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Synthesis, structure and reactivity of organogold compounds of relevance to homogeneous gold catalysis

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ABSTRACT

Organogold(I) phosphane complexes were prepared, their structure was investigated and their reactivity in reactions with Michael acceptors, sources of electrophilic halogens and protons were investigated.

1. Introduction

In the past eight years, homogeneous gold catalysis underwent an impressive development and now is an important tool in organic synthesis [1]. In many of these reactions, vinyl (**1**), aryl (**2**) or hetaryl gold complexes (**3**) are assumed as intermediates, but these have not yet directly been detected in these reactions (see Scheme 1).

On the other hand, similar organogold compounds have been known in the stoichiometric organometallic chemistry of gold for a long time [2]. We now wanted to prepare such organogold compounds and to investigate their reactivity with electrophilic reagents in elementary steps as suggested for catalytic cycles of gold-catalyzed reactions.

Since gold-catalysis has a high functional group tolerance, and our synthetic approach should also allow the synthesis of substrates with different functional groups, we decided not to use organolithium precursors [3] for the preparation of the organogold compounds. A higher functional group tolerance is shown by boronic acid derivatives, and in a recent publication the efficient synthesis of such organogold complexes from the corresponding phosphine gold(I) chlorides and boronic acids was described [4].

We here report the synthesis and characterization of a series of different organogold(I) phosphane complexes, the investigation of both their structural parameters and their reactivity with different elecrophilic reagents.

2. Results and discussion

2.1. Synthesis of the organogold(I) complexes

We decided to focus on triphenylphosphine as the ligand, which is probably most representative for the catalysts used in homogeneous gold(I) catalysis. Following the known procedure [4], the organogold(I) phosphane complexes **5** were obtained in good yields (Table 1) starting from $(Ph_3P)AuCl$, by simple reaction with boronic acids **4** in isopropanol at 50 °C in the presence of caesium carbonate as a base. The presence of different substituents on the aryl groups of aryl boronic acids did not significantly alter the reactivity. Similar yields (82–98%) were obtained with neutral (entry 1), acceptor (entry 4) or donor (entries 5 and 6) substituents. Compounds **5** with functionalities such as a formyl group (entries 2 and 3), a nitro group (entry 4) or a vinyl group (entries 7 and 8) could also be efficiently prepared. Vinyl and alkyl (entries 8 and 9) gold complexes could be prepared as well. With the sterically less demanding alkyl substituent the boron–gold exchange reaction is not diastereoselective: 20% of the (*Z*)-diastereomer is formed, too (entry 8), but full diastereoselectivity is observed with the phenyl group (entry 7).

It is not possible to prepare similar gold(III) compounds from boronic acids. In such reactions a simple oxidative homo-coupling of the organic part of the boronic acid is observed, as previously reported by Corma and co-workers [5].

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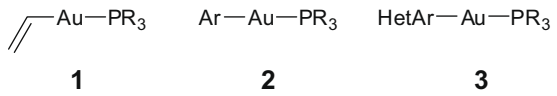
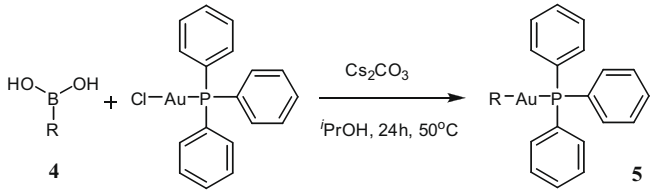


Scheme 1. Vinyl-, aryl- and hetarylgold(I) phosphanes as presumed intermediates in gold catalyzed reactions.

Table 1
Synthesis of organogold(I) triphenylphosphane complexes from boronic acids.



Entry	4	Yield of **5** (%)
1	**4a** R = C_6H_5-	**5a** (88%)
2	**4b** R = 5-formylfuran-2-yl	**5b** (88%)
3	**4c** R = 5-formylfuran-3-yl	**5c** (85%)
4	**4d** R = 3-$NO_2C_6H_5$-	**5d** (87%)
5	**4e** R = 3,5-$(CH_3)_2C_6H_5$-	**5e** (96%)
6	**4f** R = 3-(MeO)C_6H_5-	**5f** (97%)
7	(*E*)-**4g** R = (*E*)-C_6H_5-CH=CH-	(*E*)-**5g** (98%)
8	**4h** R = $CH_3(CH_2)_2CH$=CH-	**5h** (82%)[a]
9	**4i** R = C_2H_5-	**5i** (84%)

[a] 80:20 mixture of *E* and *Z* as determined by the coupling constants in ^{1}H NMR.

