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Heterometallic Complexes by Transmetalation of Alkynyl Groups from Copper or Silver to Allyl Palladium Complexes: Demetalation Studies and Alkynyl Homocoupling

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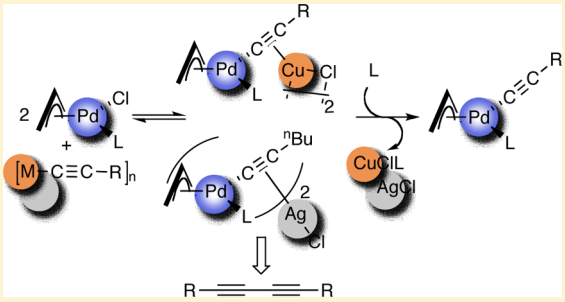
Supporting Information

ABSTRACT: The reaction of [Pd(η^3-allyl)ClL] (L = $AsPh_3$, PPh_3) with $[M(C{\equiv}CR)]_n$ (M = Cu, Ag; R = ^{n}Bu, Ph) leads to transmetalation of the alkynyl group from M to Pd. However, the group 11 metal stays η^2-bound to the new Pd−alkynyl fragment and heterometallic Pd−M complexes are formed with different nuclearities depending on M: [{Pd(η^3-allyl)(alkynyl)L}$CuCl]_2$ (**3**, **4**) or [{Pd(η^3-allyl)(alkynyl)L}$_2$AgCl] (**5**, **6**). The M-containing fragment can be eliminated to give the actual transmetalation complex [Pd(η^3-allyl)(alkynyl)L] by adding an excess of arsine or phosphine, whereas amines do not have this effect. Allyl−alkynyl reductive elimination is a slow process; therefore, complexes **3**−**6** cleanly decompose by dimerization (homocoupling) of the alkynyl group. In the decomposition process reversible alkynyl transmetalation from Pd to Cu has been observed.



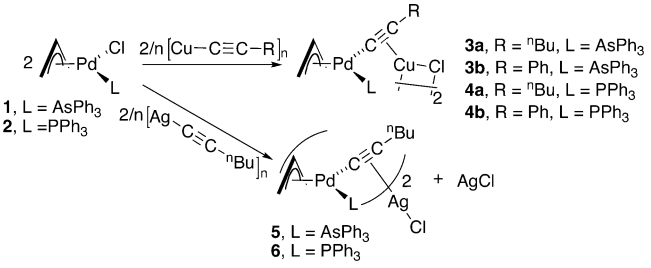
INTRODUCTION

The transmetalation of alkynyl groups from copper to palladium has been used in the synthesis of palladium alkynyls,[1] and it is a crucial step in the classical Sonogashira reaction.[2,3] In both synthetic and catalytic reactions the copper alkynyl is often formed in situ from the alkyne and the copper salt in the presence of base. Although less common, silver alkynyls have also been used for the same purposes.[4] We have studied the reaction of $[M(alkynyl)]_n$ (M = Cu, Ag) with palladium allylic complexes. The allyl moiety is a good donor ligand which introduces little steric hindrance, and it fixes a cis geometry for the remaining ligands around Pd in [Pd(allyl)XL]. Since the reductive elimination of allyl-R in [Pd(allyl)RL] complexes is generally slow, as has been shown for R = aryl[5] and also R = alkynyl groups,[6] we rationalized that other decomposition pathways for the transmetalation product [Pd(allyl)(alkynyl)L] could be studied. Indeed, we have observed that alkynyl transmetalation takes place from Cu or Ag to Pd, but interesting heterometallic derivatives, the result of a failed elimination of the group 11 metal, could be isolated. We have checked what types of ligands induce the elimination of Cu or Ag and studied the decomposition of the complexes.

RESULTS AND DISCUSSION

Synthesis of Heterometallic Cu−Pd and Ag−Pd Complexes. The reaction of a copper(I) alkynyl and the allylic complexes **1** and **2** leads to the heterometallic allyl alkynyl complexes **3** and **4**, where all of the copper is incorporated into the new derivatives (Scheme 1). The analogous reaction with a silver alkynyl leads to a different heterometallic structure, and only half of the silver added is included in the heterometallic framework (**5** and **6**; Scheme 1). Complexes **3**−**6** were completely characterized in solution. All of them except **5** could be isolated in moderate or good yields (60−90%). The molecular structures of **3b**, **4a**,**b**, and **6** were determined by X-ray crystal diffraction. Figures 1 and 2 show ORTEP drawings for complexes **3b**, **4a**, and **6**. The molecular structure of **4b** is analogous to that of the other Cu complexes and can be found in the Supporting Information.

Scheme 1. Synthesis of Heterometallic Cu−Pd and Ag−Pd Complexes



The heterometallic Cu−Pd complexes show a centrosymmetric structure and are formed by two [Pd(η^3-allyl)(alkynyl)L] units linked by a Cu_2Cl_2 unit (Figure 1). The Cu is three coordinated, bound to the alkynyl group in a η^2 symmetric fashion and two chloro atoms. This type of structural unit [(η^2-

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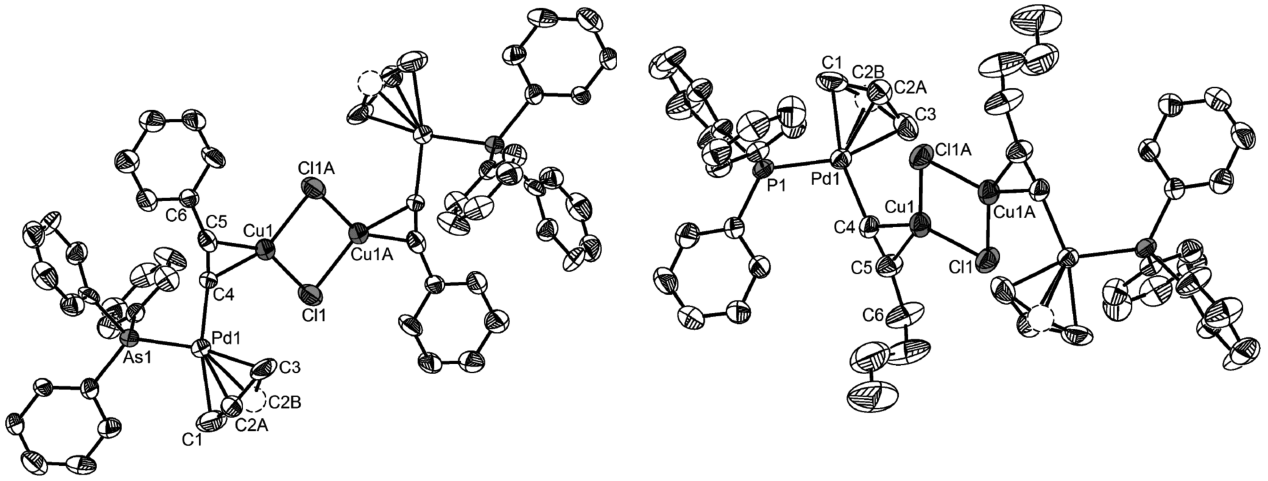

