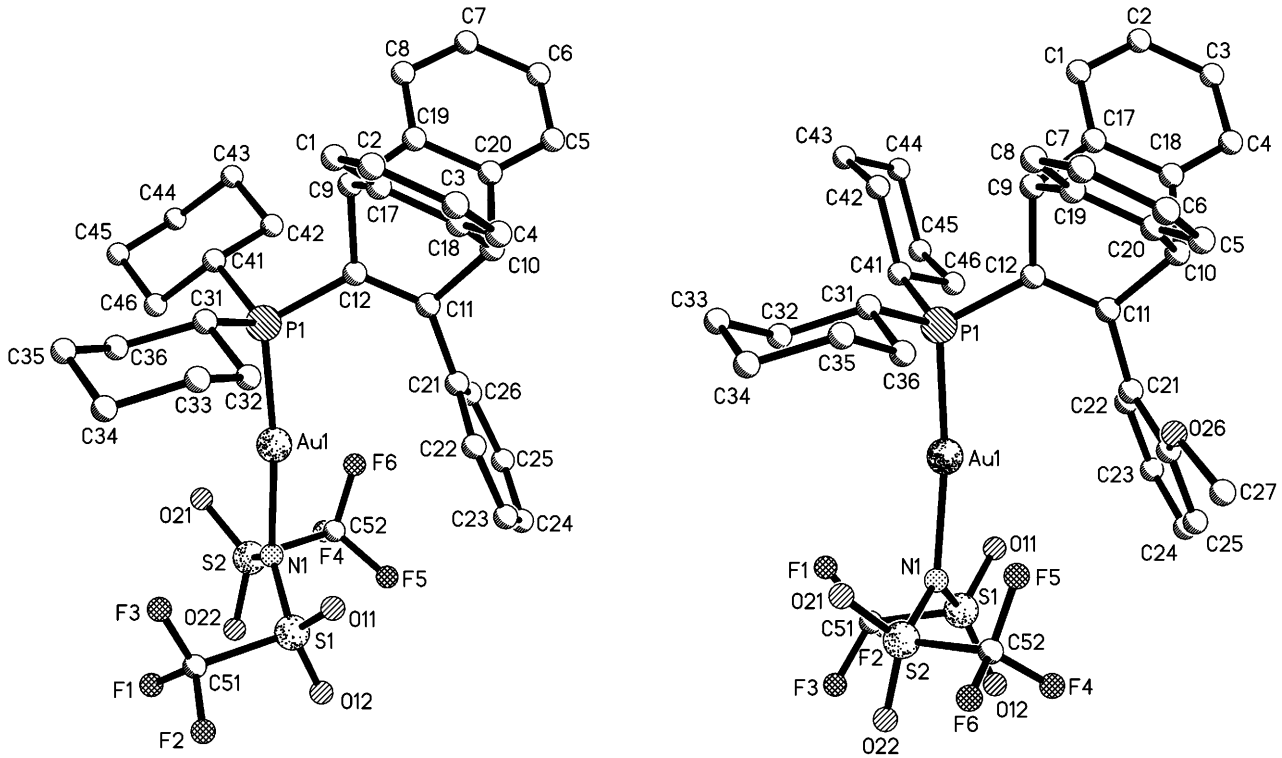


Figure 2. X-ray crystal structures of **3a** (*left*) and **3b** (*right*).

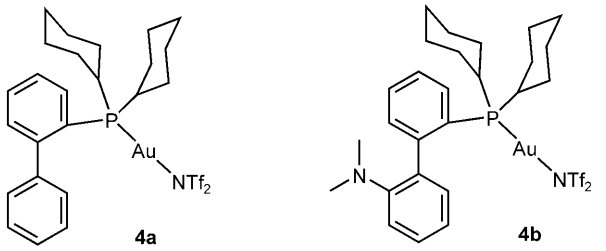


Figure 3. Buchwald ligands in **4a** and **4b** for comparison with **3a** and **3b**.

