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Regioselective Hydromethoxycarbonylation of Terminal Alkynes Catalyzed by Palladium(II)−Tetraphos Complexes

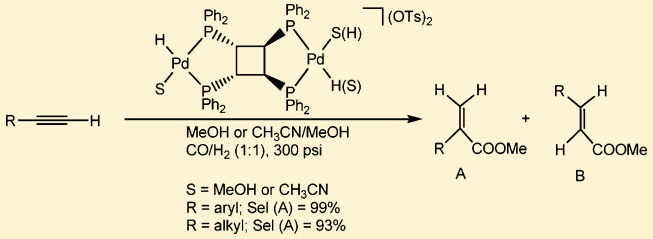
Werner Oberhauser,*[,†] Andrea Ienco,[†] Francesco Vizza,[†] Barbara Trettenbrein,[‡] Dennis Oberhuber,[‡] Christof Strabler,[‡] Teresa Ortner,[‡] and Peter Brüggeller*[,‡]

[†]Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Area di Ricerca CNR di Firenze, via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

[‡]Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 80-82, 6020 Innsbruck, Austria

Supporting Information

ABSTRACT: An in situ generated dinuclear palladium hydride complex bearing *cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphosphanyl)cyclobutane catalyzed the hydromethoxycarbonylation of terminal alkynes, giving the corresponding branched *α*,*β*-unsaturated ester (A) with high regioselectivity.



The hydromethoxycarbonylation of terminal alkynes to give *α*,*β*-unsaturated carboxylic acids or esters is a highly valuable synthetic process, which finds its major application in the synthesis of methyl methacrylate (MMA)[1] and its derivatives (i.e., application in polymer synthesis)[2] or in the synthesis of pharmaceutical products such as the optically pure anti-inflammatory drugs (*S*)-ibuprofen and (*S*)-naproxen.[3] Hydromethoxycarbonylation reactions of terminal alkynes are generally mediated by Pd(II)-phosphane-based catalyst precursors, which yield a plethora of possible products that originate from mono- and dicarbonylation reactions.[4] The chemo- and regioselectivity of the catalytic carbonylation reactions are hence important issues to be addressed. The most significant examples of regio- or chemoselective catalytic hydromethoxycarbonylation reactions of terminal alkynes reported so far are (i) the regioselective conversion of propyne into MMA by the highly active Pd(II)/2-PyPPh$_2$ catalyst system,[1] (ii) the synthesis of linear *α*,*β*-unsaturated carboxylic esters mediated by Pd(II)/diphosphane catalyst precursors (i.e., acceptable substrate conversion as well as a diphosphane bite angle dependent regioselctivity were obtained only with at least a 3-fold excess of diphosphane ligand with respect to Pd(II)),[5] (iii) the chemoselective synthesis of alkynylcarboxylic esters by PdCl$_2$/Cu-based[6a] and Pd(II)-TROPP (TROPP = 5-(diphenyl)phosphanyl-5*H*-dibenzo[*a*,*d*]cycloheptene)-based catalysts.[6b] The latter catalyst system was shown to be stereospecific when *p*-benzoquinone was used as oxidizing agent. Herein we report the synthesis and successful application of dinuclear Pd(II)-dppcb (dppcb = *cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphospanyl)cyclobutane)[7] complexes for the regioselective hydromethoxycarbonylation of terminal alkynes.

RESULTS AND DISCUSSION

The dinuclear Pd(II) complexes **1**−**3** bearing dppcb were synthesized by following the synthetic procedures shown in Scheme 1. The tetracationic Pd(II)−aqua complex **1** was obtained upon protonation of the corresponding in situ synthesized Pd(II) acetate complex[8] with *p*-toluenesulfonic acid (*p*-TsOH) with the concomitant release of acetic acid. The coordination of two water molecules to each palladium center in **1** was confirmed by a corresponding ^{1}H NMR spectrum, acquired in CD$_2$Cl$_2$, which showed a broad hump at 3.2 ppm integrating for approximately eight hydrogen atoms. Moreover, conductivity measurements of **1** in MeOH, which is the reaction medium for the catalytic hydromethoxycarbonylation reactions, corroborated its behavior as a 1:4 electrolyte.