Figure 1. ORTEP drawings of the heterometallic complexes **3b** (left) and **4a** (right).

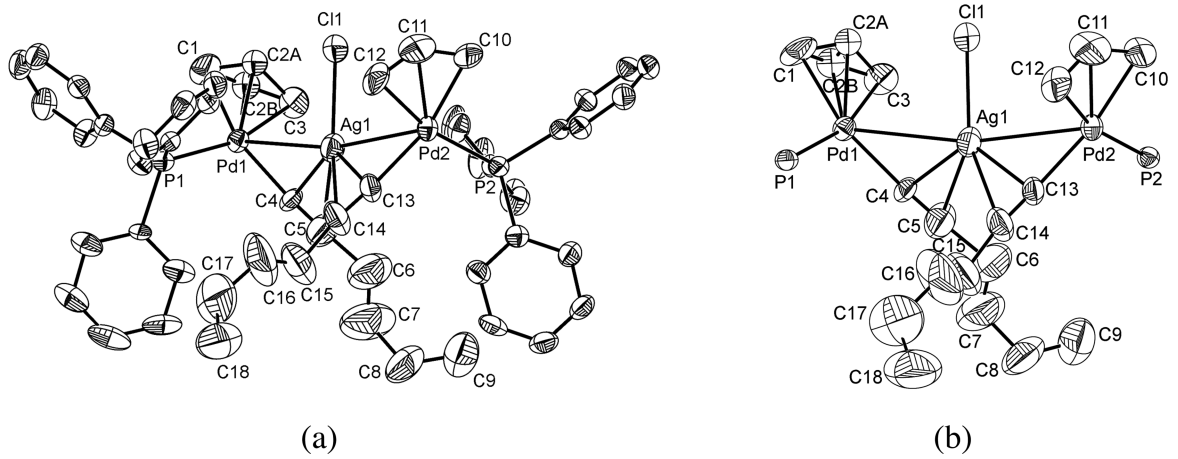

Figure 2. ORTEP drawings of the heterometallic Ag–Pd complex **6**: (a) complete structure; (b) structure with aryl rings of PPh_3 omitted for clarity.

MC≡CR)CuCl]$_2$ has also been found for other heterometallic complexes where M = Fe,[7] Ru,[8] Pt.[9]

The silver derivative **6** shows two [Pd(η^3-allyl)(alkynyl)-(PPh_3)] units bound through η^2 M–alkynyls to the same silver atom. The silver coordination sphere is completed by a Cl and shows a trigonal-planar geometry (Figure 2). This structural feature has been observed before for M = Pt.[9c,10] Silver is asymmetrically coordinated to each η^2 M–alkynyl unit, and the Ag–C_β bond length (2.600(9) Å) is longer than the Ag–C_α distance (2.374(7) Å).[9c,10d,11] The dihedral angle for both (η^2-MC≡CR)Ag planes is 61.8°.

The distances found in all the complexes fall within the expected ranges (Table 1). The allylic moieties show a disordered structure; thus, in all cases the structures were refined with C2 occupying two positions with different occupation factors. The alkynyl unit is somewhat bent, and the angle Pd–C4–C5 has a value in the range 173–168° and the angle C4–C5–C6 in the range 158–172°.

The structures of complexes **3**–**6** show that the alkynyl group is no longer σ-bound to Cu but to Pd and the dissociation of the group 11 metal has not occurred. Intermediates of this type (**A** and **B**, Scheme 2) have been proposed for the transmetalation of alkynyl groups, assuming that a good ligand such as an alkyne could play a role in anchoring both reaction counterparts.[12] Complexes **3**–**6** are

Table 1. Selected Distances (Å) and Angles (deg) for Complexes 3b, 4a, and 6

	3b	4a		6
Pd(1)–C(1)	2.171(16)	2.180(5)	Pd(2)–C(10)	2.177(8)
Pd(1)–C(2A)	2.18(2)	2.142(7)	Pd(2)–C(11)	2.135(8)
Pd(1)–C(2B)	2.17(4)	2.131(14)		
Pd(1)–C(3)	2.184(15)	2.190(4)	Pd(2)–C(12)	2.158(7)
Pd(1)–C(4)	2.039(13)	2.036(4)	Pd(2)–C(13)	2.058(8)
Pd(1)–As(1)	2.4175(18)			
Pd(1)–P(1)		2.3009(11)	Pd(2)–P(2)	2.2843(15)
Cu(1)–Cl(1)	2.305(4)	2.295(12)	Ag(1)–Cl(1)	2.4788(19)
Cu(1)-Cl(1A)	2.315(4)	2.316(13)		
Cu(1)–C(4)	2.023(12)	2.008(4)	Ag(1)–C(13)	2.374(7)
Cu(1)–C(5)	2.036(14)	2.036(4)	Ag(1)–C(14)	2.600(9)
C(4)–C(5)	1.217(17)	1.198(6)	C(13)–C(14)	1.124(10)
Pd(1)–C(4)–C(5)	168.1(11)	172.9(4)	Pd(2)–C(13)–C(14)	173.3(8)
C(4)–C(5)–C(6)	158.6(13)	164.6(5)	C(13)–C(14)–C(15)	172.0(11)

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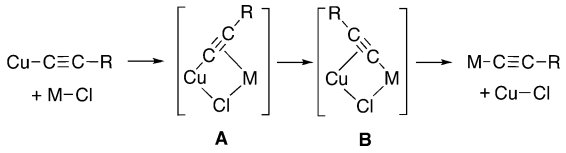
Scheme 2. Simplified Steps in the Transmetalation of Alkynyls



analogous to intermediate **B** and give strong support to the general pathway for transmetalation shown in Scheme 2.