2.2255(11) and for **3b** are Au1–N1 = 2.110(3) Å and Au1–P1 = 2.2244(10) Å. In both complexes the P–Au–N angle is close to 180° [174.0(1)° for **3**a and 172.2(1)° for **3b**]. The aryl group occupies a position close to the gold centre while the NTf_2 unit is bent away from the aryl group, which is reflected by the deviation from a perfectly linear P–Au–N angle, in much the same manner as described for gold(I) complexes of electron-rich biaryl monophosphines.[11]

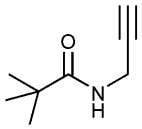
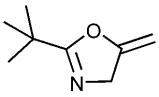
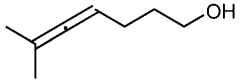
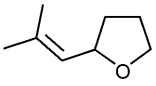
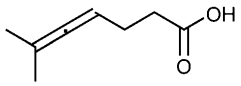
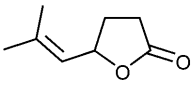
In addition, we prepared the related gold(I) complexes of two Buchwald ligands, **4a** and **4b** (Figure 3). Both were prepared by the route described for **3a** and **3b** above.

An essential aspect of this investigation was to evaluate the efficiency of the newly developed catalysts and for this we selected four different gold(I)-catalysed cycloisomerizations that have been developed in Heidelberg as screening reactions for new catalysts; the results of which are listed in Table 1. Complexes **3a** and **3b** were each tested in the cyclisation of ω-alkynylfurans[12] (entries 1–8), the cyclisation of 2-alkynylaryl epoxides[13] (entries 9–16) and *N*-propargylcarboxamides[14] (entries 17–24) as well as the intramolecular hydroalkoxylation (entries 25–30) and hydroxycarboxylation (entries 31–36) of allenes.[15] Gratifyingly, **3a** and **3b** both proved to be highly efficient cata-

Table 1. Gold(I)-catalysed cyclisations with **3a** and **3b**.

Entry	Reactant	Product[a]	Catalyst	Catalyst [mol%]	Solvent	Yield [%][b]	TON
1	5	**6**	**3a**	0.05	$CDCl_3$	90	1800
2	**5**	**6**	**3b**	0.05	$CDCl_3$	95	1900
3	**5**	**6**	**4a**	0.05	$CDCl_3$	28	560
4	**5**	**6**	**4b**	0.05	$CDCl_3$	0	0
5	**7**	**8**	**3a**	0.25	$CDCl_3$	60	240
6	**7**	**8**	**3b**	0.25	$CDCl_3$	70	280
7	**7**	**8**	**4a**	0.25	$CDCl_3$	71	284
8	**7**	**8**	**4b**	0.25	$CDCl_3$	10	40
9	**9**	**10**	**3a**	2	C_6D_6	58	29
10	**9**	**10**	**3b**	2	C_6D_6	69	35
11	**9**	**10**	**4a**	2	C_6D_6	86	43
12	**9**	**10**	**4b**	2	C_6D_6	80	40
13	**11**	**12**	**3a**	2	C_6D_6	34	17
14	**11**	**12**	**3b**	2	C_6D_6	50	25
15	**11**	**12**	**4a**	2	C_6D_6	25	13
16	**11**	**12**	**4b**	2	C_6D_6	21	11

Table 1. (Continued)

Entry	Reactant	Product[a]	Catalyst	Catalyst [mol%]	Solvent	Yield [%][b]	TON
17	**13** 	**14** 	**3a**	2	CD_2Cl_2	98	49
18	**13**	**14**	**3a**	0.5	CD_2Cl_2	97	194
19	**13**	**14**	**3a**	0.1	CD_2Cl_2	99	990
20	**13**	**14**	**3b**	2	CD_2Cl_2	92	46
21	**13**	**14**	**3b**	0.5	CD_2Cl_2	97	194
22	**13**	**14**	**3b**	0.1	CD_2Cl_2	94	940
23	**13**	**14**	**4a**	0.1	CD_2Cl_2	96	960
24	**13**	**14**	**4b**	0.1	CD_2Cl_2	81	810
25	**15** 	**16** 	**3a**	0.5	C_6D_6	98	196
26	**15**	**16**	**3a**	0.05	C_6D_6	99	1980
27	**15**	**16**	**3b**	0.5	C_6D_6	95	190
28	**15**	**16**	**3b**	0.05	C_6D_6	99	1980
29	**15**	**16**	**4a**	0.05	C_6D_6	97	1940
30	**15**	**16**	**4b**	0.05	C_6D_6	93	1860
31	**17** 	**18** 	**3a**	0.5	C_6D_6	97	194
32	**17**	**18**	**3a**	0.05	C_6D_6	75[c]	1500
33	**17**	**18**	**3b**	0.5	C_6D_6	98	196
34	**17**	**18**	**3b**	0.05	C_6D_6	65[c]	1300
35	**17**	**18**	**4a**	0.05	C_6D_6	78[c]	1560
36	**17**	**18**	**4b**	0.05	C_6D_6	89[c]	1780