The neutral bimetallic compound **2** was obtained upon reaction of dppcb with [PClMe(*η*^{4}-COD)] in CH$_2$Cl$_2$. The ^{31}P{^{1}H} NMR spectrum of **2** exhibited two singlets centered at 70.3 and 54.7 ppm and two doublets at 69.4 and 56.1 ppm with a *J*(PP) value of 5.8 Hz. This spectroscopic finding is in accordance with the occurrence of two geometrical isomers (i.e., *cis* and *trans* isomers (centrosymmetric)) in an 1:2 ratio. On the basis of the significantly different *trans* influences of chloride and a methyl group in square-planar Pd(II) complexes, the high-frequency ^{31}P NMR signals at 70.3 and 69.4 ppm were assigned to the phosphorus atoms located *trans* to chloride.

The reaction of **2** with Ag(OTs) in CH$_2$Cl$_2$ gave the corresponding bis-cationic isomers of **3** in the same ratio as those of **2**. The ^{1}H NMR spectrum of **3**, acquired in CD$_2$Cl$_2$, showed the absence of a signal which might be attributed to palladium-coordinating water molecules. As a consequence, tosylate coordinates to palladium in the solid state and CD$_2$Cl$_2$. On the other hand, **3** was completely soluble in MeOH and behaved as a 1:2 electrolyte in the latter solvent.[9] The bis-cationic complex **4**, which was straightforwardly obtained,

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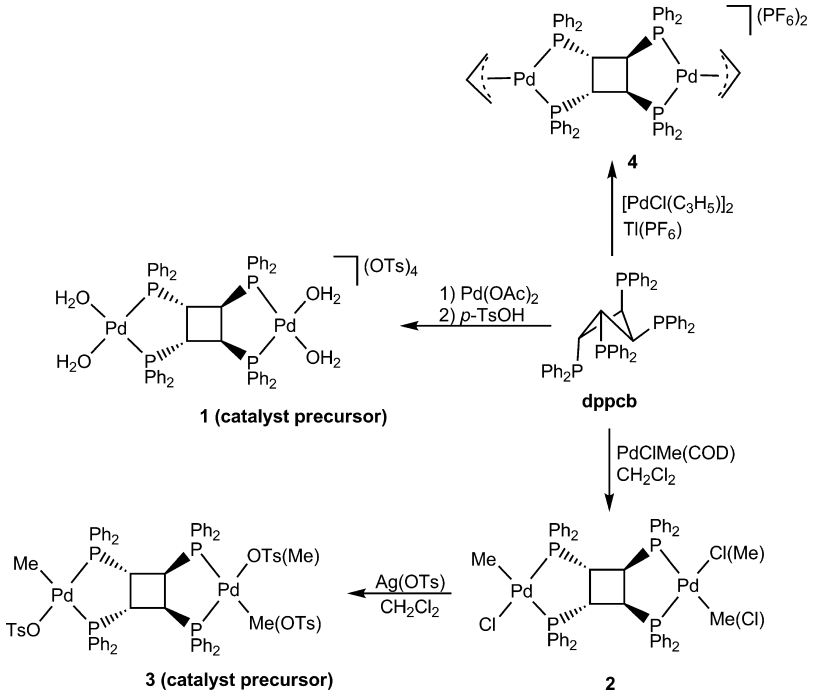
Scheme 1



showed only in DMSO-d_6 or CD_3CN a slight solubility. The dynamic allyl coordination to palladium in **4** was evidenced in solution by broad ^1H NMR singlets for the allyl hydrogen atoms at 3.62 and 5.96 ppm.

The single-crystal X-ray structure analyses of *trans*-**2**·4DMF[10] (Figure 1) and of **4**·CH_2Cl_2 (Supporting Information) confirmed the planarity of the cyclobutane carbon ring and the envelope conformation of the five-membered palladium−diphosphane cycles defined by Pd(1), P(1), P(2), C(1), and C(2) and their symmetry-equivalent counterparts.