2.2. Structural data

Four of these compounds, namely **5a**, **5c**, **5d** and (*E*)-**5g** delivered single crystals which were suitable for X-ray crystal structure investigation [6]. The structures are shown in Fig. 1, selected data are shown in Table 2. As one can see, there is no strong dependence of the P–Au and the C–Au bond on the group R on gold, which is not surprising, as all four groups R are bonded to gold by sp^2-carbon atoms. In all cases the carbon–gold–phosphorous bond angle shows a small deviation from linearity, which probably bases on packing effects in the crystal.

Table 2
Selected data for the structures of **5a**, **5c**, **5d** and (*E*)-**5g**.

Compound	P–Au (Å)	C–Au (Å)	C1–Au1–P1 (°)
5a	2.30	2.05	174.6
5c	2.28	2.04	176.4
5d	2.30	2.05	176.6
(*E*)-**5g**	2.29	2.04	176.4

2.3. Reactivity studies

Having in hand a series of organogold(I) compounds **5**, we then investigated the reactivity of these species. For this, we chose the reaction with three typical types of electrophiles known from gold catalysis: Michael acceptors, sources of electrophilic halogens and Bronsted acids.

2.3.1. Reactions with Michael acceptors

We started with methyl vinyl ketone (**6**), a simple Michael acceptor which has been reported to react with electron-rich arenes in gold-catalyzed reactions [7]. It was unclear, whether the arene is aurated and then adds to the Michael acceptor or the gold catalyst acts as a carbophilic Lewis acid, activating the Michael acceptor (see Scheme 2).

Efforts to obtain such 1,4-addition products all failed. Neither **5a**, nor **5c** or (*E*)-**5g** reacted with **6** in different solvents like benzene, dichloromethane or acetonitrile to give **7**.

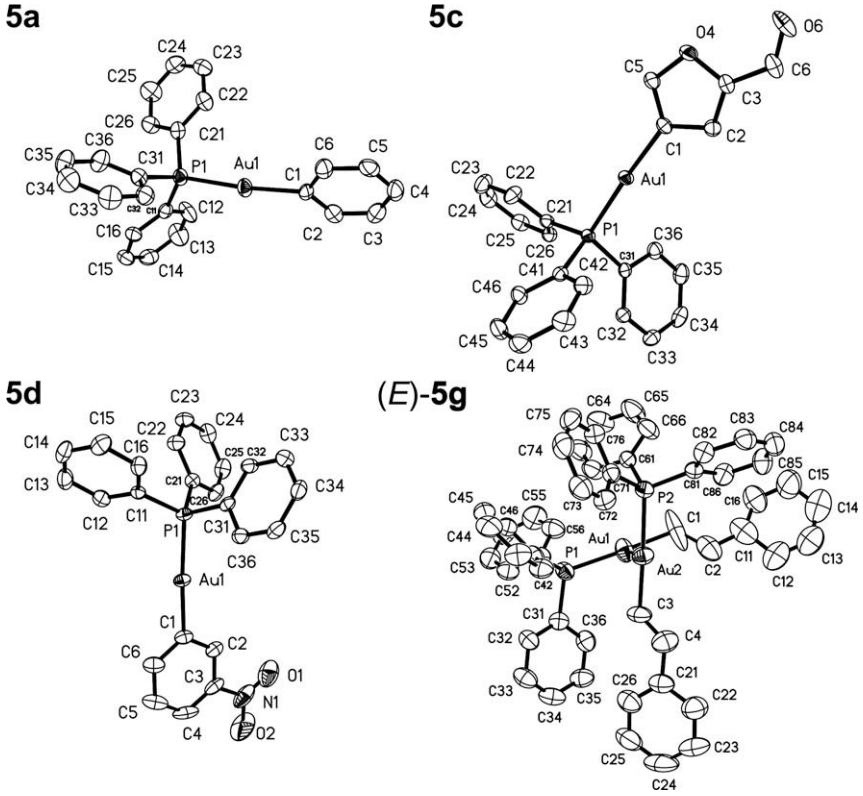
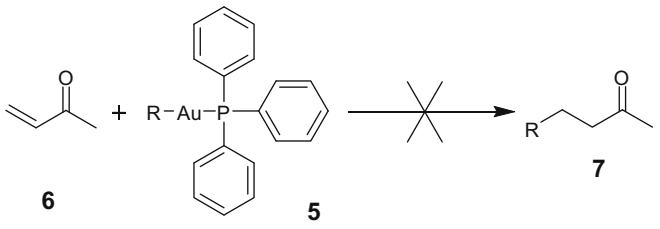


Fig. 1. Ortep-plots of the solid state structures of **5a**, **5c**, **5d** and (*E*)-**5g** (hydrogen atoms have been omitted for clarity).



Scheme 2.