[a] *Reaction conditions:* all catalysed reactions were performed in NMR tubes. Before adding the catalyst, an NMR spectrum was measured.
[b] The yield was determined by integration and comparison with an internal standard.
[c] Slow reaction, yield after 40 h.

lysts for the cycloisomerisation of **5** to give the phenol **6** in conversions of 90 and 95%, respectively, with 0.05 mol% catalyst, which corresponds to turnover numbers of 1800 and 1900, respectively (entries 1 and 2). The complexes **4a** and **4b** proved to be inferior, under the same conditions with **4a** only 28% of **6** were obtained, **4b** was inactive for this substrate (entries 3 and 4). Both **3a** and **3b** also catalysed the more challenging cyclisation of ω-alkynylfuran **7**, but required a catalyst loading of 0.25 mol%, corresponding to TONs of 240 and 280 for **3a** and **3b**, respectively. For comparison, $AuCl_3$ catalysed the same cyclisations but required 5 mol% loading to achieve 64 and 71% conversion to **6** and **8**, respectively, which corresponds to turnover numbers of 13 and 28,[12] and highlights the efficiency of the gold(I)/KITPHOS systems (entries 5 and 6). Moreover, with **4a** only slightly better results were obtained (71%, entry 7), while **4b** had a much lower activity (10%, entry 8). The cyclisation of 2-alkynylaryl epoxides **9** and **11** was also catalysed by **3a** and **3b** (2 mol%) both of which gave good conversion to the corresponding 3-acylindene with significantly higher TONs than previously reported.[13] For example, the TONs of 16 and 7 obtained with 5 mol% $[(Ad)_2(n\text{-Bu})PAu[NTf_2)]$ for the cyclisation of **9** and **11**, respectively, are significantly lower than those obtained with **3a** and **3b** (entries 9, 10, 13 and 14). Again, the comparison with **4a** and **4b** is most interesting, for **9** superior results were observed (entries 11 and 12), but for **11** these catalysts were less active than the KITPHOS gold(I) complexes (entries 15 and 16).

While gold(III) complexes have been used to catalyse the cycloisomerisation of propargylic amides, the encouraging performance of **3a** and **3b** for the cyclisations described above prompted us to investigate their use in the electrophilic activation/cyclisation of *N*-propargylcarboxamide **13** to afford oxazole **14**. In this reaction, the catalyst based on **3a** outperformed that generated from **3b**, the former giving TONs of up to 990 compared with 940 for the latter (entries 17–22), both of which are a marked improve-

ment on that of 19 obtained with $AuCl_3$.[14] Compared with catalysts **4a** and **4b** (TONs of 960 and 810, entries 23 and 24), the results of **3a** and **3b** are only slightly superior.

Finally, the intramolecular hydroalkoxylation of allenol **15** and the hydroxycarboxylation of allene-carboxylate **17** have recently been catalysed by 2.5 mol% of [dppm$(AuCl)_2$] activated with 5 mol% of silver salt to afford tetrahydropyran **16** and lactone **18** in 89 and 91% yield, respectively.[15] In contrast, **3a** and **3b** both catalyse these cyclisations in each case for **15** and one case for **17** giving conversions in excess of 90% (entries 25–28 and 31–34) with a catalyst loading of just one hundredth of that required for the dppm-based system, which further highlights the efficacy of Au/KITPHOS as a cyclisation catalyst (TONs up to 1980). In conversions of **15** the complexes **4a** and **4b** (entries 29 and 30) delivered results comparable to **3a** and **3b**, for **17** with **4a** and **4b** (entries 35 and 36) even slightly better results were obtained.

In conclusion, gold(I) complexes of KITPHOS are highly efficient catalysts for a range of cyclisations and in this regard could find widespread applications in organic synthesis, particularly since they can be prepared in an operationally straightforward procedure from commercially available ligands.[16] When compared to the corresponding gold(I) complexes of related Buchwald ligands, the results strongly depend on the test reaction.

Experimental Section

General

The first multiplicity reported for ^{13}C NMR refers to coupling with protons. If there were couplings with other heteroatoms (^{31}P, ^{19}F), the multiplicity is listed separately after the muliplicity based on protons.