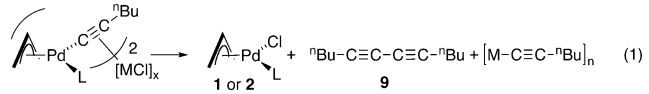
Decomposition of the Heterometallic Complexes. For a successful classical Sonogashira coupling an efficient transmetalation step followed by a fast reductive elimination is desirable and, at some point, elimination of the group 11 metal atom needs to occur. Thus, we have carried out several experiments to find out what types of ligands, usually present in Sonogashira couplings, can eliminate the group 11 metal atom in complexes **3**−**6**. The addition of PPh_3 to a solution of **4a** or **6** in the ratio PPh_3:Pd = 3:1 at 243 K leads to the elimination of Cu or Ag and the formation of $[Pd(\eta^3\text{-allyl})(C{\equiv}Cn\text{-Bu})(PPh_3)]$ (**7**) and a solid identified as $CuClPPh_3$ for **4a** and AgCl for **6**. Complex **7** was synthesized independently by reaction of **2** and a 5-fold molar amount of $SnBu_3C{\equiv}Cn\text{-Bu}$. Figure 3 shows the ^{1}H NMR spectra before and after addition of phosphine and the comparison with **7**.

Similar experiments were carried out with the arsine complexes **3a** and **5**. Upon addition of $AsPh_3$ to **3a** in the ratio $AsPh_3$:Pd = 10:1, $[Pd(\eta^3\text{-allyl})(C{\equiv}C^nBu)(AsPh_3)]$ (**8**) and $CuClAsPh_3$ (or AgCl for **5**) were observed. Complex **8** was synthesized as described above for **7**, and it has been reported before.[6] In this case, a higher ligand to Pd ratio was necessary to drive the equilibrium toward the formation of CuClL, due to the lower coordination ability of $AsPh_3$ in comparison to that of PPh_3.[13] In the case of the silver heterometallic complexes the elimination of the silver follows the same trend and the decoordination of the η^2-alkynyl from Ag is easier for the more coordinating PPh_3. The formation of AgCl as the final product seems to be favored, and this is the solid observed.

Other ligands do not have the same effect. Thus, the addition of an excess of an amine (NEt_3), commonly used as a base in Sonogashira couplings, to complex **3a** does not lead to the elimination of Cu and the formation of **8**. Palladium complexes with arsine or phosphine ligands $[PdCl_2L_2]$ are commonly used in Sonogashira couplings, and according to our results, this is beneficial to complete the transmetalation step. In other type of catalysts such as the so-called "ligandless catalytic systems" (simple palladium salts without other ligands present except for the solvent, reagents and products) this effect is not possible. Hierso el at. have reported that the use of a multidentate ferrocenylphosphine complex of copper instead of CuI makes Sonogashira couplings more efficient. The use of these ligands may affect other steps of the catalytic cycle but also avoids copper coordination to the alkynyl, leading to bimetallic species.[14]

The evolution of complexes **3**−**6** with or without added ligands was followed by ^{1}H NMR. Since the reductive elimination of the allyl and the alkynyl fragments is very slow, the allyl−alkynyl coupling was not observed in any of the experiments and conversely the homocoupling of alkynyl fragments took place. This is a competitive reaction in alkynyl cross-coupling processes but can also be synthetically useful (Glaser reaction).[15]

The decomposition of **3a** (L = $AsPh_3$) at room temperature is slow, and it is complete after 3 days. The products observed by NMR are just the dialkyne $^nBuC{\equiv}CC{\equiv}C^nBu$ (**9**) and **1** (eq 1). The **1**:**9** molar ratio found in solution is 4:1. This is



M = Cu, x = 2: **3a** (L = $AsPh_3$) **4a** (L = PPh_3)
M = Ag, x = 1: **5** (L = $AsPh_3$) **6** (L = PPh_3)

different than the expected ratio (4:2) if all of the alkynyl fragment of **3a** results in the formation of **9**. The remaining alkyne fragment forms $[Cu(C{\equiv}C^nBu)]_n$, which precipitates out and was characterized by IR. The formation of the copper alkynyl clearly shows that Cu−Pd transmetalation is a reversible process. This was also found by Osakada, Sakata, and Yamamoto when they studied the equilibria between $[Pd(C{\equiv}CPh)Ar(PR_3)_2]$ and CuI.[16] The same decomposition pattern and product ratio was observed for **4a**, **5**, and **6**. The

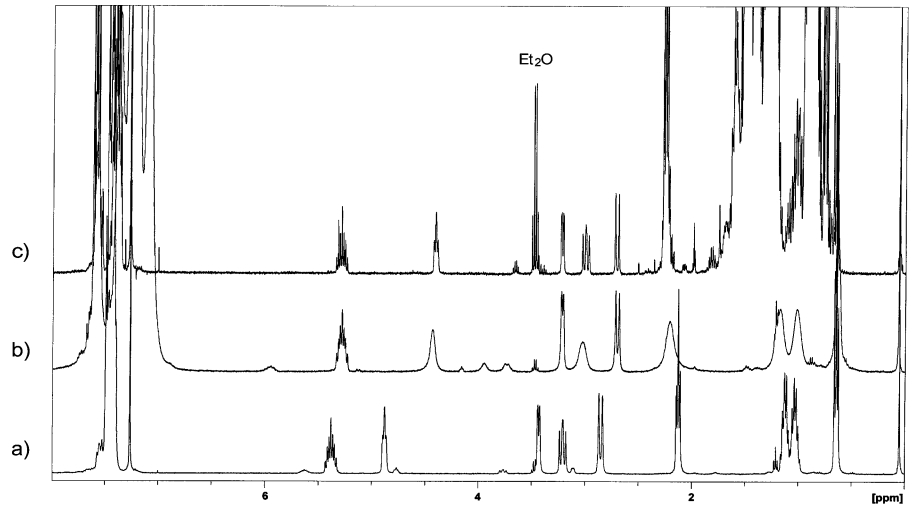


Figure 3. Addition of PPh_3 to **4a** at 243 K: (a) ^{1}H NMR of **4a** before ligand addition; (b) ^{1}H NMR after the addition of PPh_3 (Pd:P = 1:3); (c) ^{1}H NMR of **7** obtained independently by reaction of **2** and $SnBu_3C{\equiv}C^nBu$ (Pd:Sn = 1:5; an excess of stannane is present in the spectrum).

