Supplementary information to:

Decisive Ligand Metathesis Effects in Au/Pd Bimetallic Catalysis

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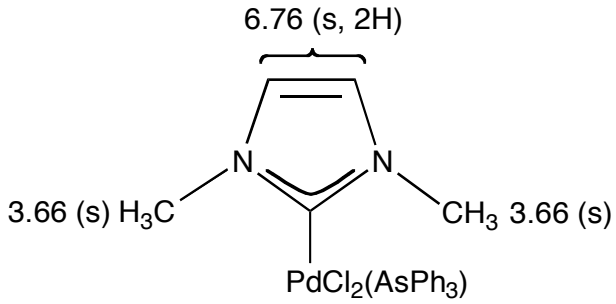
Experimental section

General methods. All reactions were carried out under N_2 or Ar. All solvents were dried using standard techniques. NMR spectra were recorded on a Bruker AV 400 instrument equipped with a VT-100 variable-temperature probe, a Varian 400-MR, or a Varian 500-MR. Chemical shifts are reported in ppm from tetramethylsilane (^{1}H), CCl_3F (^{19}F), or 85% H_3PO_4 (^{31}P), with positive shifts downfield, at ambient probe temperature unless otherwise stated. The temperature for the NMR probe was calibrated using ethylene glycol (T > 300K) and methanol (T < 300K) as temperature standards.[1] In the ^{19}F and ^{31}P spectra measured in non-deuterated solvents, a coaxial tube containing acetone-d_6 was used for the lock ^{2}H signal. The Gas Chromatgraphy-Mass analyses were performed in a Thermo-Scientific DSQ II GC/MS Fows GL. Combustion CHN analyses were made on a Perkin-Elmer 2400 CHN microanalyzer. Unless specified, all the compounds were used from commercial sources and used without further purification. The compounds $[AuCl(PPh_3)]$,[2] $[AuCl(AsPh_3)]$,[3] [AuCl(IDM)],[4] $[PdCl_2(AsPh_3)_2]$,[5] $[PdCl_2(PPh_3)_2]$,[6] $[PdCl_2(IDM)_2]$,[7] and mesityltributyltin,[8] were prepared by literature methods. The experimental procedure for the palladium/gold co-catalyzed Stille cross-coupling has been performed as reported.[9]

Synthesis of the complexes

$[PdCl_2(IDM)(AsPh_3)]$

A two necked flask was charged with $[PdCl_2(AsPh_3)_2]$ (102 mg 0.129 mmol) and $[PdCl_2(IDM)_2]$ (369 mg 0.129 mmol) dissolved in 100 mL of CH_3CN. The solution was stirred at 80 ºC for 30 hours. The resulting yellow solution was filtered through Celite and the solvent was removed under reduced pressure giving an brown oil. This residue was dissolved in 1 ml of CH_2Cl_2 and crystallized by the addition of 5ml of EtOH. The solid was filtered, washed with cold EtOH (3mL) and vacuum dried. Yield 69% (102 mg). Anal. Calcd for $C_{23}H_{23}As_2Cl_2N_2Pd$: C, 47.65; H, 4.00; N, 4.83. Found: C, 47.29; H 3.70; N, 5.29. ^{1}H NMR (500 MHz, CD_3CN) δ 7.57 (dd, J = 8.1, 1.2 Hz, 6H), 7.55 – 7.50 (m, 3H), 7.47 – 7.42 (m, 6H), 6.76 (s, 2H), 3.66 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.62, 133.17, 130.22, 129.09, 123.16, 37.64.



General procedure for ligand exchange reactions between gold and palladium complexes. A solution in CD_3CN (0.6 mL) of concentration $2.0 \cdot 10^{-3}$ M in the gold catalyst, $2.0 \cdot 10^{-3}$ M in the palladium catalyst and $4.1 \cdot 10^{-3}$ M in $AsPh_3$ was prepared in a NMR tube under nitrogen atmosphere. The tube was sealed and heated in an oil bath at 80ºC until completion of the reaction or specified time. All reactions were monitored by ^{1}H or ^{31}P NMR spectroscopy.