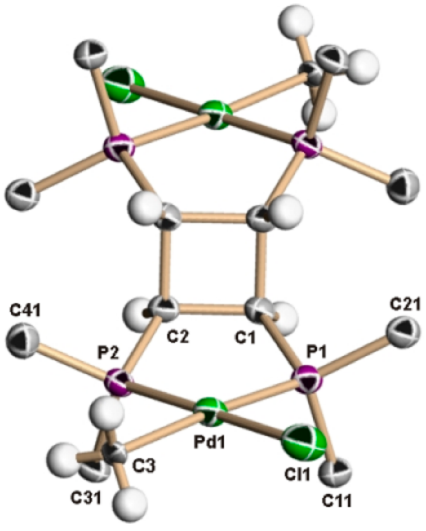


Figure 1. ORTEP plot of *trans*-**2**·4DMF. Thermal ellipsoids are shown at the 30% probability level. Solvent molecules and hydrogen atoms except for the cyclobutane carbon ring have been omitted, and only the *ipso* carbon atoms of the phenyl rings are shown for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−P(1) = 2.2969(10), Pd(1)−P(2) = 2.2246(11), Pd(1)−Cl(1) = 2.3581(12), Pd(1)−C(3) = 2.191(3), C(1)−C(2) = 1.564(5), C(1)−C(2)$^{\#}$ = 1.556(4); P(1)−Pd(1)−P(2) = 85.42(4), C(3)−Pd(1)−Cl(1) = 86.61(11). Symmetry-equivalent position: (#) $-x, -y, -z$.

A comparison of the envelope angles (i.e., defined as the interplanar angle between the least-squares planes through P(1), P(2), C(1), C(2) and Pd(1), P(1), P(2), respectively) found in *trans*-**2**·4DMF and **4**·CH_2Cl_2 showed only a slight dependence on the nature of the ancillary ligand present (i.e., 26.25(0.13)° in *trans*-**2**·4DMF and 32.61(0.10)° in **4**·CH_2Cl_2). A direct consequence of the envelope conformation of the palladium−diphosphane cycles is a fixed spatial orientation of the phenyl rings with respect to the palladium coordination plane defined by Pd(1), P(1), and P(2) with the axially oriented phenyl rings (i.e., C(11) and C(31)) pointing in the same direction.

Catalyst precursors **1** and **3** have been screened in the hydromethoxycarbonylation reaction of selected terminal alkynes carried out in neat MeOH or a 9:1 solvent mixture of CH_3CN and MeOH. The optimal CO pressure was revealed to be 150 psi, and catalytic reactions carried out under syngas conditions (i.e., CO/H_2 (150/150 psi); a hydrogen pressure higher than 150 psi gave no beneficial effect in terms of substrate conversion) showed significantly higher substrate conversion in comparison to identical reactions conducted in the absence of hydrogen.[5b] The catalytic performance of dppcb-based precursors (i.e., **1** and **3**) (Table 1) has been compared with that of $[Pd(H_2O)_2(PP)](OTs)_2$ (PP = *meso*-2,3-bis(diphenylphosphanyl)butane (**5**) and 1,2-bis(diphenylphosphanyl)ethane (**6**)), which are characterized by a comparable ligand bite angle of ca. 85° but a typical twist conformation of the five-membered palladium−diphosphane cycle, as shown by the corresponding single-crystal X-ray structure analysis (Supporting Information). In addition, the catalytic performance of **1** has been compared with that of $[Pd(H_2O)_2(dppf)](OTs)_2$ (**7**; dppf = 1,1′-bis(diphenylphosphanyl)ferrocene),[11] since dppf-based palladium precursors are known to be among the most active catalysts for the hydromethoxycarbonylation of terminal alkynes.[5]

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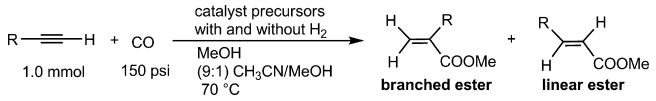
Table 1. Pd(II)-Phosphane Catalyzed Hydromethoxycarbonylation of Terminal Alkynes[a]