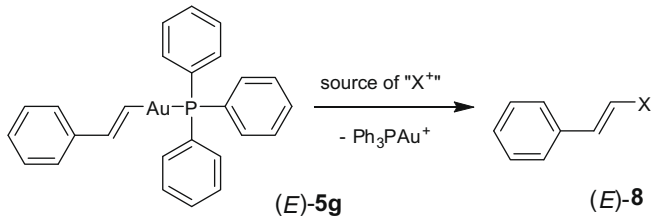
The reaction was also unsuccessful with butyn-2-one. With respect to other gold(I)-catalyzed hydroarylations of electron-deficient alkynes [8]. This fully supports the overall *anti*-addition initiated by an electrophilic attack of the alkyne, which is co-ordinated to the gold catalyst, at the aryne and excludes a significant participation of aurated arenes in the catalytic cycle.

2.3.2. Electrophilic halogen transfer reagents

In a number of gold catalyzed cycloisomerization reactions, the intermediate vinylgold species had been claimed to be trapped by electrophilic halogens, for example from NIS and related reagents [9]. Since these reactions are also possible with only the source of electrophilic halogen and only a kinetically faster reaction indicated the participation of the gold catalyst (which could also have been a Lewis-acid type interaction with the NIS, making the latter a more active I^+ donor), a proof of the elementary step between a vinylgold species and electrophilic halogen was needed [10].

We investigated the reaction of different sources of electrophilic halogen (Table 3). With NIS, NBS and NCS in a clean reaction took place without any detectable side-reaction and the corresponding (*E*)-configurated iodo- (entry 1, **8a**), bromo- (entry 2, **8b**) and chloro-styrenes (entry 3, **8c**) were formed. With selectfluor on the other hand, the corresponding fluorostyrene could not be detect (entry 4), which probably originates from solubility problems.

Table 3
Reaction of (*E*)-**5g** with different electrophilic halogen sources.



Entry	Source of "X^+"	Product **8** (Yield)
1	NIS	**8a** X = I (96%)
2	NBS	**8b** X = Br (95%)
3	NCS	**8c** X = Cl (95%)
4	Selectfluor	**8d** X = F (–)
5	Py_2I^+ BF_4^-	**8a** X = I (88%)
6	*N*-fluorobenzenesulfonimide	**9** (91%)

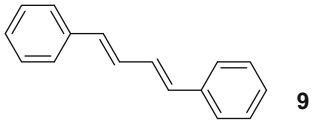
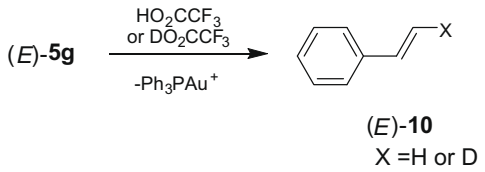


Fig. 2. Compound **9** as the product of an oxidative coupling.



Scheme 3. Diastereoselectivity in the protodeauration step.

The Barluenga reagent [11] also gave **8a** in good yield. With *N*-fluorobenzenesulfonimide only **9** (Fig. 2), the product of an oxidative coupling of the organic moiety in **5g**, was obtained, again in very good yield.

Encouraged by these conversions of (*E*)-**5g**, we tested **5a**, **5e** and **5f**, which with NBS gave 81%, 89% and 94% of the corresponding bromo compounds.

These results show that a direct halogenation of vinylgold intermediates is possible with excellent selectivity and good yield.

2.3.3. Bronsted acids

The proto-deauration is one of the most important elementary steps in homogeneous gold catalysis. In order to check the stereoselectivity of this step, we subjected (*E*)-**5g** to trifluoro acetic acid, which delivered styrene **10**. Due to the volatility of this product, we only could detect a selective conversion with over 95% yield with respect to an internal NMR standard, an separation from the solvent was not possible. The next step was to use the deuterated trifluoro acetic acid (65% conversion), which indeed only delivered the (*E*)-diastereomer of the deuterostyrene, confirming the diastereoselectivity for this elementary step as discussed previously for related reactions [12] (see Scheme 3).

A similar deutero-deauration was possible with the arylgold complex **5f** (92% conversion against the internal NMR standard).

3. Conclusion

The boronic acid route allows a quick synthesis of functionalized organogold(I) compounds. The study of the reactivity of these compounds allowed to identify and to exclude possible reaction pathways of gold-catalyzed reactions. Similar investigation for other elementary steps will deliver valuable mechanistic information in the future.