Figure 1

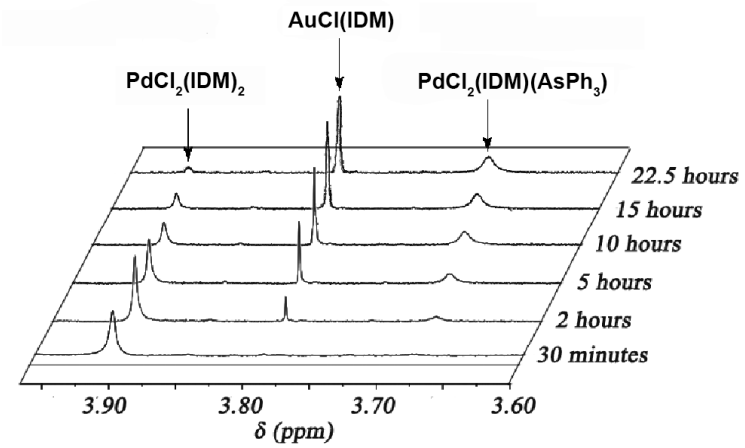


Figure 1. Ligand exchange between $[PdCl_2(IDM)_2]$ and $[AuCl(AsPh_3)]$, at 80 ˚C in CD_3CN, monitored by ^{1}H NMR on the Me signals of IDM.

Reaction between $[PdCl_2(IDM)_2]$ and $[AuCl(AsPh_3)]$

Corresponding to reaction "a" in Scheme 3 in the main text.

$$[PdCl_2(IDM)_2] + [AuCl(AsPh_3)] \xrightarrow[AsPh_3]{CD_3CN,\ 80\ ^oC} [PdCl_2(IDM)(AsPh_3)] + [AuCl(IDM)]$$

The reaction between $[PdCl_2(IDM)_2]$ and $[AuCl(AsPh_3)]$ produces quantitatively $[AuCl(IDM)]$ and $[PdCl_2(IDM)(AsPh_3)]$ in 24 hours.