				conversn (%)[b] [TOF][c]		selectivity br. ester (%)
entry	cat. precursor	substrate (R)	$p(H_2)$ (psi)	1 h	2 h	1 h/2 h
1	**1**	phenyl	0	31 [31]	54 [27]	99/99
2	**1**	phenyl	150	n.d.	95 [48]	n.d./99
3[d]	**1**	phenyl	0	49 [196]	n.d.	99/n.d.
4[d]	**1**	phenyl	150	65 [260]	100 [200]	99/99
5	**1**	4-methoxyphenyl	150	n.d.	80 [40]	n.d./99
6	**1**	4-chlorophenyl	150	n.d.	97 [49]	n.d./99
7	**1**	2-methoxyphenyl	150	n.d.	98 [49]	n.d./99
8	**1**	hexyl	150	n.d.	51 [26]	n.d./93
9[d]	**1**	hexyl	150	12 [48]	20 [40]	87/87
10	**1**	decyl	150	n.d.	40 [20]	n.d./93
11	**3**	phenyl	0	15 [15]	24 [12]	99/99
12	**3**	phenyl	150	n.d.	94 [47]	n.d./99
13	**5**	phenyl	0	20	37 [19]	85/85
14	**5**	phenyl	150	n.d.	54 [27]	n.d./85
15[d]	**5**	phenyl	150	6 [24]	n.d.	86/n.d.
16	**6**	phenyl	0	14	16 [8]	85/85
17	**6**	phenyl	150	n.d.	36 [18]	n.d./84
18	**6**	2-methoxyphenyl	150	n.d.	21 [11]	n.d./84
19	**6**	hexyl	150	n.d.	46 [23]	n.d./45
20	**6**	decyl	150	n.d.	37 [19]	n.d./52
21[d]	**7**	phenyl	150	12 [48]	16 [32]	30/30

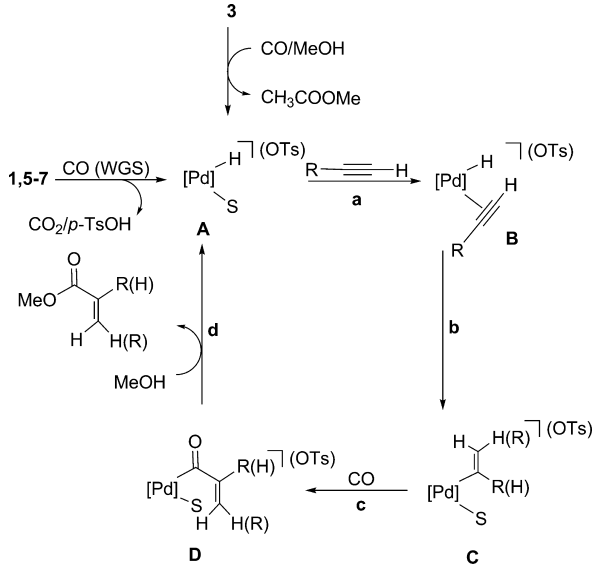
[a]Conditions: catalyst precursor (0.01 mmol Pd), substrate (1.00 mmol), MeOH (10.0 mL), CO (150 psi), T (70 °C). [b]Substrate conversion determined by GC using *n*-decane as internal standard. [c]TOF defined as mmol of substrate converted ((mmol of precursor) h)$^{-1}$. [d]Conditions: precursor (0.005 mmol Pd), substrate (2.00 mmol), 9:1 solvent mixture of CH_3CN and MeOH (10.0 mL).

Under the applied experimental conditions the corresponding α,β-unsaturated branched and linear esters (Table 1) were the only carbonylation products obtained. Two experimental facts were found: (i) the conversion was increased on conducting catalytic reactions in the presence of hydrogen gas (i.e., hydrogen gas stabilizes Pd−H species and unlike protic acids avoids the hydration of alkynes giving ketones) and (ii) analogous reactions carried out in the presence of 2,6-dimethoxybenzoquinone gave not even traces of the α,β-unsaturated esters, the corresponding alkynyl-methoxycarboxylate[6] being obtained instead. This experimental fact proves that Pd−OCH_3 is not the catalytically active species.[12] As a consequence, the unsaturated esters were obtained by a Pd−H-based catalytic cycle,[13] as shown in Scheme 2.

The palladium hydride (Scheme 2, A), which is the key intermediate in the catalytic cycle, was generated from either Pd−aqua complexes (i.e., **1**, **5**−**7**) by a water-gas shift (WGS) reaction[14] or from a palladium−alkyl species[12] (i.e., **3**) upon CO insertion and a subsequent methanolysis reaction releasing methyl acetate, the presence of which in the catalyst solution was proved by GC-MS analysis. The stabilizing effect of *p*-TsOH for the catalyst, formed upon the WGS reaction of Pd−aqua complexes, is nicely demonstrated by carrying out catalytic reactions of **1** and **3** in MeOH in the absence of hydrogen pressure (Table 1, entries 1 and 11).