4. Experimental

*4.1. Phenyl(triphenyl-λ^5-phosphanyl)gold (**5a**)*

In dry isopropanol (5 mL) the phenyl boronic acid (35.0 mg, 290 μmol) was dissolved and Cs_2CO_3 (92.0 mg, 280 μmol) was added. To this suspension was added [(Ph_3P)AuCl] (74.0 mg, 150 μmol) under N_2 and the resultant mixture was stirred at 50 °C for 24 h and taken to dryness via rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated in vacuo to dryness, washed with pentane and dried. The solid was re-extracted into a minimum of benzene, filtered, and was washed with pentane to get colorless solid, which was washed with methanol, pentane and dried. Yield: 65.0 mg (88%). IR (film): ν = 3050, 1480, 1436, 1369, 1330, 1261, 1182, 1071, 1025, 997, 909, 746, 728, 693 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz): δ = 8.10 (t, J = 6.42 Hz, 2H, C_6H_5), 7.50 (td, J = 7.86 Hz, 2H, C_6H_5), 7.38–7.42 (m, 6H, $P(C_6H_5)_3$), 7.24 (t, J = 7.28 Hz, 1H, C_6H_5), 6.89–6.97 (m, 9H, $P(C_6H_5)$); ^{31}P NMR (C_6D_6, 101 MHz): δ = 44.55 (s) ppm; HRMS (LIFDI): m/z (%) = 536 (100) $[M]^+$, 995 (23), 1072 (20); Anal. Calc. for $C_{20}H_{20}AuP$: C, 53.74; H, 3.76. Found: C, 53.66; H, 3.83%. This data is in accordance with the published data [4].

*4.2. (5-Formylfuran-2-yl)(triphenyl-λ^5-phosphanyl)gold (**5b**)*

In dry isopropanol (5 mL) 2-furyl-5-boronic acid (42.5 mg, 300 μmol) was dissolved and Cs_2CO_3 (99.0 mg, 300 μmol) was added. To this suspension was added [(Ph_3P)AuCl] (84.0 mg, 170 μmol) under N_2 and the resultant mixture was stirred at 50 °C for 24 h and taken to dryness via rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated in vacuo to dryness, washed with pentane and dried. The solid was re-extracted into a minimum of benzene, filtered, and was washed with pentane to get yellowish brown solid, which was washed with methanol, pentane and dried. Yield: 83.2 mg (88%). Decomposition temperature = 141 °C; IR (film): ν = 1662, 1572, 1552, 1543, 1480, 1435, 1101, 1019, 998, 959, 796, 754, 693 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 9.78 (s, 1H, CHO), 7.20–7.27 (m, 6H, $P(C_6H_5)_3$), 6.85–6.95 (m, 9H, $P(C_6H_5)_3$), 6.97–6.98 (m, 1H, C_4H_2), 6.67 (d, J = 3.32 Hz, 1H, C_4H_2); ^{13}C NMR (C_6D_6, 75 MHz): δ = 176.30 (s), 156,67 (s), 134.47 (d, $J_{C\text{-}P}$ = 13.4 Hz), 131.34 (s), 129.24 (d, $J_{C\text{-}P}$ = 10.8 Hz), 130.69 (s), 128.32 (s), 122.42 (s); ^{31}P NMR (C_6D_6, 101 MHz): δ = 43.53 (q) ppm; HRMS (LIFDI) m/z (%) = 554 (100) $[M]^+$, 721 (8), 1013 (9); Anal. Calc. for $C_{23}H_{18}AuO_2P$: C, 49.83; H, 3.27. Found: C, 50.04; H, 3.33%.

*4.3. (5-Formylfuran-3-yl)(triphenyl-λ^5-phosphanyl)gold (**5c**)*

In dry isopropanol (5 mL) 2-furyl-4-boronic acid (85.0 mg, 608 μmol) was dissolved and Cs_2CO_3 (198 mg, 608 μmol) was added. To this suspension was added [(Ph_3P)AuCl] (168 mg, 340 μmol) under N_2 and the resultant mixture was stirred at 50 °C for 24 h and taken to dryness via rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated in vacuo to dryness, washed with pentane and dried. The solid was re-extracted into a minimum of benzene, filtered, and was washed with pentane to get pale yellow solid, which was washed with methanol, pentane and dried. Yield: 157 mg (85%). Decomposition temperature = 173 °C; IR (film): ν = 1668, 1539, 1480, 1460, 1449, 1436, 1330, 1114, 1101, 942, 911, 765, 750, 710 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 9.69 (s, 1H, CHO), 7.55 (s, 1H, (C_4H_2O)), 7.44 (s, 1H, (C_4H_2O)), 7.28–7.36 (m, 6H, $P(C_6H_5)_3$), 6.91–6.94 (m, 9H, $P(C_6H_5)_3$); ^{13}C NMR (C_6D_6, 75 MHz): δ = 177.69 (s), 154.76 (d, J = 7.4 Hz), 134.28 (d, J = 13.7 MHz), 131.42 (d, J = 2.09 Hz), 130.70 (s), 129.98 (s), 129.16 (d, J = 10.97 Hz), 128.31 (s); ^{31}P NMR (C_6D_6, 101 MHz): δ = 45.7 (s) ppm; HRMS (LIFDI): m/z (%) = 554 (100) $[M]^+$, 1013 (9), 1108 (12).