Dicyclohexyl(12-phenyl-9,10-dihydro-9,10-ethenoanthracen-11-yl)phosphanegold Chloride (2a)

(tht)AuCl (64.1 mg, 200 μmol) was dissolved in dichloromethane (DCM) (1 mL) and a solution of **1a** (95.3 mg, 200 μmol) in DCM (1 mL) was added. The reaction mixture was stirred for 15 min and the solvent was removed under reduced pressure to afford **2a** as a colourless powder; yield: 141 mg (199 μmol, 99%); mp >310 °C (could not be measured); IR (KBr): $\nu = 2927$, 2851, 1619, 1488, 1475, 1190, 1157, 767, 751, 698 cm^{-1}; MS (FAB$^+$): $m/z = 731.2$ [M+Na$^+$], 673.2 [M$^+$−Cl]; HR-MS (FAB$^+$): $m/z = 673.2288$, calcd. for $C_{34}H_{37}PAu$: 673.2298.

It was not possible to measure NMR spectra because of the low solubility in all solvents.

Dicyclohexyl(12-phenyl-9,10-dihydro-9,10-ethenoanthracen-11-yl)phosphanegold Bis(trifluoromethane)sulfonimide (3a)

Compound **2a** (81.6 mg, 115 μmol) and $AgNTf_2$ (44.8 mg, 115 μmol) were suspended in DCM (5 mL) and stirred for 1.5 h. The reaction mixture was filtered through silica gel and the solvent was removed under reduced pressure at room temperature to afford of the complex as a colourless solid; yield: 99.1 mg (104 μmol, 90%); mp 208–210 °C (decomposition); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.02$–1.40 (m, 12H), 1.61–1.70 (m, 4H), 1.76–1.98 (m, 4H), 2.15–2.27 (m, 2H), 5.25 (d, $^4J = 3.4$ Hz, 1H), 5.41 (d, $^4J = 5.7$ Hz, 1H) 6.97 (bs, 2H), 7.03–7.09 (m, 4H), 7.31–7.39 (m, 4H), 7.40–7.45 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 25.7$ (t, 2 C), 26.5 (t, d: $J_{C,P} = 12.9$ Hz, 2 C), 26.5 (t, d: $J_{C,P} = 14.3$ Hz, 2 C), 30.2 (t, 2 C), 30.8 (t, d: $J_{C,P} = 1.8$ Hz, 2 C), 35.4 (d, d: $^1J_{C,P} = 36.2$ Hz, 2 C), 53.6 (d), 61.5 (d), 119.4 (s, q: $^1J_{C,F} = 323.8$ Hz, 2 C), 123.1 (d, 2 C), 123.8 (d, 2 C), 125.5 (d, 2 C), 125.9 (d, 2 C), 126.9 (d, 2 C), 129.0 (d, 2 C), 129.6 (d, 2 C), 140.0 (s), 141.0 (s), 143.6 (s, 2 C), 144.0 (s, 2 C), 170.2 (s); ^{31}P NMR (202 MHz, $CDCl_3$); $\delta = 36.04$; IR (KBr): $\nu = 2929$, 2852, 1621, 1463, 1449, 1351, 1333, 1199, 1137, 1060, 767, 743, 698 cm^{-1}; MS (FAB$^+$): $m/z = 673.3$ [M−NTf$_2$]$^+$; HR-MS (FAB$^+$): $m/z = 673.2263$, calcd. for $C_{34}H_{37}PAu$: 673.2298.

Dicyclohexyl[12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracen-11-yl]phosphanegold Chloride (2b)