Regardless of the substrate and reaction medium employed, dppcb-based precursors gave the highest regioselectivity for the branched esters (i.e., 99% and 93% for aromatic and aliphatic terminal alkynes, respectively) (Table 1). In order to rationalize this experimental result, the corresponding regioselectivity-determining Pd−hydride alkyne intermediate[15] (i.e., the terminal alkyne hydrogen atom is pointing toward the Pd−H moiety) (Scheme 2, B) in the case of dppcb-based precursors was mimicked by a geometry-optimized model compound that bears *cis*-1,2-bis(diphenylphosphanyl)cyclobutane (L) as a model ligand.

Scheme 2



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Importantly, the model ligand exhibits all the characteristics of monocoordinated dppcb (i.e., rigid and planar cyclobutane carbon ring, which was theoretically realized by forcing the dihedral angle of the four carbon atoms to be 0°). Both possible model compounds of $[Pd(H)(L)(C_6H_5C_2H)]^+$ were calculated using the B97-D method, which takes into account the dispersion forces.[16] The most interesting structural features arising from the model compound calculated for the pro-branched isomer, as shown in Figure 2, are (i) the carbon−carbon triple

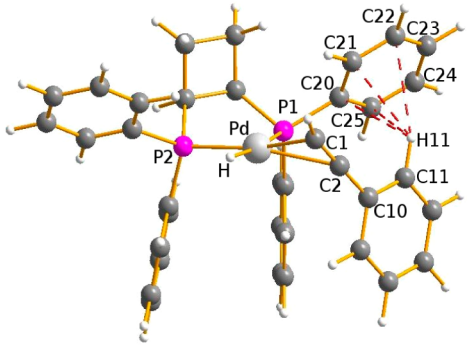

Figure 2. Optimized theoretical model of the pro-branched $[Pd(H)(L)(C_6H_5C_2H)]^+$. Short intramolecular contacts between H11 and some carbon atoms of the equatorial ligand phenyl ring are highlighted in red. Selected bond and intramolecular distances (Å) as well as angles (deg): Pd−C1 = 2.21, Pd−C2 = 2.47, Pd−P1 = 2.27, Pd−P2 = 2.39, Pd−H = 1.58, C1−C2 = 1.25, H11···C20 = 2.75, H11···C21 = 2.69, H11···C22 = 2.84, H11···C25 = 2.93; P1−Pd−P2 = 84.3, C1−Pd−C2 = 30.2.

bond of phenylacetylene is tilted with respect to the Pd coordination plane of 46.4° and (ii) the short intramolecular interactions between H11 of the substrate phenyl ring and four carbon atoms of one equatorially oriented ligand phenyl ring are shorter than 3 Å. As a consequence, the model compound with the terminal alkyne hydrogen atom pointing toward Pd−H is 2.00 kcal mol^{-1} (i.e., energy difference in methanol) lower in energy in comparison to its counterpart (Supporting Information). The importance of the dispersion force was evidenced by comparing the same optimized models using the *classical* B3LYP method. In the latter case the short interactions between the phenyl rings of phenylacetylene and of the ligand are lost and the energy difference between the two isomers is significantly 2.25 kcal mol^{-1} in favor of the model compound, with the phenyl ring pointing toward Pd−H (Supporting Information). Analogous theoretical calculations with 1-hexyne instead of phenylacetylene showed that the energy difference is slightly in favor of the model compound, showing the butyl carbon chain which points toward Pd−H (0.28 kcal mol^{-1}). The latter theoretical result is in line with the lower regioselectivity for the branched esters found for aliphatic in comparison to aromatic terminal alkynes (Table 1). In addition, it is rational to assume that an increasing diphosphane flexibility significantly decreases weak interactions between the substrate and the ligand phenyl rings. Accordingly, dppe- and *meso*-2,3-dppb-based catalyst precursors showed a lower regioselectivity versus the branched esters in comparison to the dppcb counterpart (Table 1).

The highest substrate conversion was obtained with **1**, significantly exceeding that of **7** (Table 1, entry 4 vs 21), by carrying out catalytic reactions in a 9:1 solvent mixture of CH_3CN and MeOH under syngas conditions. A comparison of the catalytic activities of **1**, **5**, and **6** under identical experimental conditions unambiguously showed that an increasing rigidity of the diphosphane ligand (i.e., dppe < *meso*-2,3-dppb < dppcb) led to an increased substrate conversion. This experimental finding is in accordance with slower overall deactivation processes triggered by phosphane on−off coordination to Pd(II) in the case of dppcb. *Operando* high-pressure $^{31}P\{^1H\}$ NMR experiments carried out with **1** and **6** in MeOH-d_4 in the presence of phenylacetylene under syngas conditions showed only in the case of **6** the formation of $[Pd(dppe)_2](OTs)_2$[17] (i.e., completely inactive under the chosen experimental conditions) at 70 °C as a result of the formation of Pd(0) and the concomitant release of diphosphane, which coordinates a cationic $[Pd(dppe)]^{2+}$ unit. In the absence of experimental evidence for the formation of a related Pd(II) complex in the case of dppcb, we calculated computational models for both possible conformers **8a,b** (Figure 3), using the model ligand introduced above (L).