*4.4. (3-Nitrophenyl)(triphenyl-λ^5-phosphanyl)gold (**5d**)*

In dry isopropanol (5 mL) 3-nitrophenyl boronic acid (126 mg, 755 μmol) was dissolved and Cs_2CO_3 (199 mg, 607 μmol) was added. To this suspension was added [(Ph_3P)AuCl] (166 mg, 340 μmol) under N_2 and the resultant mixture was stirred at 50 °C for 24 h and taken to dryness via rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated in vacuo to dryness, washed with pentane and dried. The solid was re-extracted into a minimum of benzene, filtered, and was washed with pentane to get colorless solid, which was washed with methanol, pentane and dried. Yield: 171 mg (87%). Melting point = 148 °C; IR (film): ν = 3053, 1511, 1480, 1436, 1341, 1309, 1261, 1183, 1100, 998, 909, 865, 803, 745, 728, 710, 693 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.42 ((bs, 1H, 3-$NO_2(C_6H_4)$), 7.84–7.91 (m, 1H, 3-$NO_2(C_6H_4)$), 7.53–7.60 (m, 6H, $P(C_6H_5)_3$), 7.44–7.51 (m, 9H, $P(C_6H_5)_3$), 7.34–7.41 (dd, J = 15.4 Hz, 2H, 3-$NO_2(C_6H_4)$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 145.98 (s), 134.29 (d, $J_{C\text{-}P}$ = 13.7 Hz), 133.50 (s), 131.36 (d, J = 2.1 Hz), 130.82 (s), 130.21 (d, J = 9.9 Hz), 129.16 (d, $J_{C\text{-}P}$ = 10.83 Hz), 128.31 (s), 127.48 (s), 120.53 (s); ^{31}P NMR (C_6D_6, 121 MHz): δ = 42.74 (s) ppm; HRMS (LIFDI) m/z (%) = 581 (100) $[M]^+$, 721 (8); Anal. Calc. for $C_{24}H_{19}AuNO_2P$: C, 49.58; H, 3.29, N, 2.41. Found: C, 49.90; H, 3.41; N, 2.60%.

*4.5. (3,5-Dimethylphenyl)(triphenyl-λ^5-phosphanyl)gold (**5e**)*

In dry isopropanol (5 mL) the 3,5-dimethylphenyl boronic acid (113 mg, 755 μmol) was dissolved and Cs_2CO_3 (198 mg, 607 μmol) was added. To this suspension was added [(Ph_3P)AuCl] (166 mg, 340 μmol) under N_2 and the resultant mixture was stirred at 50 °C for 24 h and taken to dryness via rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated in vacuo to dryness, washed with pentane and dried. The solid was re-extracted into a minimum of benzene, filtered, and was washed with pentane to get colorless solid, which was washed with methanol, pentane and dried. Yield: 185 mg (96%). Decomposition temperature = 132 °C; IR (film): ν = 2995, 2921, 2856, 1725, 1480, 1436, 1283, 1181, 1100, 998, 746, 709, 694 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz): δ = 7.43–7.51 (m, 6H, $P(C_6H_5)_3$), 7.31–7.37 (m, 9H, $P(C_6H_5)_3$), 7.12 (s, 1H, ($C_6H_3(CH_3)_2$)), 7.07–7.09 (d, J = 5.8 Hz 2H, ($C_6H_3(CH_3)_2$)), 2.13 (s, 6H, ($C_6H_3(CH_3)_2$)); ^{13}C NMR (C_6D_6, 75 MHz): δ = 172.05 (s), 170.51 (s), 137.04 (s), 136.36 (d, J = 6.33 Hz), 134.41 (d, $J_{C\text{-}P}$ = 13.7 Hz), 131.52 (s), 131.08 (s), 129.00 (d, $J_{C\text{-}P}$ = 10.7 Hz), 128.35 (s), 127.73 (s), 125.11 (s), 21.41 (s); ^{31}P NMR (C_6D_6, 121 MHz): δ = 43.46 (d) ppm; HRMS (LIFDI) m/z (%) = 564.2 (100) $[M]^+$, 396.3 (32), 262.1 (46); Anal. Calc. for $C_{26}H_{24}AuP$: C, 55.23; H, 4.28. Found: C, 55.33; H, 4.29%.