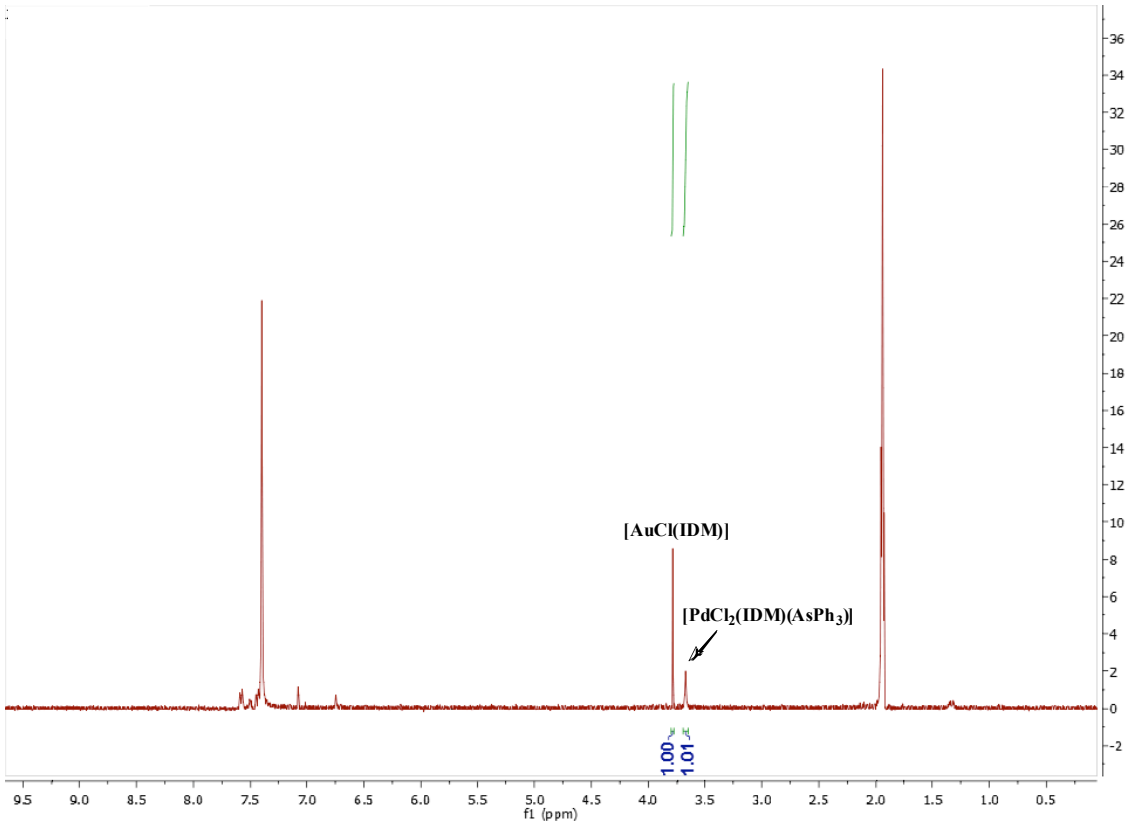


Figure S1. Spectra of $[PdCl_2(IDM)_2]$ and $[AuCl(AsPh_3)]$ after 24 h in CD_3CN at 80C. The signals from the methyl IDM groups in both metals (marked with arrows) have been used for quantitative purposes.

Reaction between $[PdCl_2(IDM)(AsPh_3)]$ and [AuCl(IDM)]

Corresponding to reaction "a" in Scheme 3 in the main text.

$$[PdCl_2(IDM)(AsPh_3)] + [AuCl(IDM)] \xrightarrow[AsPh_3]{CD_3CN,\ 80\ ^oC} \text{No reaction}$$

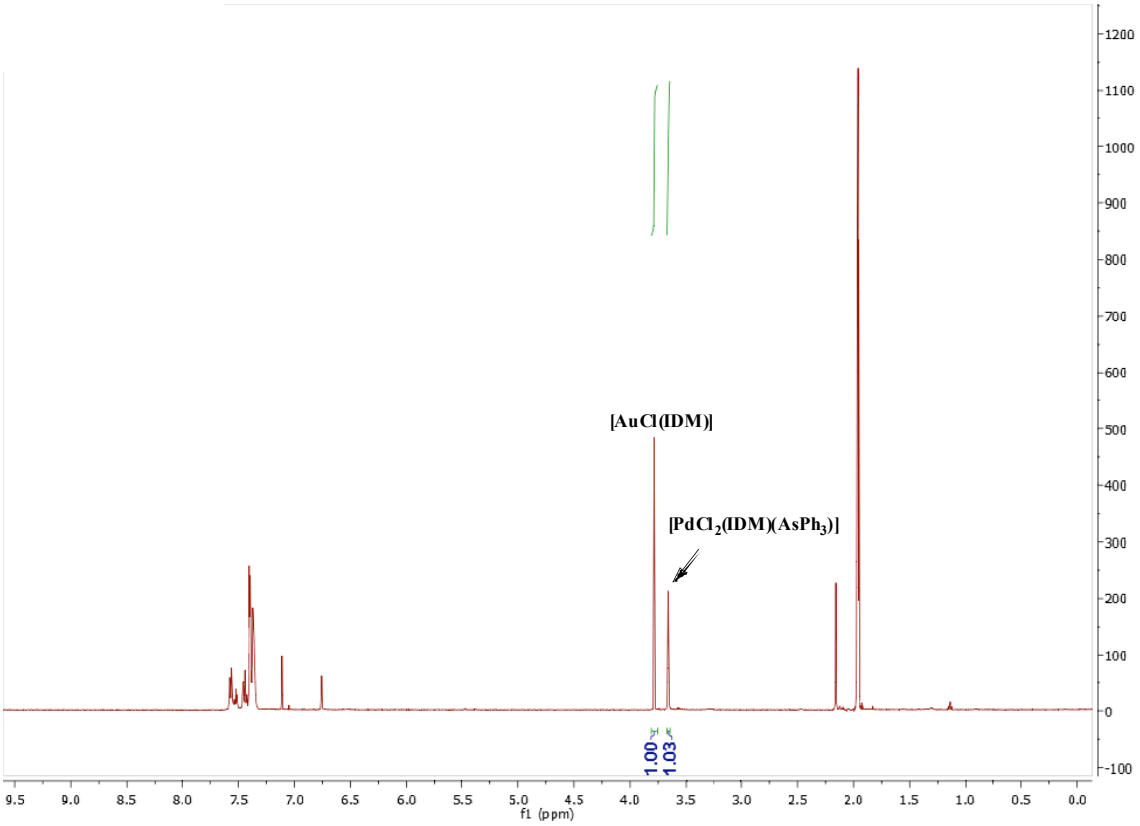


Figure S2. Spectra of $[PdCl_2(IDM)(AsPh_3)]$ and [AuCl(IDM)] after 24 h in CD_3CN at 80C.