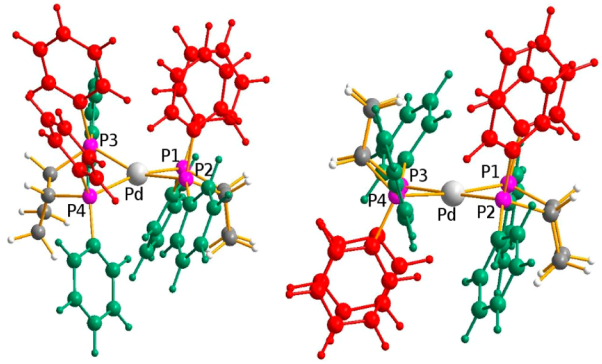

Figure 3. Optimized theoretical models of the possible conformers of $[Pd(L)_2]^{2+}$. The axial and equatorial phenyl rings are red and green, respectively. Selected bond distances (Å) and angles (deg) for **8a** (left): Pd−P(1) = 2.38, Pd−P(2) = 2.36, Pd−P(3) = 2.35, Pd−P(4) = 2.36; P(1)−Pd−P(2) = 84.6, P(3)−Pd−P(4) = 85.1. Selected bond distances (Å) and angles (deg) for **8b** (right): Pd−P(1) = 2.36, Pd−P(2) = 2.37, Pd−P(3) = 2.43, Pd−P(4) = 2.39; P(1)−Pd−P(2) = 83.8, P(3)−Pd−P(4) = 82.3.

The rigidity of the model ligand induces strain, due to equatorial phenyl−phenyl repulsions. The strain present in both model compounds is minimized by either a stark distortion of the square-planar Pd coordination geometry, as in the case of **8a** (i.e., interplanar angle between P(1)−Pd−P(2) and P(3)−Pd−P(4) of 23.8°, while the analogous angle in **8b** is 8.4°), or by a significant increase of the Pd−P bond lengths of one ligand, as in the case of **8b** (i.e., Pd−P(1) = 2.36 Å, Pd−P(2) = 2.37 Å vs Pd−P(3) = 2.43 Å and Pd−P(4) = 2.39 Å). Nevertheless, **8a** is 2.71 kcal mol^{-1} more stable than **8b**. At this point it is important to consider that the formation of **8a,b** is kinetically much more disfavored in comparison to $[Pd(dppe)]^{2+}$, since in the case of the rigid ligand two coordination sites have to be provided simultaneously.

CONCLUSION

The fixed orientation of the phenyl rings in the Pd−dppcb hydride alkyne complex favors the Markovnikov insertion of the terminal alkynes into the Pd−H bond, yielding branched α,β-unsaturated esters with high regioselectivity (up to 99%), which is unique for an isolated Pd complex. The overall rigidity of coordinated dppcb notably stabilizes the Pd(II) center in the

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course of the catalytic carbonylation reaction, precluding the formation of catalytically inactive Pd−bis(chelate) complexes.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. [PdClMe(η^4-COD)],[18] [PdCl(η^3-C_3H_5)]$_2$,[19] $PdCl_2$(dppe),[20] $PdCl_2$(*meso*-2,3-dppb)],[20] [$Pd(H_2O)_2$(dppf)](OTs)$_2$,[11] and dppcb[7] were prepared according to literature methods. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were obtained on a Bruker Avance DRX-400 spectrometer at 400.13, 100.62, and 161.98 MHz. Chemical shifts (δ) are reported in ppm relative to TMS (^{1}H and ^{13}C NMR) or 85% H_3PO_4. Infrared spectra were recorded on a FT-IR Perkin-Elmer BX spectrometer. Carbonylation reactions were performed in homemade 80 mL stainless steel autoclaves, equipped with a magnetic stirrer and temperature and pressure controller. GC analyses were performed on a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column, using *n*-decane as internal standard. GC-MS analyses were performed on a GC-MS QP2010S instrument which was equipped with the same capillary column. Elemental analyses were carried out with a NA 1500 Carlo Erba elemental analyzer.