*4.6. (3-Methoxyphenyl)(triphenyl-λ^5-phosphanyl)gold (**5f**)*

In dry isopropanol (5 mL) the 3-methoxyphenyl boronic acid (98.0 mg, 640 μmol) was dissolved and Cs_2CO_3 (194 mg, 640 μmol) was added. To this suspension was added [(Ph_3P)AuCl] (148 mg, 300 μmol) under N_2 and the resultant mixture was stirred at 50 °C for 24 h and taken to dryness via rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated in vacuo to dryness, washed with pentane and dried. The solid was re-extracted into a minimum of benzene, filtered, and was washed with pentane to get colorless fluffy solid, which was washed with methanol, pentane and dried. Yield: 165 mg (97%). Decomposition temperature = 123 °C; IR (film): ν = 3050, 2927, 2829, 1572, 1497, 1480, 1468, 1436, 1397, 1276, 1233, 1217, 1180, 1100, 998, 828, 747, 710, 693 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz): δ = 7.54–7.58 (m, 5H, $P(C_6H_5)_3$), 7.42–7.49 (m, 7H, $P(C_6H_5)_3$), 7.26–7.34 (m, 2H $P(C_6H_5)_3$), 7.21 (d, J = 2.8 Hz, 1H, 3-$(C_6H_4)OCH_3$), 7.17 (d, J = 6.5 Hz, 1H, 3-$(C_6H_4)OCH_3$), 6.88–6.94 (m, 1H, 3-$(C_6H_4)OCH_3$), 6.68 (dq, J = 8.2 Hz, 1H, 3-$(C_6H_4)OCH_3$), 3.79 (s, 3H, OCH_3); ^{13}C NMR (C_6D_6, 125 MHz): δ = 158.83 (s), 134.31 (d, $J_{C\text{-}P}$ = 13.6 Hz), 131.26 (s), 129.40 (s), 129.07 (d, $J_{C\text{-}P}$ = 10.9 Hz), 128.16 (s), 124.62 (s), 12.60 (s), 55.08 (s); ^{31}P NMR (C_6D_6, 202 MHz): δ = 42.06 (s) ppm; HRMS (LIFDI) m/z (%) 566 (100) $[M]^+$. This data is in accordance with data published for this substance [13].

*4.7. [(E)-2-Phenylethenyl](triphenyl-λ^5-phosphanyl)gold ((E)-**5g**)*

In dry isopropanol (5 mL) (*E*)-styrylboronic acid (100 mg, 676 μmol) was dissolved and Cs_2CO_3 (220 mg, 676 μmol) was added. To this suspension was added [(Ph_3P)AuCl] (167 mg, 338 μmol) under N_2 and the resultant mixture was stirred at 50 °C for 24 h and taken to dryness via rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated in vacuo to dryness, washed with pentane and dried. The solid was re-extracted into a minimum of benzene, filtered, and was washed with pentane to get colorless solid, which was washed with methanol, pentane and dried. Yield: 186 mg (98%). Decomposition temperature = 98 °C; IR (film): ν = 3054, 2917, 1595, 1556,

1490, 1480, 1435, 1276, 1182, 1100, 989, 828, 747, 709, 692 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz): δ = 8.48–8.52 (d, J = 19.2 Hz, 1H, CH=CH–C_6H_5), 7.67 (d, J = 7.1 Hz, 2H, C_6H_5), 7.52 (d, J = 19.2 Hz, 1H, CH=CH–C_6H_5), 7.38–7.42 (m, 6H, $P(C_6H_5)_3$), 7.22 (t, J = 7.6 MHz, 2H, C6H5), 7.030–7.06 (tt, J = 8.4 Hz, 1H, C_6H_5), 6.90–6.98 (m, 9H, $P(C_6H_5)_3$); ^{13}C NMR (C_6D_6, 125 MHz): δ = 144.74 (s), 134.55 (d, J_{C-P} = 13.8 Hz) 131.87 (s), 131.49 (s), 130.93 (s), 129.09 (d, J_{C-P} = 10.6 Hz), 128.74 (s), 128.53 (s), 128.29 (s), 126.32 (s), 126.12(s); ^{31}P NMR (C_6D_6, 121 MHz): δ = 43.9 (s) ppm; HRMS (LIFDI) m/z (%) = 562 (100) $[M]^+$, 830 (11), 913 (4), 387 (4), 262 (60), 206 (21)). The data is in accordance with some data published on this compound before [14].

4.8. [(1E)- and (1Z)-Pent-1-en-1-yl](triphenyl-λ^5-phosphanyl)gold (**5h**)