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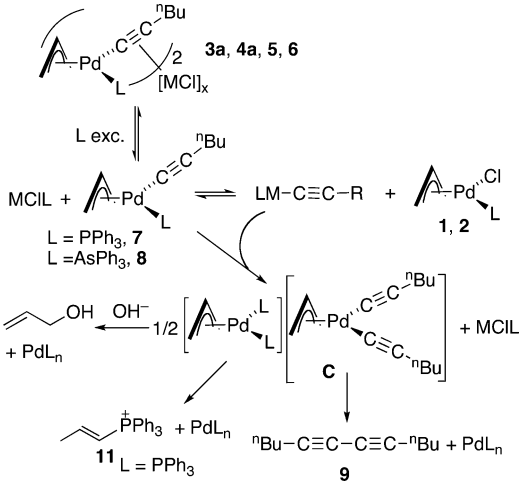
decomposition of the triphenylphosphine complexes takes longer for completion than that of the $AsPh_3$ analogues (cf. 13 days for **4a** vs 3 days for **3a** or 16 h for **6** vs 10 min for **5**). The silver complexes are less stable than the copper derivatives.

Upon addition of an excess of $AsPh_3$ to **3a** (10-fold) and of PPh_3 to **4a** (3-fold) at 243 K, copper demetalation takes place as described above and complexes **8** and **7** formed. These solutions were warmed to room temperature, and the decompositions of the $[Pd(allyl)(C{\equiv}CPh)(EPh_3)]$ complexes in the mixture were monitored (Scheme 3). In comparison to

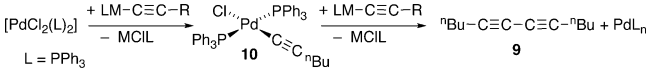
Scheme 3. Decomposition Pathways for Complexes 7 and 8 Formed by Addition of L to Complexes 3−6



the reactions shown in eq 1, the presence of ligands increases the rate of decomposition and the conversion of the alkynyl fragment to **9** is quantitative: the expected molar ratio of allyl-containing compounds to **9** of 2:1 is obtained. Along with **9**, the solution contains complex **1** or **2**, allylic alcohol, and, in the case of **4a**, the phosphonium salt $[PPh_3(1\text{-propenyl})]Cl$ (**11**). Scheme 3 summarizes the decomposition processes, which are analogous for the Cu and Ag complexes bearing the same L.

Alkynyl transfer from complexes **7** or **8** to Cu can occur, as we observed for the decomposition of the heterometallic complexes **3−6** in the absence of added ligand (eq 1). Complex **1** or **2** is observed in most decompostion mixtures (entries 1−3, Table 2). The key intermediate in the formation of the final alkynyl product **9** must be the *cis*-dialkynyl complex **C**, which we did not detect, and it could be formed by two different pathways: (i) ligand rearrangement in complex **7** (or **8**); (ii) transmetalation of an alkynyl fragment from $[Cu(C{\equiv}C^nBu)L]$ to **7**. A reductive elimination in **C** leads to **9**. The excess ligand induces the formation of cationic species $[Pd(\eta^3\text{-}C_3H_5)L_2]^+$, represented as a cation for **C**, where nucleophilic attack on the allyl ligand is quite favorable; thus, the presence of small quantities of water give an allylic alcohol (Scheme 3). When L = PPh_3, a reductive elimination of the phosphine and an allyl group to give $(CH_2{=}CHCH_2PPh_3)Cl$ occurs, although under the reaction conditions, isomerization of the double bond takes place and the thermodynamically more stable **11** is observed (entries 2 and 4, Table 2).[17,18] This process has been observed before and has been proposed to occur in $[Pd(\sigma\text{-allyl})ClL_2]$ complexes.[17] The phosphonium salt $(CH_2{=}CHCH_2PPh_3)Cl$ and **11** are also formed when an excess of PPh_3 is added to **2**, and this has been checked in an independent experiment (see the Supporting Information). The complex *trans*-$[Pd(C{\equiv}C\text{-}nBu)Cl(PPh_3)_2]$ (**10**) was also observed in the experiments with triphenylphosphine, and it eventually decomposes to **9** through a plausible second alkynyl transmetalation, isomerization, and reductive elimination. **10** is the result of an alkynyl transfer to $[PdCl_2(PPh_3)_2]$, formed in the reaction media ($CDCl_3$) presumably by oxidation of PdL_n species (Scheme 4). Alkynyl

Scheme 4. Proposed Pathway for the Formation of 10 and Its Decomposition to 9



palladium complexes analogous to **10** with other alkynyl groups have been reported before,[12,19,20] and we checked the identity of **10** by reacting $ClC{\equiv}C^nBu$[21] and $Pd(PPh_3)_4$ as previously described.[20]

It is noteworthy that, in the decomposition reactions in the presence of excess of ligand, the ^1H NMR spectra of complexes **1** and **2** show the typical fluxional behavior for allylic compounds via fast exchange between (i) η^3- and σ-allylic complexes and (ii) free and coordinated ligand, as well as neutral and cationic species. This kind of behavior has been studied in detail elsewhere.[22] In the presence of a large excess of triphenylphosphine (for example PPh_3:Pd = 10:1), the new alkynyl complex **7** also shows syn−anti exchange for the protons attached to C3 (cis to the phosphine ligand) as well as exchange of free and coordinated phosphine. These fluxional processes are faster as the concentration of L in the solution becomes greater; therefore, it is observed that the appearance of the ^1H NMR spectrum of the complexes (specially **7**) changes as the decomposition proceeds and L is released.