Reaction between $[PdCl_2(IDM)(AsPh_3)]$ and $[AuCl(AsPh_3)]$

Corresponding to reaction "b" in Scheme 3 in the main text.

$$[PdCl_2(IDM)(AsPh_3)] + [AuCl(AsPh_3)] \xrightarrow[AsPh_3]{CD_3CN,\ 80\ ^oC} [PdCl_2(AsPh_3)_2] + [AuCl(IDM)]$$

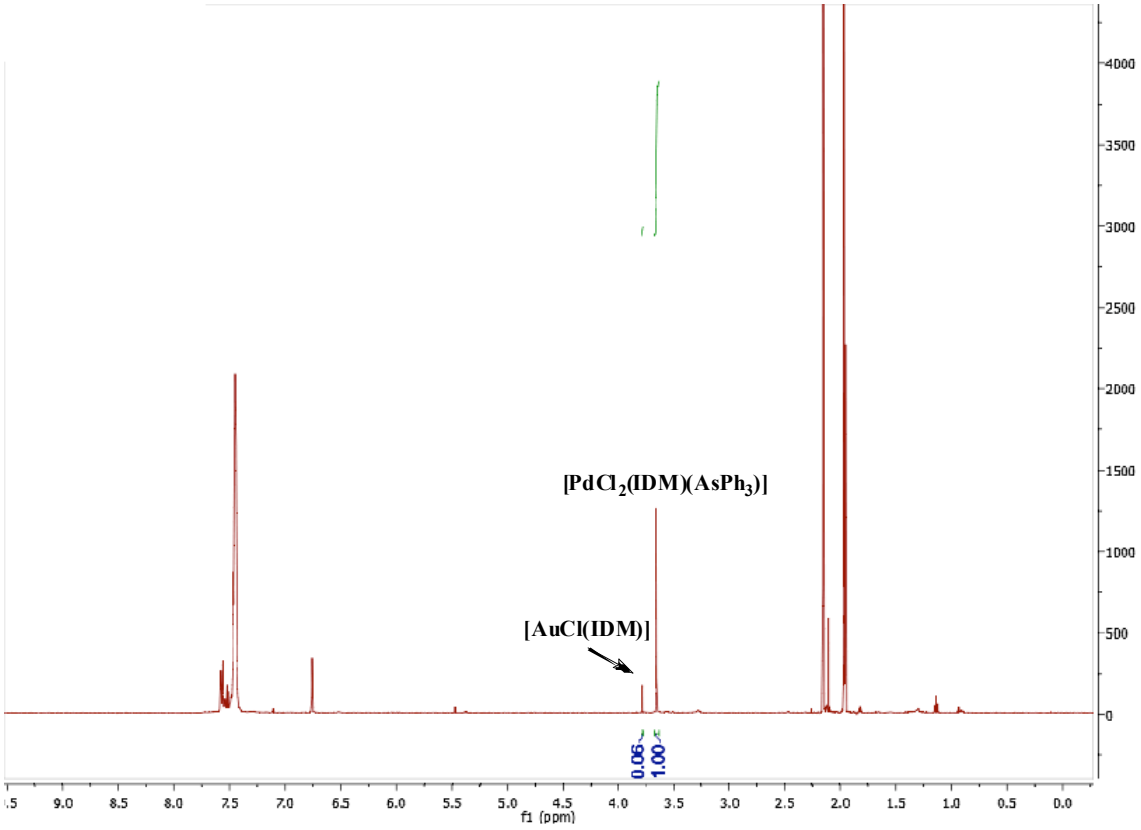
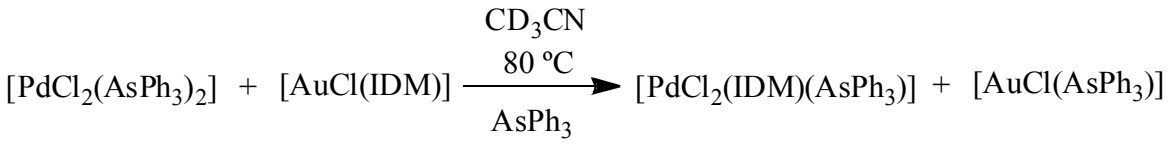