(tht)AuCl (64.1 mg, 200 μmol) was dissolved in DCM (1 mL) and a solution of **1b** (101 mg, 200 μmol) in DCM (1 mL) was added. The reaction mixture was stirred for 15 min and the solvent was removed under reduced pressure to afford **2b** as a colourless powder; yield: 151 mg (200 μmol, quantitative). mp 300–303 °C (decomposition); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.02$–1.40 (m, 11H), 1.49–1.99 (m, 9H), 2.11–2.22 (m, 2H), 3.62 (s, 3H), 5.17 (d, $^4J = 3.3$ Hz, 1H), 5.36 (d, $^4J = 5.4$ Hz, 1H), 6.68 (dd, $J = 7.6$ Hz, $J = 1.7$ Hz, 1H), 6.92–6.97 (m, 2H), 6.98–7.08 (m, 4H), 7.23–7.26 (m, 1H), 7.30–7.35 (m, 3H), 7.46 (td, $J = 7.9$ Hz, $J = 1.7$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 25.7$ (t), 26.5 (t, d: $J_{C,P} = 13.3$ Hz), 26.7 (t, d: $J_{C,P} = 14.4$ Hz, 2 C), 26.8 (t, d: $J_{C,P} = 12.3$ Hz), 29.8 (t), 29.8 (t, d: $J_{C,P} = 3.7$ Hz), 29.9 (t), 31.2 (t, d: $J_{C,P} = 4.1$ Hz), 35.2 (d, d: $^1J_{C,P} = 36.2$ Hz), 35.4 (d, d: $^1J_{C,P} = 35.5$ Hz), 54.7 (d, d: $J_{C,P} = 3.0$ Hz), 55.0 (q), 60.4 (d, d: $J_{C,P} = 7.8$ Hz), 111.5 (d), 121.1 (d), 122.7 (d), 122.8 (d), 123.8 (d), 123.9 (d),124.8 (d), 125.2 (d), 125.2 (d), 125.5 (d), 127.8 (s, d: $J_{C,P} = 6.7$ Hz), 129.3 (d), 130.5 (d), 132.5 (s, d: $J_{C,P} = 49.8$ Hz), 143.6 (s), 144.2 (s), 144.9 (s, d: $J_{C,P} = 1.3$ Hz), 145.0 (s, d: $J_{C,P} = 2.2$ Hz), 156.7 (s), 168.3 (s, d: $J_{C,P} = 11.4$ Hz); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 37.19$; IR (KBr): $\nu = 2928$, 2851, 1618, 1585, 1486, 1460, 1267, 1243, 1116, 1023, 764, 749 cm^{-1}; MS (FAB$^+$): m/z: 761.2 [M+Na]$^+$, 738.2 [M$^+$], 703.2 [M$^+$−Cl]; HR-MS (FAB$^+$): $m/z = 738.2108$, calcd. for $C_{35}H_{39}O^{35}ClPAu$: 738.2093, $m/z = 703.2416$, calcd. for $C_{35}H_{39}OPAu$: 703.2416.

Dicyclohexyl[12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracen-11-yl]phosphanegold Bis(trifluoromethane)sulfonimide (3b)

Compound **2b** (75.7 mg, 102 μmol) and $AgNTf_2$ (39.7 mg, 102 μmol) were suspended in DCM (3 mL) and stirred for 1.5 h. The reaction mixture was filtered through silica gel and the solvent was removed under reduced pressure at room temperature to affordthe complex as a colourless solid; yield: 87.8 mg (89.2 μmol, 87%); mp 219–221 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.92$–2.25 (m, 22 H), 3.64 (s, 3 H), 5.19 (d, $^4J = 3.5$ Hz, 1 H), 5.36 (d, $^4J = 5.9$ Hz, 1 H), 6.69 (dd, $J = 7.6$ Hz, $J = 1.5$ Hz, 1 H), 6.93–7.11 (m, 6 H), 7.21–7.27 (m, 1 H), 7.29–7.44 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 25.7$ (t), 25.8 (t), 26.4 (t, d: $J_{C,P} = 13.0$ Hz), 26.6 (t, d: $J_{C,P} = 14.1$ Hz), 29.7 (t, d: $J_{C,P} = 12.8$ Hz, 2 C), 29.9 (t), 30.2 (t, d: $J_{C,P} = 2.7$ Hz), 30.3 (t), 31.4 (t, d: $J_{C,P} = 4.0$ Hz), 35.3 (d, d: $^1J_{C,P} = 36.9$ Hz), 35.5 (d, d: $^1J_{C,P} = 36.8$ Hz), 54.8 (d, d: $J_{C,P} = 4.8$ Hz), 54.9 (q), 60.6 (d, d: $J_{C,P} = 8.1$ Hz), 111.9 (d), 119.4 (s, q: $^1J_{C,F} = 323.5$ Hz, 2 C), 121.2 (d), 122.7(d), 122.8(d), 123.9 (d), 124.0 (d), 124.9 (d), 125.3 (d), 125.4 (d), 125.6 (d), 126.9 (s, d: $J_{C,P} = 6.7$ Hz), 129.1 (d), 129.8 (s), 130.6 (d), 143.3 (s, d: $J_{C,P} = 1.7$ Hz), 143.9 (s, d: $J_{C,P} = 2.0$ Hz), 144.7 (s, d: $J_{C,P} = 2.4$ Hz), 144.8 (s, d: $J_{C,P} = 1.8$ Hz), 156.7 (s), 169.4 (s, d: $J_{C,P} = 10.1$ Hz); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 36.25$; IR (KBr): $\nu = 2929$, 2852, 1620, 1486, 1460, 1450, 1333, 1268, 1241, 1198, 1141, 1059, 764, 749 cm^{-1}; MS (FAB$^+$): $m/z = 703.3$ $[M-NTf_2]^+$; HR-MS (FAB$^+$): $m/z = 703.2346$, calcd. for $C_{35}H_{39}OPAu$: 703.2416.