In conclusion, stable heterometallic Pd−Cu and Pd−Ag complexes can be formed in the transmetalation of alkynyl ligands from the group 11 metals to palladium. This is a stage of transmetalation where the carrier metal stays bound to the transferred fragment, and it can be completely eliminated by addition of soft ligands such as phosphines and arsines. Amines do not have the same effect, and elimination of the group 11 metal does not occur. A slow reductive elimination in $[PdR(C{\equiv}C^nBu)L_2]$ complexes, as is the extreme case with R

Table 2. Decomposition Data (%) for Complexes 3−6 in the Presence of an Excess of L[a]

entry	complex	L	Pd:L (mol)	time	**9**	**10**	**1** or **2**	C_3H_5OH	**11**
1	**3a**	$AsPh_3$	1:10	5 h	34		38	28	
2	**4a**[b]	PPh_3	1:3	12 h	33		38	17	10
3	**5**	$AsPh_3$	1:10	2 h	31		52	17	
4	**6**[b]	PPh_3	1:3	7 days	22	18		6	46

[a]Molar percentages were determined by integration of ^1H NMR signals. [b]A small amount of unidentified allylic compounds was detected, which is responsible for the total percentage being lower than 100% (each unidentified compound less than 3%).

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= η^3-allyl, drives the reaction quite effectively to the homocoupling of alkynyls, which is a major competitive process in Sonogashira couplings.

EXPERIMENTAL SECTION

General Methods. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Bruker AC-300, ARX-300, and AV-400 spectrometers. Chemical shifts (in δ units, ppm) were referenced to Me_4Si (^{1}H and ^{13}C) and H_3PO_4 (85%, ^{31}P). The spectral data were recorded at 293 K unless otherwise noted. Signal assignments were made with the aid of heteronuclear ^{1}H−^{13}C HMQC and HMBC experiments. IR spectra were recorded on Perkin-Elmer IR 883 and Perkin-Elmer FT-IR 1720X spectrophotometers. C, H, and N elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyzer.

All of the manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried using an SPS PS-MD-5 solvent purification system or distilled from appropriate drying agents under nitrogen, prior to use. The compounds copper(I) butylacetylide,[23] copper(I) phenylacetylide,[23] silver butylacetylide,[4a,24] $SnBu_3(C{\equiv}C^nBu)$,[25,26] $[\{Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)\}_2]$,[27] $[Pd(\eta^3\text{-}C_3H_5)Cl(AsPh_3)]$ (**1**),[22a,28] $[Pd(\eta^3\text{-}C_3H_5)Cl(PPh_3)]$ (**2**),[28] and $[PdCl_2(PPh_3)_2]$[29] were prepared according to literature methods. The complex $[Pd(\eta^3\text{-}C_3H_5)(C{\equiv}C^nBu)(AsPh_3)]$ (**8**) has been described before.[6] Allyl alcohol and **9** are commercially available and their NMR spectra were compared with authentic samples.

Synthesis of the Heterometallic Complexes $[CuCl\{Pd(\eta^3\text{-}C_3H_5)(C{\equiv}CR)L\}]_2$. *$[CuCl\{Pd(\eta^3\text{-}C_3H_5)(C{\equiv}C^nBu)(AsPh_3)\}]_2$ (**3a**).* $[Cu(C{\equiv}C^nBu)]_n$ (0.2706 g, 1.870 mequiv) was added to a solution of $[Pd(\eta^3\text{-}C_3H_5)Cl(AsPh_3)]$ (0.9147 g, 1.870 mmol) in CH_2Cl_2 (25 mL) at room temperature. The reaction mixture was stirred until the copper(I) acetylide dissolved and the initial yellow solution slowly turned dark reddish. After this time, the mixture was filtered through activated carbon and Celite and then evaporated to dryness. Et_2O (10 mL) was added to the residue, and a grayish solid was obtained, which was filtered, washed with Et_2O (2 × 5 mL), and air-dried. Yield: 0.9270 g (78%). The solid can be recrystallized from a mixture of acetone and hexane at −20 °C. Anal. Calcd for $C_{54}H_{58}As_2Cl_2Cu_2Pd_2$: C, 51.15; H, 4.62. Found: C, 50.95; H, 4.42. ^{1}H NMR (300 MHz, δ, $CDCl_3$): 7.53−7.46 (m, 6H; H_{ortho} $AsPh_3$), 7.45−7.37 (m, 9H; H_{meta}, H_{para} $AsPh_3$), 5.35 (br, 1H; H^2), 4.95 (br, 1H; H^1_{syn}), 3.82 (br, 1H; H^3_{syn}), 3.33 (d, J = 13.4 Hz, 1H; H^1_{anti}), 2.86 (d, J = 13.4 Hz, 1H; H^3_{anti}), 2.20 (t, J = 7.2 Hz, 2H; H^6), 1.32−1.08 (m, 4H; H^7, H^8), 0.73 (t, J = 7.2 Hz, 3H; H^9); ^{13}C{^{1}H} NMR (75.4 MHz, δ, $CDCl_3$, 243 K): 133.9 (s, 3C; C_{ipso} $AsPh_3$), 133.2 (s, 6C; C_{orto} $AsPh_3$), 130.2 (s, 3C; C_{para} $AsPh_3$), 128.9 (s, 6C; C_{meta} $AsPh_3$), 124.4 (s, C^5), 117.3 (s, C^2), 88.5 (s, C^4), 67.1 (s, C^3), 66.9 (s, C^1), 31.6 (s, C^7), 22.8 (s, C^6), 21.7 (s, C^8), 13.6 (s, C^9).

Complexes **3b** and **4a,b** were prepared in the same way by reacting the corresponding palladium complex **1** or **2** and the copper alkynyl.