Figure S3. Spectra of $[PdCl_2(IDM)(AsPh_3)]$ and $[AuCl(AsPh_3)]$ after 24 h in CD_3CN at 80C.

Reaction between [AuCl(IDM)] and [$PdCl_2(AsPh_3)$]

Corresponding to reaction "b" in Scheme 3 in the main text.



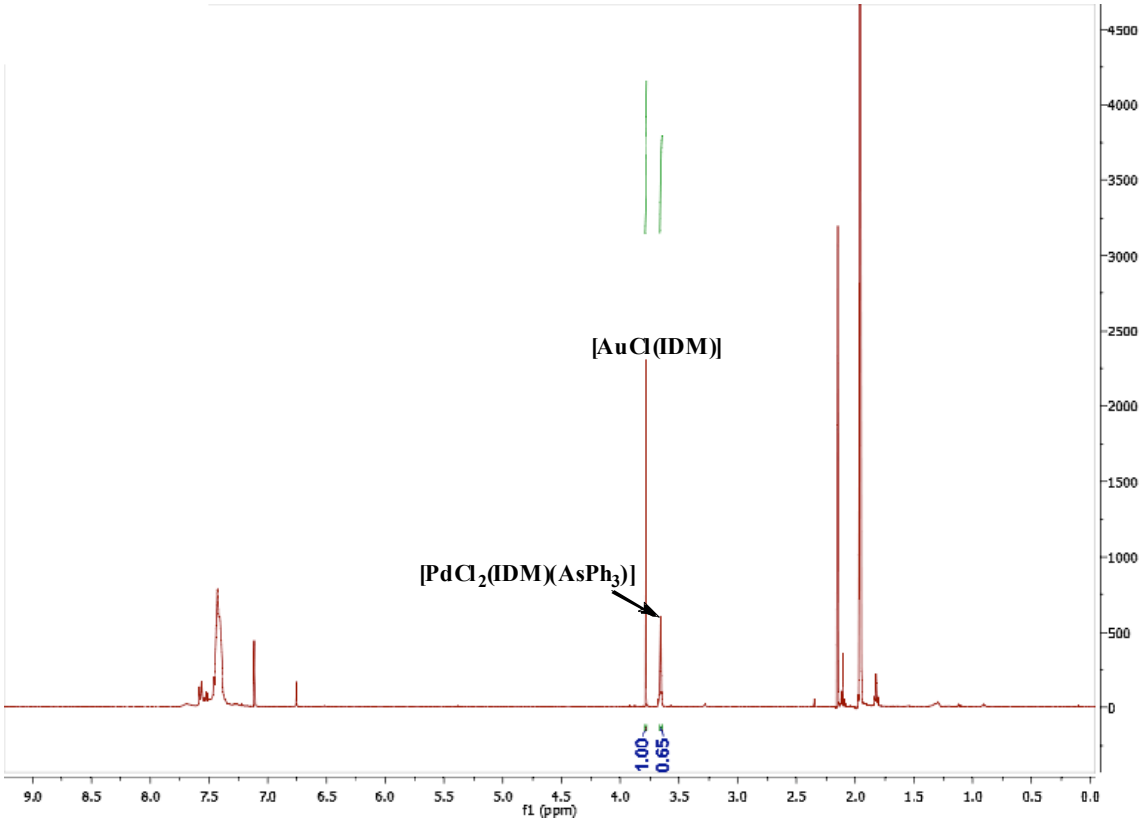


Figure S4. Spectra of [AuCl(IDM)] and [$PdCl_2(AsPh_3)$] after 24 h in CD_3CN at 80C.

