

Electronic Supplementary Information

Methoxycarbonylation of phenylethyne

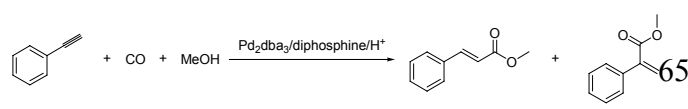
The carbonylation of phenylethyne was carried out using a variety of different ligands to palladium, metal precursors and alcohols as nucleophiles. The results of these studies are collected here.

Alternative ligands

As indicated in the main text, a catalyst comprised of Pd/BDTBPMB/MsOH is highly active for the methoxycarbonylation of phenyl ethyne (Table S1, entry 1). In the absence of BDTBPMB, the only product observed was acetophenone, (Table 4, entry 2). This product has previously been formed during the methoxycarbonylation of phenylethyne and attributed to a non-catalytic reaction with water formed from methanol by methane sulfonic acid catalysed ether formation.^{S1}

Less electron donating and sterically demanding phosphines, such as 1,4-bis(diphenylphosphino)butane (dppb) or 1,2-bis(diphenylphosphinomethyl)benzene (BDPPMB) were found to be less active and selective than BDTBPMB and resulted in an increased acetophenone (Table S1, entries 3 and 4). Despite previous studies showing that 1,2-bis(diterbutylphosphinomethyl)ferrocene, (BDTBPMB) is an effective analogue of BDTBPMB for carbonylation chemistry,^{S2} it promoted lower yields and an increase in acetophenone production in comparison to BDTBPMB, (Table S1, entry 5).

Table S1. Methoxycarbonylation of phenylethyne catalysed by Pd/Phosphine systems.^a



Entry	Diphosphine	Ester yield (%)	Linear Sel. (%)	Acetophenone
1	BDTBPMB	>99	91	0
2	-	0	-	52
3	dppb	65	51	30
4	BDPPMB	52	29	12
5	BDTBPMB	65	91	8

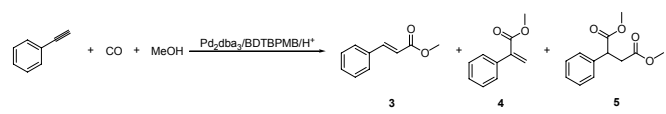
^a Conditions: Phenylethyne (1 cm³, 9.1 mmol), [Pd₂dba₃] (4.2 mg, 0.0046 mmol), diphosphine (0.055 mmol), MsOH/Pd ratio (30:1), T = 80°C, p_{CO} = 30 bar, MeOH (10 cm³), 3 h.

Alternative palladium precursors

The air-stable [Pd₂dba₃] has highly labile dba ligands, which allows this palladium (0) species to be an effective catalyst precursor for carbonylation reactions. Despite this it has been shown that the displacement of the dba by a phosphine or substrate can be difficult and on occasion may not take place at all.^{S3} Studies using other precatalysts (Table S2) show that [Pd(MeCN)₂Cl₂] is slightly better in terms of linear selectivity, and whereas [Pd₂dba₃] does not produce the

dicarbonylation product, **5**, under the conditions studied (Pd 0.1 mol %), [Pd(MeCN)₂Cl₂] does produce small amounts (Table S2, entry 2). This may indicate some effect of the halide. [Pd(BDTBPMB)Cl₂] can form under related conditions since crystals of this complex, which has been characterised crystallographically, see below, were isolated from a hydroxycarbonylation reaction when using [Pd(MeCN)₂Cl₂] under similar conditions.

Table S2. Other palladium precatalysts for the methoxycarbonylation of phenylethyne.^a



Entry	Palladium precatalyst	Additive	Ester (3+4) yield (%)	Linear Sel. (%)	5 yield (%)	Acetophenone (%)
1	[Pd ₂ dba ₃]	-	>99	91	0	0
2	[Pd(MeCN) ₂ Cl ₂]	-	98	>99	2	0
3	[Pd ₂ dba ₃]	NBu ₄ I (5 mol %)	98	95	2	0
4	[Pd ₂ dba ₃]	NBu ₄ F (5 mol %)	>99	90	0	0
5	[Pd(OAc) ₂]	-	96	90	0	4
6	[Pd(1)dba] ^{b, c}	-	14	90	0	10
7	[Pd(1)dba]	-	95	>99	5	0
8	[Pt(MeCN) ₂ Cl ₂]	-	97	97	3	0

^a Conditions: Phenylethyne (1 cm³, 9.1 mmol), "Pd" (0.0091 mmol), BDTBPMB (22 mg, 0.055 mmol), additive (as indicated), MsOH/Pd ratio (30:1), T = 80°C, p_{CO} = 30 bar, MeOH (10 cm³), 3 h; ^b Pd black formation was observed; ^c No additional ligand was added.