3b: off-white solid; 77% yield. Anal. Calcd for $C_{58}H_{50}As_2Cl_2Cu_2Pd_2$: C, 53.27; H, 3.86. Found: C, 53.53; H, 4.19. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.53 (m, 6H; H_{ortho} $AsPh_3$), 7.46−7.35 (m, 9H; H_{meta}, H_{para} $AsPh_3$), 7.22−7.10 (m, 3H; H_{meta}, H_{para} Ph), 7.06 (m, 2H; H_{ortho} Ph), 5.44 (br, 1H; H^2), 5.07 (br, 1H; H^1_{syn}), 3.92 (br, 1H; H^3_{syn}), 3.41 (br, 1H; H^1_{anti}), 2.95 (br, 1H; H^3_{anti}); ^{13}C{^{1}H} NMR (100.61 MHz, δ, $CDCl_3$, 243 K): 134.1 (s, 3C; C_{ipso} $AsPh_3$), 133.4 (s, 6C; C_{ortho} $AsPh_3$), 131.3 (s, 2C; C_{ortho} Ph), 130.2 (s, 3C; C_{para} $AsPh_3$), 129.1 (s, 6C; C_{meta} $AsPh_3$), 128.1 (s, 2C; C_{meta} Ph), 127.8 (s, 1C; C_{para} Ph), 124.5 (s, 1C; C_{ipso} Ph), 123.2 (a, C^5), 117.8 (s, C^2), 100.7 (a, C^4), 67.7 (s, C^3), 67.4 (s, C^1).

4a: off-white solid; 86% yield. Anal. Calcd for $C_{54}H_{58}P_2Cl_2Cu_2Pd_2$: C, 54.97; H, 4.96. Found: C, 54.86; H, 4.79. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.60−7.47 (m, 6H; H_{ortho} PPh_3), 7.46−7.35 (m, 9H; H_{meta}, H_{para} PPh_3), 5.39 (br, 1H; H^2), 4.88 (a, 1H; H^1_{syn}), 3.45 (br, 1H; H^3_{syn}), 3.26 (br, 1H; H^1_{anti}), 2.83 (d, J = 13.2 Hz, 1H; H^3_{anti}), 2.16 (t, J = 7.2 Hz, 2H; H^6), 1.21 (m, 2H; H^7), 1.14 (m, 2H; H^8), 0.71 (t, J = 7.2 Hz, 3H; H^9); ^{31}P{^{1}H} NMR (161.97 MHz, δ, $CDCl_3$): 26.4 (s); ^{13}C{^{1}H} NMR (100.61 MHz, δ, $CDCl_3$, 243 K): 133.8 (d, $^2J_{P-C}$ = 13.1 Hz, 6C; C_{ortho} PPh_3), 132.2 (d, $^1J_{P-C}$ = 43.3 Hz, 3C; C_{ipso} PPh_3), 130.7 (s, 3C; C_{para} PPh_3), 128.7 (d, $^3J_{P-C}$ = 10.1 Hz, 6C; C_{meta} PPh_3), 123.6 (s, C^5), 119.0 (d, $^2J_{P-C}$ = 6.0 Hz; C^2), 90.2 (d, $^2J_{P-C}$ = 24.1 Hz; C^4), 69.0 (d, $^2J_{P-C}$ = 3.0 Hz; C^3), 68.3 (d, $^2J_{P-C}$ = 31.2 Hz; C^1), 31.7 (s, C^7), 22.9 (s, C^6), 21.8 (s, C^8), 13.8 (s, C^9).

4b: off-white solid; 75% yield. Anal. Calcd for $C_{58}H_{50}P_2Cl_2Cu_2Pd_2$: C, 57.10; H, 4.14. Found: C, 57.42; H, 4.37. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 7.63−7.51 (m, 6H; H_{ortho} PPh_3), 7.50−7.37 (m, 9H; H_{meta}, H_{para} PPh_3), 7.20−7.07 (m, 3H; H_{meta}, H_{para} Ph), 7.02 (m, 2H; H_{ortho} Ph), 5.46 (br, 1H; H^2), 5.00 (br, 1H; H^1_{syn}), 3.53 (br, 1H; H^3_{syn}), 3.33 (br, 1H; H^1_{anti}), 2.90 (d, J = 12.4 Hz, 1H; H^3_{anti}); ^{31}P{^{1}H} NMR (161.97 MHz, δ, $CDCl_3$): 26.3 (s); ^{13}C{^{1}H} NMR (100.61 MHz, δ, $CDCl_3$, 243 K): 133.9 (d, $^2J_{P-C}$ = 12.1 Hz, 6C; C_{ortho} PPh_3), 132.4 (d, $^1J_{P-C}$ = 42.3 Hz, 3C; C_{ipso} PPh_3), 131.4 (s, 2C; C_{ortho} Ph), 130.9 (s, 3C; C_{para} PPh_3), 128.9 (d, $^3J_{P-C}$ = 11.1 Hz, 6C; C_{meta} PPh_3), 128.1 (s, 2C; C_{meta} Ph), 127.7 (s, 1C; C_{para} Ph), 124.7 (s, 1C; C_{ipso} Ph), 122.4 (s, C^5), 119.4 (d, $^2J_{P-C}$ = 6.0 Hz; C^2), 102.5 (d, $^2J_{P-C}$ = 24.1 Hz; C^4), 69.8 (s, C^3), 68.4 (d, $^2J_{P-C}$ = 31.2 Hz; C^1).

Synthesis of the Heterometallic Complexes $[AgCl\{Pd(\eta^3\text{-}C_3H_5)(C{\equiv}C^nBu)L\}_2]$. *Detection of $[AgCl\{Pd(\eta^3\text{-}C_3H_5)(C{\equiv}C^nBu)(AsPh_3)\}_2]$ (**5**).* $[Pd(\eta^3\text{-}C_3H_5)Cl(AsPh_3)]$ (0.0200 g, 0.041 mmol) was dissolved in $CDCl_3$ (0.6 mL) under nitrogen at 243 K in a 5 mm NMR tube. Silver butylacetylide (0.0085 g, 0.045 mequiv) was added to the solution. The reaction was then monitored by ^{1}H NMR spectroscopy at 243 K, and the formation of complex **5** was observed. ^{1}H NMR (400 MHz, δ, $CDCl_3$, 243 K): 7.60−7.45 (m, 6H; H_{ortho} $AsPh_3$), 7.44−7.32 (m, 9H; H_{meta}, H_{para} $AsPh_3$), 5.33 (m, J = 13.2, 6.0 Hz, 1H; H^2), 4.67 (d, J = 6.5 Hz, 1H; H^1_{syn}), 3.78 (d, J = 6.5 Hz, 1H; H^3_{syn}), 3.25 (d, J = 13.2 Hz, 1H; H^1_{anti}), 2.88 (d, J = 13.2 Hz, 1H; H^3_{anti}), 2.19 (t, J = 7.2 Hz, 2H; H^6), 1.19 (m, 2H; H^7), 1.06 (m, 2H; H^8), 0.66 (t, J = 7.3 Hz, 3H; H^9). ^{13}C{^{1}H} NMR (100.61 MHz, δ, $CDCl_3$, 243 K): 134.4 (s, 3C; C_{ipso} $AsPh_3$), 133.4 (s, 6C; C_{ortho} $AsPh_3$), 130.1 (s, 3C; C_{para} $AsPh_3$), 129.0 (s, 6C; C_{meta} $AsPh_3$), 123.9 (a, C^5), 117.3 (s, C^2), 79.5 (a, C^4), 67.2 (s, C^3), 64.8 (s, C^1), 32.3 (s, C^7), 21.8 (s, C^6), 21.5 (s, C^8), 13.9 (s, C^9).