Reaction between $[PdCl_2(PPh_3)_2]$ and $[AuCl(AsPh_3)]$:

Corresponding to reaction "c" in Scheme 3 in the main text.

a) In CD_3CN

$$[PdCl_2(PPh_3)_2] + [AuCl(AsPh_3)] \xrightarrow[AsPh_3]{CD_3CN,\ 80\ ^oC} [AuCl(PPh_3)] + [PdCl_2(PPh_3)_2] \rightleftharpoons [PdCl_2(AsPh)_3(PPh_3)] \rightleftharpoons [PdCl_2(AsPh_3)_2]$$

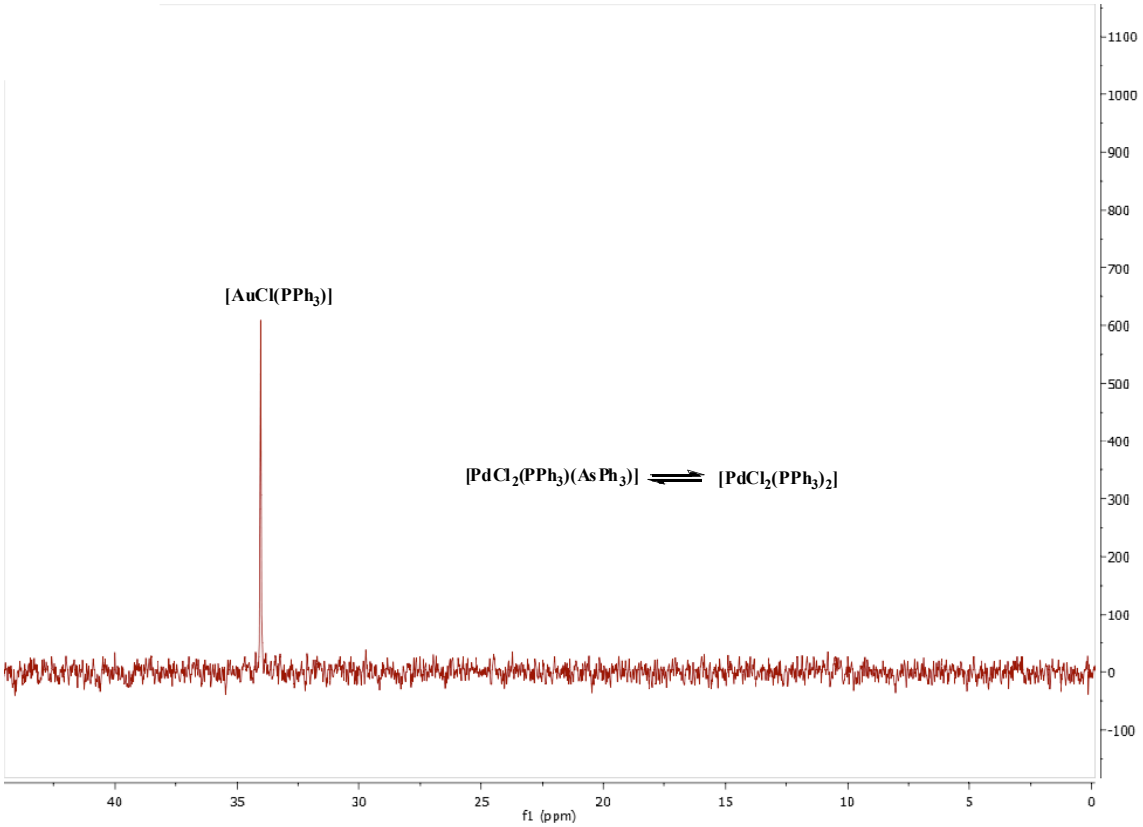


Figure S5. Spectra of $[PdCl_2(PPh_3)_2]$ and $[AuCl(AsPh_3)]$ in CD_3CN at 80ºC after 5 minutes.

b) After evaporating the CD_3CN and dissolving the residue in $CDCl_3$.