To explore the possibility of a halide effect,^{S4} two experiments were carried out. The methoxycarbonylation was carried out under normal conditions in the presence of an iodide (NBu₄I) or fluoride (NBu₄F) source. Fluoride does not result in any apparent change in activity (Table S2, entry 3), but iodide improves catalyst efficiency and yields some **5** (Table S2, entry 4). However this catalyst system is unstable giving appreciable formation of palladium black.

The reaction catalysed by [Pd(OAc)₂]/BDTBPMB gave slightly lower yields (Table S2, entry 5), perhaps because of the known generation of a palladacycle by coordination of only one P atom and C-H activation of the aromatic C-H bond *ortho* to the coordinated P.^{S5} This catalyst was also unstable.

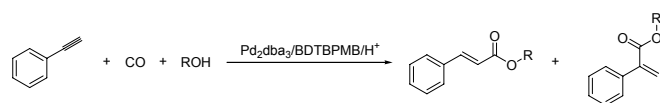
[Pd(BDTBPMB)dba] without added excess ligand was unstable, precipitating palladium black (Table S2, entry 6), but was stabilised by addition of excess BDTBPMB. A significant increase in complex stability was observed in the presence of excess ligand giving similar results to those obtained when the complex was formed *in situ* (Table S2, entry 7).

A few cases of platinum catalysed methoxycarbonylations have been reported.^{S6, S7} In the case of platinum complexes of BDTBPMB, methoxycarbonylation of alkenes is slower than for the palladium analogues.^{S7} Unusually, we find that the platinum analogue shows high conversion and selectivity for

phenylethyne carbonylation, (Table S2, entry 8).

Alternative alcohols

Table S3. Alkoxy carbonylation of phenylethyne using different alcohols.^a 30



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Entry	Alcohol	Ester yield (%)	Linear Sel. (%)
1	EtOH	>99	99
2	ⁱ PrOH	>99	93
3 ^b	PhOH	78	82

^a Conditions: Phenylethyne (1 cm³, 9.1 mmol), [Pd₂dba₃] (4.2 mg, 0.0046 mmol), BDTBPMB (22 mg, 0.055 mmol), MsOH/Pd ratio (30:1), T = 80°C, pCO = 30 bar, ROH (10 cm³), 3 h; ^b PhOH (10 g).

As expected, similar results were obtained when the alkoxy carbonylation reaction was carried out in the presence of ethanol instead of methanol, generating the corresponding ethyl ester (Table S3, entry 1). No double carbonylation was detected in the crude reaction products. High yields were also obtained when using the more hindered *isopropanol* (Table S3, entry 2).

It has been reported^{S8} that, in the alkoxy carbonylation of alkenes catalysed by [Pd(PPh₃)₂Cl₂]/SnCl₂, the reaction rate was significantly decreased when using phenol, a poorer nucleophile than methanol.^{S8, S9} Similarly a significant decrease in ester yield and regioselectivity was observed when the phenoxy carbonylation of phenylethyne was carried out in phenol using Pd/BDTBPMB as the catalyst. (Table S3, entry 3).

X-ray crystal and molecular structure of BDTBPMB

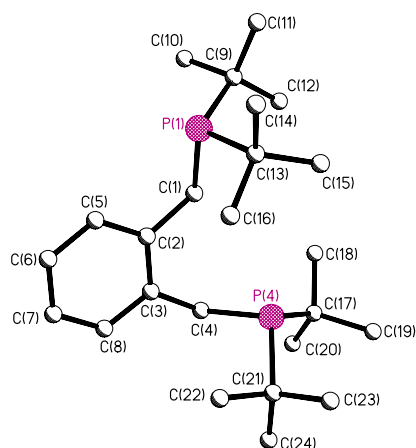


Fig S1 X-Ray structure and numbering scheme for BDTBPMB, 1. H atoms are omitted for clarity

The structure of BDTBPMB (1) is as expected with the phosphines orientated away from one another to reduce steric repulsions between the bulky Bu^t groups.