*Synthesis of $[AgCl\{Pd(\eta^3\text{-}C_3H_5)(C{\equiv}C^nBu)(PPh_3)\}_2]$ (**6**).* Silver butylacetylide (0.06 g, 0.317 mequiv) was added to a solution of $[Pd(\eta^3\text{-}C_3H_5)Cl(PPh_3)]$ (0.1282 g, 0.288 mmol) in CH_2Cl_2 (10 mL) at room temperature. The reaction mixture was stirred until total dissolution of the silver acetylide occurred. The initial yellow suspension slowly turned dark. The mixture was filtered through activated carbon and Celite and then evaporated to dryness. Et_2O (10 mL) was added to the residue, and a grayish solid was obtained which was filtered, washed with Et_2O (2 × 5 mL), and air-dried (62% yield). The solid can be recrystallized from a mixture of acetone and hexane at −20 °C. Anal. Calcd for $C_{54}H_{58}AgClP_2Pd_2$: C, 57.64; H, 5.21. Found: C, 57.78; H, 5.46. ^{1}H NMR (400 MHz, δ, $CDCl_3$, 243 K): 7.60−7.35 (m, 15H; PPh_3), 5.39 (m, J = 12.4, 6.5 Hz, 1H; H^2), 4.67 (t, J = 5.8 Hz, $^3J_{P-H}$ = 5.8 Hz, 1H; H^1_{syn}), 3.44 (d, J = 7.2 Hz, 1H; H^3_{syn}), 3.18 (dd, J = 11.6 Hz, $^3J_{P-H}$ = 11.6 Hz, 1H; H^1_{anti}), 2.85 (d, J = 13.2 Hz, 1H; H^3_{anti}), 2.15 (t, J = 6.8 Hz, 2H; H^6), 1.15 (m, 2H; H^7), 1.03 (m, 2H; H^8), 0.66 (t, J = 7.2 Hz, 3H; H^9). ^{31}P{^{1}H} NMR (161.97 MHz, δ, $CDCl_3$, 243 K): 25.5 (s). ^{13}C{^{1}H} NMR (100.61 MHz, δ, $CDCl_3$, 243 K): 133.8 (d, $^2J_{P-C}$ = 12.1 Hz, 6C; C_{ortho} PPh_3), 132.3 (d, $^1J_{P-C}$ = 43.3 Hz, 3C; C_{ipso} PPh_3), 130.7 (s, 3C; C_{para} PPh_3), 128.7 (d, $^3J_{P-C}$ = 10.1 Hz, 6C; C_{meta} PPh_3), 123.9 (s, C^5), 119.1 (d, $^2J_{P-C}$ = 5.0 Hz; C^2), 77.9 (d, C^4) (signals overlapped with solvent resonances), 69.2 (s, C^3), 66.7 (d, $^2J_{P-C}$ = 33.2 Hz; C^1), 32.3 (s, C^7), 21.8 (s, C^8), 21.5 (s, C^6), 13.8 (s, C^9).

Characterization of $[Pd(\eta^3\text{-}C_3H_5)(C{\equiv}C^nBu)(PPh_3)]$ (7). A 5 mm NMR tube was charged with $SnBu_3(C{\equiv}C^nBu)$ (0.0104 g, 0.028 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl(PPh_3)]$ (**2**; 0.0027 g, 0.006 mmol). Then $CDCl_3$ (0.6 mL) was added under nitrogen at 243 K. The reaction was then monitored by ^{1}H NMR spectroscopy at this temperature, and the formation of complex **7** was observed. ^{1}H NMR (400 MHz, δ, $CDCl_3$, 243 K): 7.70−7.55 (m, 6H; PPh_3), 7.45−7.33 (m, 9H; PPh_3), 5.29 (m, J = 13.6, 7.2 Hz, 1H; H^2), 4.40 (t, $^3J_{P-H}$ = 6.8 Hz, 1H; H^1_{syn}), 3.22 (dd, J = 7.2, 2.0 Hz, 1H; H^3_{syn}), 3.00 (dd, J = 13.5, $^3J_{P-H}$ = 10.7 Hz, 1H; H^1_{anti}), 2.70 (d, J = 13.1 Hz, 1H; H^3_{anti}), 2.25 (t, J = 7.2 Hz, 2H; H^6), 1.30−1.15 (m, 2H; H^7), 1.14−0.95 (m, 2H; H^8), 0.65 (t, J = 7.4 Hz, 3H; H^9). ^{31}P{^{1}H} NMR (161.97 MHz, δ, $CDCl_3$, 243 K): 24.6 (s).

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$^{13}C\{^1H\}$ NMR (100.61 MHz, δ, $CDCl_3$, 243 K): 134.1 (d, $^2J_{P-C}$ = 13.1 Hz, 6C; C_{ortho} PPh_3), 133.7 (d, $^1J_{P-C}$ = 41 Hz, 3C; C_{ipso} PPh_3), 130.7 (d, $^4J_{P-C}$ = 2 Hz, 3C; C_{para} PPh_3), 128.3 (d, $^3J_{P-C}$ = 10.1 Hz, 6C; C_{meta} PPh_3), 118.8 (d, $^2J_{P-C}$ = 6.0 Hz; C^2), 117.2 (s, C^5), 92.3 (d, $^2J_{P-C}$ = 24.1 Hz; C^4), 67.8 (s, C^3), 63.5 (d, $^2J_{P-C}$ = 34 Hz; C^1), 32.4 (s, C^7), 21.9 (s, C^8), 21.4 (s, C^6), 14.0 (s, C^9).