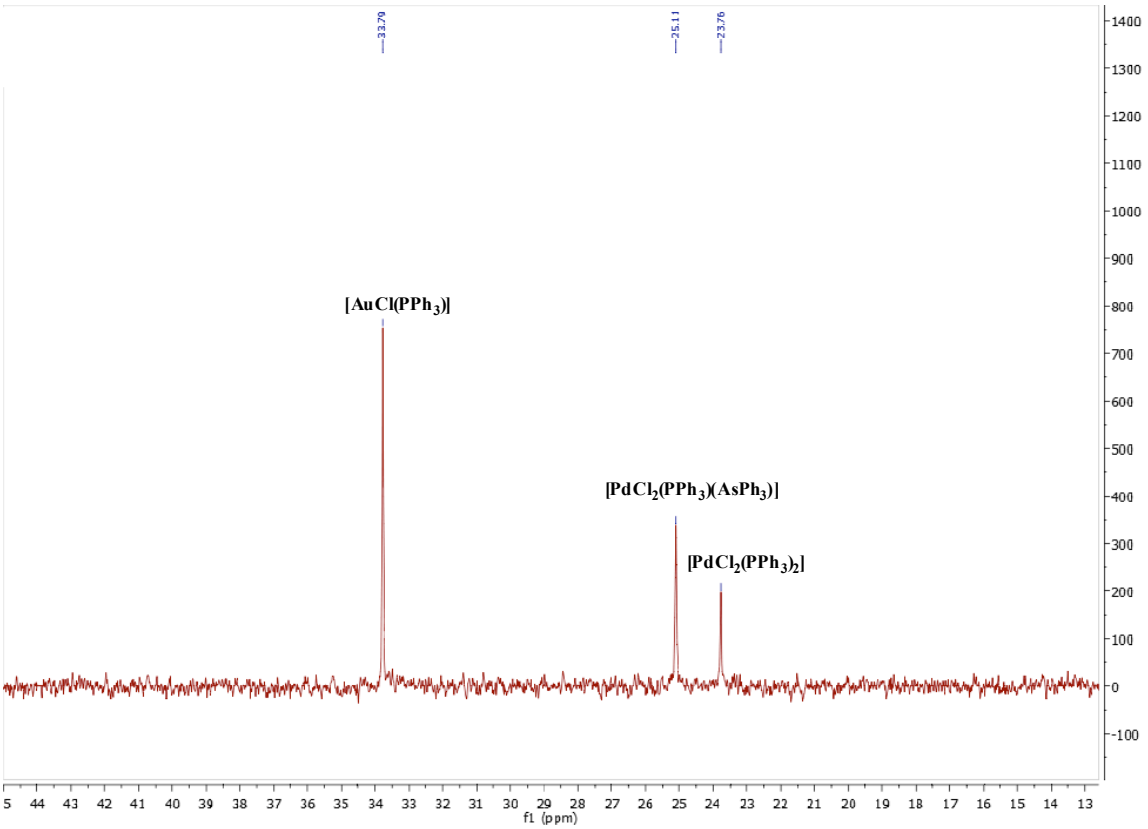


Figure S6. Spectra of $[PdCl_2(PPh_3)_2]$ and $[AuCl(AsPh_3)]$ in $CDCl_3$.

Reaction between $[PdCl_2(AsPh_3)_2]$ and $[AuCl(PPh_3)]$

Corresponding to reaction "c" in Scheme 3 in the main text.

$$[PdCl_2(AsPh_3)_2] + [AuCl(PPh_3)] \xrightarrow[AsPh_3]{CD_3CN,\ 80\ ^oC} \text{No reaction}$$

The reaction between $[PdCl_2(AsPh_3)_2]$ and $[AuCl(PPh_3)]$ in the reported conditions provided only $[AuCl(PPh_3)]$ after 5 minutes in the ^{31}P spectra, either in CD_3CN or $CDCl_3$.