2-(Dicyclohexylphosphino)biphenylgold Bis(trifluoromethane)sulfonimide (4a)

(tht)AuCl (96.7 mg, 301 μmol) was dissolved in DCM (2 mL) and 2-(dicyclohexylphosphino)biphenyl (106 mg, 301 μmol) was added. The solution was stirred for 30 min and then the solvent was removed under reduced pressure without heating to obtain a white solid. Next the solid was dissolved in DCM (2 mL) and $AgNTf_2$ (117 mg, 301 μmol) was added. After stirring for 30 min the solvent was removed under reduced pressure without heating to afford the product as a white foam; yield: 229 mg (277 μmol, 92%); mp: 83–85 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.10$–1.45 (m, 10 H), 1.54–2.15 (m, 12 H), 7.19 (d, $J = 6.9$ Hz, 2 H), 7.31 (m, 1 H), 7.43–7.59 (m, 5 H), 7.73 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 25.7$ (t, 2 C), 26.5 (t, d: $J_{C,P} = 14.5$, 2 C), 26.6 (t, d: $J_{C,P} = 13.1$, 2 C), 30.0 (t, 2 C), 31.5 (t, d: $J_{C,P} = 3.2$, 2 C), 36.7 (t, d: $J_{C,P} = 34.2$, 2 C), 128.0 (d, d: $J_{C,P} = 10.2$ Hz), 128.6 (d), 129.1 (d, 2 C), 129.3 (d, 2 C), 131.5 (d), 132.8 (d, d: $J_{C,P} = 7.7$ Hz, 2 C); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 45.94$; IR (KBr): $\nu = 2929$, 2852, 1629, 1345, 1196, 1144, 1061, 756, 701, 656, 603, 574, 513 cm^{-1}; MS (FAB$^+$): $m/z = 547.2$ $[M-NTf_2]^+$; HR-MS (FAB$^+$): $m/z = 547.1852$, calcd. for $C_{24}H_{31}AuNP$: 547.1829.

2-(Dicyclohexylphosphino)-2′-(*N*,*N*-dimethylamino)-biphenylgold Bis(trifluoromethane)sulfonimide (4b)

(tht)AuCl (96.2 mg, 300 μmol) was dissolved in DCM (2 mL) and 2-(dicyclohexylphosphino)-2′-(*N*,*N*-dimethylamino)biphenyl (118 mg, 300 μmol) was added. The solution was stirred for 30 min and then the solvent was removed under reduced pressure without heating to obtain a white solid. Next the solid was dissolved in DCM (2 mL) and $AgNTf_2$ (116 mg, 300 μmol) was added. After stirring for 30 min the solvent was removed under reduced pressure without heating to afford the product as a white foam; yield: 241.85 mg (278 μmol, 93%); mp 48–50 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.00$–2.18 (m, 22 H), 2.47 (s, 6 H), 6.96–7.18 (m, 3 H), 7.36–7.48 (m, 2 H), 7.52–7.68 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 25.8$ (t), 25.9 (t), 26.5 (t), 26.6 (t), 26.7 (t, d: $J_{C,P} = 13.3$ Hz), 27.1 (t, d: $J_{C,P} = 13.0$ Hz), 29.9 (t), 30.6 (t), 31.2 (t), 31.7 (t), 36.3 (d, d: $J_{C,P} = 31.1$ Hz), 37.3 (d, d: $J_{C,P} = 31.7$ Hz), 43.8 (q, 2 C), 119.1 (d), 122.2 (d), 124.5 (s), 128.1 (d), 129.8 (d), 132.1 (d), 132.6 (d), 132.8 (d), 133.6 (d), 134.6 (s), 147.8 (s),152.1 (s); ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 43.98$; IR (KBr): $\nu = 2931$, 2853, 1351, 1194, 1143, 1059, 745, 653, 616, 600, 572, 513; HR-MS (FAB$^+$): $m/z = 590.2247$ $[M-NTf_2]^+$, calcd. for $C_{26}H_{36}AuNP$: 590.2245.