In dry isopropanol (5 mL) 1-pentenyl boronic acid (35.0 mg, 303 μmol) was dissolved and Cs_2CO_3 (98.8 mg, 303 μmol) was added. To this suspension was added [(Ph_3P)AuCl] (75.0 mg, 151 μmol) under N_2 and the resultant mixture was stirred at 50 °C for 24 h and taken to dryness via rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated in vacuo to dryness, washed with pentane and dried. The solid was re-extracted into a minimum of benzene, filtered, and was washed with pentane to get reddish brown sticky substance, which was washed with methanol, pentane and dried. The product was found to be mixture of (*E*) and (*Z*) isomers from NMR analysis. *E*:*Z* = 4:1. Yield: 65.0 mg (82%). IR (film): ν = 2954, 2927, 1480, 1459, 1436, 1330, 1309, 1183, 1100, 998, 910, 812, 746, 710, 692 cm^{-1}; (*E* Isomer): ^1H NMR (C_6D_6, 500 MHz): δ = 7.58 (d, J = 11.4 Hz, 1H, (CH=CH(C_3H_7))), 7.40 (m, 6H, $P(C_6H_5)_3$), 6.92–6.97 (m, 9H, $P(C_6H_5)_3$), 2.83 (q, J = 14.2 Hz, 3H, CH_3), 1.77 (td, J = 14.8 Hz, 2H, CH_2), 1.30-1.37 (m, 2H, CH_2) 1.11 (t, J = 7.4 Hz, 3H, (CH=CH(C_3H_7))); ^{13}C NMR (C_6D_6, 125 MHz): δ = 146.41 (s), 134.52 (d, J_{C-P} = 13.8 Hz), 132.35 (d, J = 9.6 Hz), 132.14 (s), 131.76 (s), 130.84 (s), 129.03 (d, J_{C-P} = 10.5 Hz), 42.65 (s), 30.15 (s), 24.51 (s), 14.35 (d, J = 29.0 Hz); (*Z* Isomer): ^1H NMR (C_6D_6): δ 7.58 (d, J = 18.4 Hz, 1H, (CH=CH(C_3H_7))), 7.40 (m, 6H, $P(C_6H_5)_3$), 6.92–6.97 (m, 9H, $P(C_6H_5)_3$), 2.50 (q, J = 14.6 Hz, 3H, CH_3), 1.77 (td, J = 14.7 Hz, 2H, CH_2), 1.11 (t, J = 7.3 Hz, 1H, (CH=CH(C_3H_7))), 0.88 (m, 2H, CH_2); ^{13}C NMR (C_6D_6, 125 MHz): δ = 144.47 (s), 134.52 (d, J_{C-P} = 13.7 Hz), 132.35 (d, J = 9.62 Hz), 132.14 (s), 131.53 (s), 130.84 (s), 129.03 (d, J_{C-P} = 10.5 Hz), 41.45 (s), 30.15 (s), 23.82 (s), 14.35 (d, J = 29.0 Hz); ^{31}P NMR (C_6D_6): δ = 43.9 (s) ppm; HRMS (LIFDI) m/z (%) = 262 (1), 494 (1), 528 (100) $[M]^+$, 987 (95); Anal. Calc. for $C_{23}H_{24}AuP$: found: C, 52.28; H, 4.58%.

4.9. Ethyl(triphenyl-λ^5-phosphanyl)gold (**5i**)

In dry isopropanol (5 mL) ethyl boronic acid (22.5 mg, 303 μmol) was dissolved and Cs_2CO_3 (98.8 mg, 303 μmol) was added. To this suspension was added [(Ph_3P)AuCl] (75.0 mg, 152 μmol) under N_2 and the resultant mixture was stirred under argon at 50 °C for 24 h and taken to dryness via rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated in vacuo to dryness, washed with pentane and dried. The solid was re-extracted into a minimum of benzene, filtered, and was washed with pentane to get brownish sticky mass, which was washed with methanol, pentane and dried. Yield: 62 mg (84%). IR (film): ν = 2926, 1479, 1435, 1336, 1197,1092, 1026, 997, 888, 796, 745, 695 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz): δ = 7.70–7.77 (m, 3H, $P(C_6H_5)_3$), 7.34–7.40 (m, 4H, $P(C_6H_5)_3$), 6.95–7.03 (m, 8H, $P(C_6H_5)_3$), 1.21–1.39 (m, 3H, CH_3), 0.86–0.91 (m, 2H, CH_2); ^{13}C NMR (C_6D_6, 125 MHz): δ = 134.55 (d, J_{C-P} = 13.8 Hz), 132.42 (d, J = 9.68 Hz), 131.55 (s), 131.52 (s), 129.09 (d, J_{C-P} = 10.6 Hz), 128.78 (s), 31.69 (s), 30.20 (s); ^{31}P NMR (C_6D_6, 121 MHz): δ = 25.0 (d) ppm; HRMS (LIFDI) m/z (%) = 278 (100), 557 (65) [M]++3Na, 721.1 (77), 987.1 (65); Anal. Calc. for $C_{23}H_{24}AuP$: found: C, 49.19; H, 4.13%. This data is in accordance with some data published previously [15].

4.10. General procedure for Michael additions

In a dry NMR tube the gold(I) complex (1 equiv.) was dissolved in deuterated benzene (500 μL) and methyl vinyl ketone (1 equiv.) was added at room temperature. The possible conversion of the starting materials was monitored by in situ ^1H NMR, but no evidence for a reaction was observed.

4.11. Reactions with electrophilic halogens

4.11.1. (E)-2-Phenyl-1-iodo-1-ethene

In deuterated benzene (500 μL) gold(I) complex (10.0 mg, 178 μmol) was dissolved and *N*-iodosuccinimide (4.01 mg, 178 μmol) was added at room temperature. Conversion of the starting material is monitored by ^1H NMR. Yield (NMR): >95%. ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.41 (d, J = 14.9 Hz, 1H, CH=CHI), 7.17–7.19 (m, 1H, CH=CHI), 7.26–7.34 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 126.24 (s), 126.78 (s), 128.69 (s), 133.18 (s), 145.11 (s). This data is in accordance with the published data [16].