In the presence of an excess of PPh_3, **7** shows a fluxional behavior that exchanges free and coordinated phosphine and H^3 syn and anti protons.

***7* in the Presence of PPh_3 (Pd/PPh_3 = 1/10).** ^1H NMR (400 MHz, δ, $CDCl_3$, 243 K): 8.00−7.00 (m, PPh_3), 5.43 (m, 1H; H^2), 4.60 (d, J = 6.4 Hz, 1H; H^1_{syn}), 3.18 (d, J = 13.6 Hz, 1H; H^1_{anti}), 3.10 (b, 2H; H^3_{syn}, H^3_{anti}) 2.45 (t, J = 7.2 Hz, 2H; H^6), 1.40 (m, 2H; H^7), 1.22 (m, 2H; H^8), 0.83 (t, J = 7.2 Hz, 3H; H^9). $^{13}C\{^1H\}$NMR (100.61 MHz, δ, $CDCl_3$, 243 K): 138.0−128.0 (36C; PPh_3), 119.0 (s, 2C; C^2), 117.3 (s, C^5), 92.5 (s, C^4), 68.1 (s, C^3), 63.7 (s, C^1), 32.6 (s, C^7), 22.1 (s, C^8), 21.6 (s, C^6), 14.4 (s, C^9).

Decomposition of Complexes 3a, 4a, 5, and 6. Solutions of each complex (0.02−0.04 mmol) in $CDCl_3$ (0.6 mL) were prepared in 5 mm NMR tubes under nitrogen. The decompositions were monitored at room temperature by ^1H NMR, and the resulting products (**9** and complex **1** or **2**) were identified and their ratio is collected in Table 2. A brown solid precipitated out, which was identified as $[MC{\equiv}C^nBu]_n$ (M = Cu, Ag).

$[CuC{\equiv}C^nBu]_n$: IR (KBr, cm^{-1}): ν(C≡C) 1925.

$[AgC{\equiv}C^nBu]_n$: IR (KBr, cm^{-1}): ν(C≡C) 2040.

Decomposition of Complexes 3a, 4a, 5, and 6 in the Presence of Excess $AsPh_3$ or PPh_3. Solutions of each complex (0.02−0.04 mmol) in $CDCl_3$ (0.6 mL) were prepared in 5 mm NMR tubes under nitrogen at 243 K. The ligand was added: PPh_3 in the ratio Pd/L = 1/3 for complexes **4a** and **6** or $AsPh_3$ in the ratio Pd/L = 1/10 for complexes **3a** and **5**. The formation of **7** (L = PPh_3) or **8** (L = $AsPh_3$) was observed. Then, the solutions were kept at room temperature and the decompositions were monitored by ^1H NMR. The resulting products were identified, and their ratios are collected in Table 2.

*$[Pd(C{\equiv}C^nBu)Cl(PPh_3)_2]$ (**10**).* ^1H NMR (400 MHz, δ, $CDCl_3$): 8.00−7.00 (m, 30H; PPh_3), 1.39 (t, J = 7.2 Hz, 2H; $C{\equiv}CCH_2-$), 0.69 (m, 2H; $-CH_2CH_2CH_2$), 0.54 (m, 2H; $-CH_2CH_3$), 0.50 (t, J = 7.2 Hz, 3H; $-CH_3$). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): 24.5 (s). $^{13}C\{^1H\}$ NMR (100.61 MHz, δ, $CDCl_3$, 243 K): 135.0 (t, J = 6.0 Hz, 12C; C_{ortho} PPh_3), 130.8 (t, J = 24.2 Hz, 6C; C_{ipso} PPh_3), 130.0 (s, 6C; C_{para} PPh_3), 127.8 (t, J = 5.0 Hz, 12C; C_{meta} PPh_3), 111.7 (t, $^3J_{P-C}$ = 6.5 Hz, 2C; PdC≡C), 79.8 (t, $^2J_{P-C}$ = 14.6 Hz, 2C; PdC), 31.0 (s, 2C; $CH_2CH_2CH_2$), 21.6 (s, 2C; $-CH_2CH_3$), 20.8 (s, 2C; $CH_2C{\equiv}C-$), 13.9 (s, 2C; $-CH_3$).

*$(CH_3CH{=}CHPPh_3)Cl$ (**11**).*[17] ^1H NMR (400 MHz, δ, $CDCl_3$): 8.02 (ddq, 1H; $CH_3CH{=}CH-$) (signals overlapped with other resonances), 6.60 (ddq, J = 22.0, 16.4 Hz, $^2J_{P-H}$ = 6.4 Hz, 1H; $CHPPh_3$), 2.33 (ddd, J = 6.8, 2.4 Hz, $^4J_{P-H}$ = 1.6 Hz; 3H; CH_3). $^{31}P\{^1H\}$ NMR (161.97 MHz, δ, $CDCl_3$): 19.0 (s).

$CuClAsPh_3$. IR (KBr, cm^{-1}): ν($AsPh_3$) 1481 (s), 1433 (vs), 1071 (s), 738 (vs), 693 (vs), 474 (f); ν(Cu−Cl) 305 (w). Anal. Calcd for $C_{18}H_{15}ClCuAs$: C, 53.35; H, 3.74. Found: C, 53.21; H, 3.49.

$CuClPPh_3$. IR (KBr, cm^{-1}): ν(PPh_3) 1481 (s), 1435 (vs), 1093 (s), 1027 (m), 745 (vs), 694 (vs), 521 (vs), 509 (vs); ν(Cu−Cl) 304 (w). Anal. Calcd for $C_{18}H_{15}ClCuP$: C, 59.84; H, 4.19. Found: C, 60.21; H, 4.26.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, tables, text, and figures giving crystallographic data and bond lengths and angles for complexes **3b**, **4a**,**b** and **6** and an ORTEP figure for **4b** and additional experiments and selected spectra of complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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