General Procedure for Gold-Catalysed Reactions

The reagent and the internal standard were dissolved in deuterated solvent and an NMR spectrum was measured. The catalyst was added and the tube was shaken vigorouely. The yield was determined by integrating the NMR signals against the internal standard.

a) 5 (45.3 mg, 193 μmol), 1,3,5-tri-*tert*-butylbenzene (1.94 mg, internal standard), $CDCl_3$ (450 μL), **3a** (19.1 mg of a 0.5 wt% solution in $CDCl_3$, 100 nmol). 90% yield determined with internal standard.

b) 5 (46.4 mg, 198 μmol), 1,3,5-tri-*tert*-butylbenzene (2.44 mg, internal standard), $CDCl_3$ (450 μL), **3b** (19.7 mg of a 0.5 wt% solution in $CDCl_3$, 100 nmol). 95% yield determined with internal standard.

c) 7 (30.4 mg, 202 μmol), 1,3,5-tri-*tert*-butylbenzene (2 mg, internal standard), $CDCl_3$ (450 μL), **3a** (95.4 mg of a 0.5 wt% solution in $CDCl_3$, 500 nmol). 60% yield determined with internal standard.

d) 7 (30.4 mg, 202 μmol), 1,3,5-tri-*tert*-butylbenzene (2 mg, internal standard), $CDCl_3$ (450 μL), **3b** (98.3 mg of a 0.5 wt% solution in $CDCl_3$, 500 nmol). 70% yield determined with internal standard.

e) 9 (49.1 mg, 203 μmol), hexamethylbenzene (1.91 mg, internal standard), C_6D_6 (500 μL), **3a** (3.79 mg, 3.98 μmol). 58% yield determined with internal standard.

f) 9 (49.3 mg, 203 μmol), hexamethylbenzene (1.83 mg, internal standard), C_6D_6 (500 μL), **3b** (3.89 mg, 3.95 μmol). 69% yield determined with internal standard.

g) 11 (46.5 mg, 198 μmol), hexamethylbenzene (1.98 mg, internal standard), C_6D_6 (500 μL), **3a** (3.79 mg, 3.97 μmol). 34% yield determined with internal standard.

h) 11 (45.8 mg, 195 μmol), hexamethylbenzene (1.56 mg, internal standard), C_6D_6 (500 μL), **3b** (3.96 mg, 4.03 μmol). 50% yield determined with internal standard.

i) 13 (14 mg, 80.8 μmol), 1,3,5-tri-*tert*-butylbenzene (1 mg, internal standard), CD_2Cl_2 (500 μL), **3a** (1.54 mg, 1.61 μmol). 98% yield determined with internal standard.

j) 13 (16.4 mg, 94.7 μmol), 1,3,5-tri-*tert*-butylbenzene (1.56 mg, internal standard), CD_2Cl_2 (500 μL), **3b** (1.84 mg, 1.87 μmol). 92% yield determined with internal standard.

k) 15 (27.7 mg, 220 μmol), DMF (external standard), C_6D_6 (500 μL), **3a** (1.05 mg, 1.10 μmol). 98% yield determined with external standard.

l) 15 (28.2 mg, 224 μmol), DMF (external standard), C_6D_6 (500 μL), **3b** (1.10 mg, 1.12 μmol). 95% yield determined with external standard.

m) 17 (28.1 mg, 201 μmol), DMF (external standard), C_6D_6 (500 μL), **3a** (960 μg, 1.0 μmol). 97% yield determined with external standard.

n) 17 (28.5 mg, 203 μmol), DMF (external standard), C_6D_6 (500 μL), **3b** (1.0 mg, 1.02 μmol). 98% yield determined with external standard.