4.11.2. (E)-2-Phenyl-1-bromo-1-ethene

In deuterated benzene (500 μL) gold(I) complex (10.0 mg, 178 μmol) was dissolved and *N*-bromosuccinimide (3.16 mg, 178 μmol) was added at room temperature. Conversion of the starting material is monitored by ^1H NMR. Yield (NMR): >95%. ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.34 (d, J = 14.0 Hz, 1H, CH=CHBr), 7.26–7.33 (m, 6H, C_6H_5); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 106.88 (s), 126.34 (s), 128.80 (s), 129.03 (s), 137.36 (s), 147.73 (s). This data is in accordance with the published data [17].

4.11.3. (E)-2-Phenyl-1-chloro-1-ethene

In deuterated benzene (500 μL) gold(I) complex (10.0 mg, 178 μmol) was dissolved and *N*-chlorosuccinimide (2.38 mg, 178 μmol) was added at room temperature. Conversion of the starting material is monitored by ^1H NMR. Yield (NMR): >95%. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.71–7.78 (m, 2H, C_6H_5), 7.30 (d, 2H, J = 7.4 Hz, C_6H_5), 7.23 (d, J = 15.1 Hz, 1H, CH=CHCl), 6.99–7.11 (m, 6H, $P(C_6H_5)3$), 6.80–6.93 (m, 9H, $P(C_6H_5)3$), 6.49 (d, J = 15.1 Hz, 1H, CH=CHCl); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 126.78 (s), 128.62 (s), 128.63 (s), 129.65 (s), 133.18 (s).

4.11.4. (E)-2-Phenyl-1-iodo-1-ethene via Barluenga reagent

In deuterated benzene (500 μL) the gold(I) complex (10.0 mg, 178 μmol) was dissolved and bis(pyridine)iodonium tetrafluoroborate (6.62 mg, 178 μmol) was added at room temperature. Conversion of the starting material is monitored by ^1H NMR and the product formed was purified via column chromatography on silica with petrol ether and ethyl acetate as eluents. Yield: 65 mg (88%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.86 (d, J = 14.9 Hz, 1H, CH=CHI), 7.33–7.35 (m, 5H, C_6H_5), 7.46 (d, 1H, J = 14.9 Hz CH=CHI); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 125.98 (s), 128.70 (s), 128.36 (s), 145.0 (s).

4.11.5. (E,E)-1,4-Diphenyl-1,3-butadiene

In deuterated benzene (500 μL) gold(I) complex (21.5 mg, 382 μmol) was dissolved and *N*-fluorobenzenesulfonimide (12.0 mg, 382 μmol) was added at room temperature. Conversion of the starting material is monitored by ^1H NMR. Yield (NMR): >95%. Isolated Yield: 5.0 mg (64%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.35 (d, 4H, J = 8.6 Hz, ArH), 7.31–7.23 (m, 4H, ArH), 7.16–7.13 (m, 2H, ArH), 6.91–6.86 (dd, 2H, J = 12.0 Hz, J = 14.8 Hz, CH), 6.62–6.58 (dd, 2H, J = 11.9 Hz, J = 14.8 Hz, CH); ^{13}C NMR ($CDCl_3$,

75 MHz): δ = 137.35, 132.81, 130.87, 129.24, 128.79, 127.55, 126.37 ppm; HRMS (EI, 70 eV) *m*/*z* (%) = 206 (100) [M^+], 205 (51), 191 (36), 165 (15), 128 (21), 91 (21). This data is in accordance with the published data [18].

4.12. Protodeaurations

4.12.1. Styrene

In deuterated benzene (500 μL) gold(I) complex (10.1 mg, 179 μmol) was dissolved and trifluoroacetic acid (2.04 mg, 179 μmol) was added at room temperature. Conversion of the starting material is monitored by ^{1}H NMR. Yield: >95%. ^{1}H NMR (C_6D_6, 250 MHz): δ = 5.03 (dd, *J* = 10.9 Hz, *J* = 1.0 Hz, 1H), 5.58 (dd, *J* = 17.6 Hz, *J* = 1.0 Hz, 1H), 6.56 (dd, 1H, *J* = 17.6 Hz, *J* = 11.0 Hz), 7.20–7.24 (m, 5H, C_6H_5). This data is in accordance with the published data [19]. A similar experiment with DO_2CCF_3 showed only a disappearance of the *cis* hydrogen signal, the *trans* signal and the *trans* coupling remained.

5. Supplementary material

CCDC 705031–705034 contain the supplementary crystallographic data for compounds **5a**, **4c**, **4d** and (*E*)-**4g**, respectively. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.034.

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