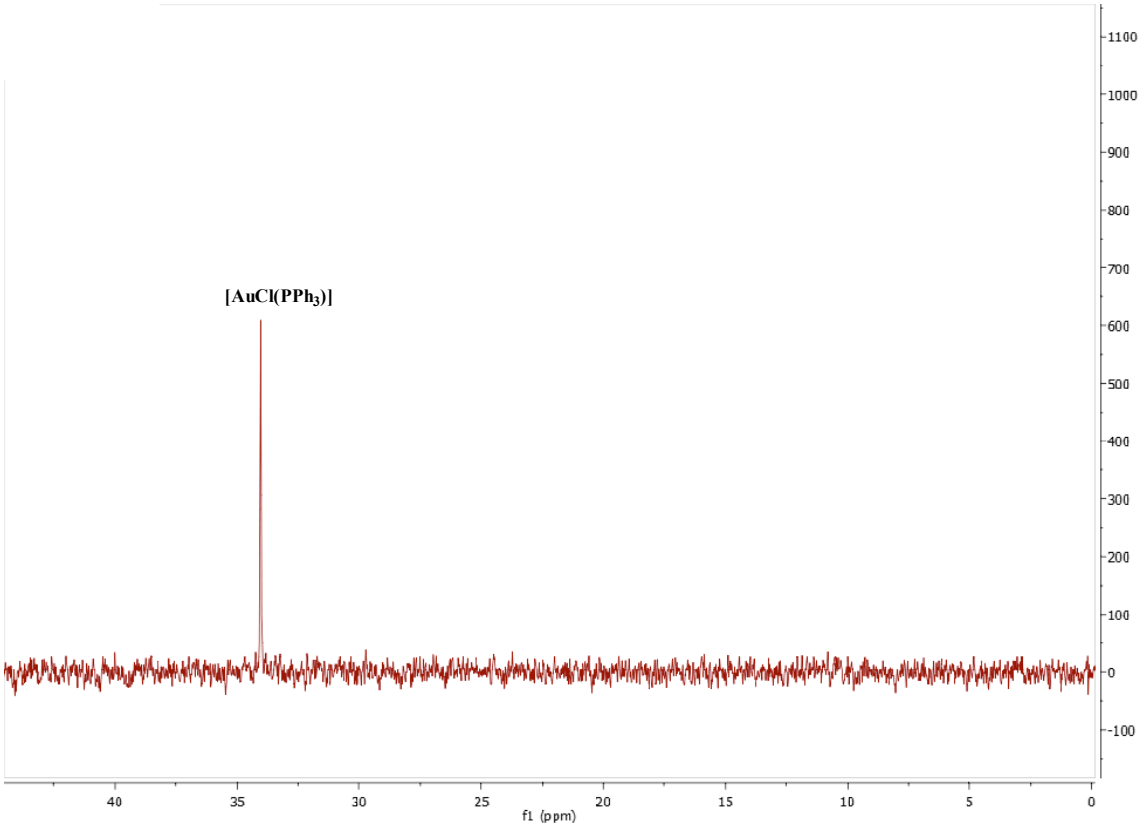


Figure S7. Spectra of $[PdCl_2(AsPh_3)_2]$ and $[AuCl(PPh_3)]$ in CD_3CN after 5 minutes at 80ºC.

References

[1] C. Amman, P. Meier and A. E. Merbach, *J. Magn. Reson.* **1982**, *46*, 319-321

[2] P.Sinha, A. K. Wilson, and M.A.Omary, *J. Am. Chem. Soc.*, **2005**, *127 (36),* 12488–12489.

[3] C. Nieto-Oberhuber, S. López, A. M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178-6179.

[4] H. M. J. Wang, C. Sekhar Vasam, T. Y. R. Tsai, S. Chen, A. H. H. Chang, I. J. B. Lin, *Organometallics,* **2005,** *24* (4), 486-493.

[5] A. H. Norbury, A. L. P. Sinha, *J. Inorg. Nucl. Chem*. **1973**, *35*, 1211-1218.

[6] N. Miyaura, A. Suzuki, *Org. Synth. Coll.* **1993**, *Vol.* 8, 532, (note 8).

[7] E. Lee, D. V. Yandulov, *J. Organometallic Chem.* **2011**, 696, 4095-4103.

[8] A. F. Littke, L.Schwarz, G. C. Fu, *J. Am. Chem. Soc.* **2002**, *124*, 6343–6348.

[9] J. delPozo, D. Carrasco, M. H. Pérez-Temprano, M. García-Melchor, R. Álvarez, J. A. Casares, P. Espinet, *Angew. Chem. Int. Ed.* **2013***, 52,* 2189–2193.