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References

[1] a) G. Dyker, *Angew. Chem.* **2000**, *112*, 4407–4409; *Angew. Chem. Int. Ed.* **2000**, *39*, 4237–4239; b) A. S. K. Hashmi, *Gold Bull.* **2003**, *36*, 3–9; c) A. S. K. Hashmi, *Gold Bull.* **2004**, *37*, 51–65; d) N. Krause, A. Hoffmann-Röder, *Org. Biomol. Chem.* **2005**, *3*, 387–391; e) A. S. K. Hashmi, *Angew. Chem.* **2005**, *117*, 7150–7154; *Angew. Chem. Int. Ed.* **2005**, *44*, 6990–6993; f) A. S. K. Hashmi, G. Hutchings, *Angew. Chem.* **2006**, *118*, 8064–8105 ; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; g) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211.

[2] D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378.

[3] A. S. K. Hashmi, J. P. Weyrauch, M. Rudolph, E. Kurpejovic, *Angew. Chem.* **2004**, *116*, 6707–6709; *Angew. Chem. Int. Ed.* **2004**, *43*, 6545–6547.

[4] a) Y. Ito, M. Sawamura, T. Hayashi, *J. Am. Chem. Soc.* **1986**, *108*, 6405–6406; b) A. Togni, S. D. Pastor, *J. Org. Chem.* **1990**, *55*, 1649–1664; c) J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem.* **1998**, *110*, 1475–1478; *Angew. Chem. Int. Ed.* **1998**, *37*, 1415–1418.

[5] N. Marion, S. P. Nolan, *Chem. Soc. Rev.* **2008**, *37*, 1776–1785.

[6] A. S. K. Hashmi, M. C. Blanco, E. Kurpejovic, W. Frey, J. W. Bats, *Adv. Synth. Catal.* **2006**, *348*, 709–713.

[7] N. Mezailles, L. Ricard, F. Gagosz, *Org. Lett.* **2005**, *7*, 4133–4136.

[8] S. Doherty, J. G. Knight, C. H. Smyth, G. A. Jorgenson, *Adv. Synth. Catal.* **2008**, *350*, 1801–1806.

[9] a) C. Nieto-Oberhuber, M. P. Munos, S. López, E. Jiménez-Núnez, R. Nevado, E. Herrero-Gómez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1677–1693; b) X. Han, R. A. Widenhoefer, *Angew. Chem.* **2006**, *118*, 1779–1781; *Angew. Chem. Int. Ed.* **2006**, *45*, 1747–1749; c) Z. Zhang, C. Liu, R. E. Kinder, X. Han, H. Qian, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2006**, *128*, 9066–9073; d) C. F. Bender, R. A. Widenhoefer, *Chem. Commun.* **2006**, 4143–4144; e) A. K. Buzas, F. M. Istrate, F. Gagosz, *J. Am. Chem. Soc.* **2006**, *128*, 12614–12615; f) A. K. Buzas, F. M. Istrate, F. Gagosz, *Angew. Chem.* **2007**, *119*, 1159–1162; *Angew. Chem. Int. Ed.* **2007**, *46*, 1141–1144; g) S. Böhringer, F. Gagosz, *Adv. Synth. Catal.* **2008**, *350*, 2617–2630.

[10] CCDC 707171 (**3a**) and CCDC 707172 (**3b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336–033; or deposit@ccdc.cam.ac.uk).

[11] a) E. Herrero-Gómez, C. Nieto-Oberhuber, S. López, J. Benet-Buchholz, A. M. Echavarren, *Angew. Chem.* **2006**, *118*, 5581–5585; *Angew. Chem. Int. Ed.* **2006**, *45*, 5455–5459; b) D. V. Partyka, T. J. Robilotto, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics* **2008**, *27*, 28–32.

[12] A. S. K. Hashmi, M. Wölfle, F. Ata, M. Hamzic, R. Salathé, W. Frey, *Adv. Synth. Catal.* **2006**, *348*, 2501–2508.

[13] a) A. S. K. Hashmi, M. Bührle, R. Salathé, J. W. Bats, *Adv. Synth. Catal.* **2008**, *350*, 2059–2064; b) G.-Y. Lin, C.-W. Li, S.-H. Hung, R.-S. Liu, *Org. Lett.* **2008**, *10*, 5059–5062.

[14] A. S. K. Hashmi, J. P. Weyrauch, W. Frey, J. W. Bats, *Org. Lett.* **2004**, *6*, 4391–4394.

[15] G. L. Hamilton, E. J. Kang, M. Mba, F. D. Toste, *Science* **2007**, *317*, 496–499.

[16] H-KITPHOS and *o*-MeO-KITPHOS monophosphines **1a** and **1b**, respectively, are commercially available from Strem Chemical Co.