X-ray crystal and molecular structure of [BDTBPMBH₂][BF₄]₂

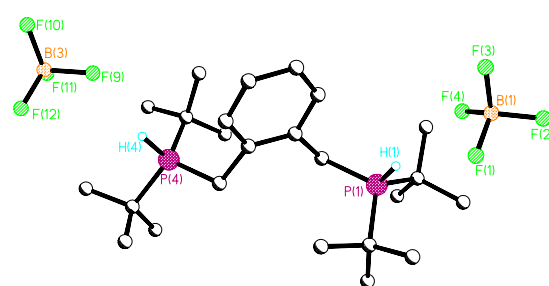


Fig. S2. X-ray structure and partial numbering scheme for [BDTBPMBH₂][BF₄]₂

The structure of [BDTBPMBH₂][BF₄]₂ (Figure S2) contains two independent molecules in the asymmetric unit. The bond lengths and angles are within normal ranges. The phosphorus atoms lie above and below the aryl ring [values for second independent molecule in parentheses] P(1) 1.57(1) [1.52(1)] P(4) -1.66(1) [-1.54(1)] Å, the P..P separation is > 6 Å. The P-H hydrogen atoms interact with the [BF₄]⁻ anions: H1 - F4 2.40(3), P1 - H1 - F4 140.1; H4 - F9 2.32(2) P4 - H4 - F9 157.0; H31 - F11 2.44(4) P31 - H31 - F11 139.5; H34 - F2' 2.30(3) P34 - H34 - F2' 148.8°.

45 X-ray crystal and molecular structure of [PdCl₂(BDTBPMB)]

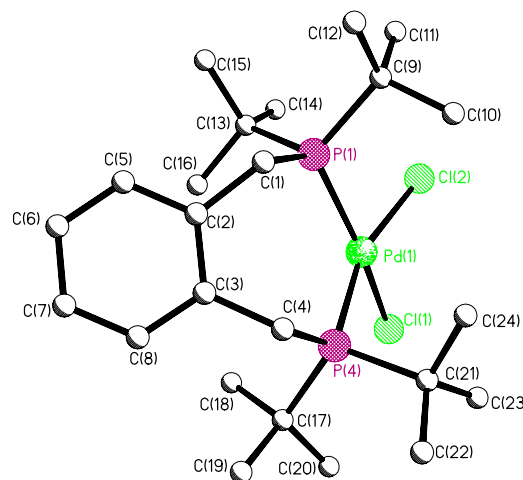


Fig S3. X-ray structure and numbering scheme for [PdCl₂(BDTBPMB)] (Hydrogen atoms omitted for clarity).

Selected bond lengths and angles for [Cl₂Pd(BDTBPMB)] (Figure S3) are collected in Table S4. Interestingly the Pd-P bond lengths are noticeably different from each other in this complex (Pd-P(1) 2.3094(8), Pd-P(4) 2.3288(8) Å) and the complex is quite distorted from square planar with the Cl-Pd-Cl mean plane twisted by 20.8° with respect to the P-Pd-P

mean plane with Cl(1) and Cl(2) lying 0.52(1) above and -0.59(1) Å below the P₂Pd mean plane. The ligand is hinged about the C(1)...C(4) axis; with the Pd-P(1)-P(4)-C(1)-C(4) section of the complex being essentially planar and inclined by 54 ° to the C(1)-C(8) mean plane. The Cl-Pd-Cl angle in [Pd(BDTBPMB)Cl₂] is *ca.* 7 ° smaller than that in [Pd(BDPPMB)Cl₂].^{S10} The difference can be attributed to the appreciable difference in steric effects between the Bu^t and phenyl substituents on the phosphorus atoms of the ligands. Steric effects are probably also responsible for the longer Pd-P distances (by *ca.* 0.05 Å) in [Pd(BDTBPMB)Cl₂] than in [Pd(BDPPMB)Cl₂].

Table S4. Selected bond lengths and angles for [Pd(BDTBPMB)Cl₂]

Selected bond lengths (Å)

Pd(1)-P(1)	2.3094 (8)
Pd(1)-P(4)	2.3288 (8)
Pd(1)-Cl(1)	2.3645 (7)
Pd(1)-Cl(2)	2.3602 (8)

Selected angles(°)

P(1)-Pd(1)-P(4)	101.88 (3)
P(1)-Pd(1)-Cl(2)	88.38 (3)
P(4)-Pd(1)-Cl(2)	162.26 (3)
P(1)-Pd(1)-Cl(1)	162.72 (3)
P(4)-Pd(1)-Cl(1)	89.97 (3)
Cl(2)-Pd(1)-Cl(1)	83.60 (3)

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- S9 For an interesting example of alkoxy-carbonylation of alkynes using phenol, see ref 4c.
- S10 M. D. Brown, W. Levason, G. Reid and R. Watts, *Polyhedron*, 2005, **24**, 75