[$Pd_2(H_2O)_4$(dppcb)](OTs)$_4$ (1). $Pd(OAc)_2$ (92.2 mg, 0.411 mmol) was added to a deaerated solution of dppcb (162.4 mg, 0.205 mmol) in CH_2Cl_2 (10 mL) at room temperature. The reaction solution was stirred for 4 h at room temperature. Afterward water (5 mL) and *p*-TsOH·H_2O (234.5 mg, 1.233 mmol) were added, giving a biphasic reaction mixture which was vigorously stirred at room temperature for 2 h. Afterward the organic phase was separated from the water phase, washed with water, dried over $MgSO_4$, and then concentrated to dryness, giving the product as a beige solid. Yield: 288.9 mg (80%). Anal. Calcd (found) for $C_{80}H_{80}O_{16}P_4S_4Pd_2$: C, 54.54; H, 4.54. Found: C, 54.32; H, 4.63. Λ_M = 0.051 Ω^{-1} cm^2 mol^{-1}.

Synthesis of [$Pd_2Cl_2Me_2$(dppcb)] (2). PdClMe(η^4-COD) (108.6 mg, 0.410 mmol) was added to a deaerated solution of dppcb (162.4 mg, 0.205 mmol) in CH_2Cl_2 (6 mL) at room temperature. During the reaction (1 h) the product precipitated from solution as an off-white product. To complete precipitation, *n*-pentane (5 mL) was added, and the product was separated by filtration and dried by a flow of nitrogen. Yield: 182 mg (85%). Anal. Calcd (found) for $C_{54}H_{50}Cl_2P_4Pd_2$: C, 58.63; H, 4.52. Found: C, 58.43; H, 4.60.

Synthesis of [Pd_2(OTs)$_2Me_2$(dppcb)] (3). Compound **2** (120.0 mg, 0.108 mmol) was suspended in deaerated CH_2Cl_2, followed by the addition of Ag(OTs) (63.3 mg, 0.227 mmol). The suspension was allowed to react for 2 h. Then AgCl was removed by filtration of the suspension through Celite and the resulting solution was concentrated to dryness, giving an off-white solid. Yield: 104.1 mg (70%). Anal. Calcd (found) for $C_{68}H_{64}O_6P_4S_2Pd_2$: C, 59.29; H, 4.64. Found: C, 59.15; H, 4.56. Λ_M = 0.029 Ω^{-1} cm^2 mol^{-1}.

Synthesis of [$Pd_2(\eta^3$-$C_3H_5)_2$(dppcb)] (4). To a deaerated solution of dppcb (80.0 mg, 0.101 mmol) in CH_2Cl_2 (20 mL) was added [PdCl(η^3-C_3H_5)]$_2$ (37.0 mg, 0.101 mmol) at room temperature. The reaction solution was stirred for 1 h, followed by the addition of Tl(PF_6) (74.1 mg, 0.212 mmol). The reaction was continued for $^1/_2$ h. Then the suspension was filtered through Celite and the solution concentrated to half of its original volume, causing the partial precipitation of the product. On addition of petroleum ether the precipitation was complete and the off-white product separated by filtration and dried in vacuo. Yield: 117.0 mg (84%). Anal. Calcd (found) for $C_{58}H_{54}F_{12}P_6Pd_2$: C, 50.58; H, 3.92. Found: C, 50.62; H, 3.99.

Synthesis of [$Pd(H_2O)_2$(*meso*-2,3-dppb)](OTs)$_2$ (5) and [$Pd(H_2O)_2$(dppe)](OTs)$_2$ (6). $PdCl_2$(*meso*-2,3-dppb) and $PdCl_2$(dppe) (0.132 mmol) were suspended in deaerated CH_2Cl_2 (10 mL) at room temperature. To the latter suspension was added Ag(OTs) (77.3 mg, 0.277 mmol), and the suspension was stirred for 2 h, followed by its filtration through Celite and the concentration of the resulting solution to dryness, giving brownish and yellow powders, respectively. **5**: yield 93.8 mg (78%). Anal. Calcd (found) for $C_{42}H_{46}O_8P_2S_2Pd$: C, 55.38; H, 5.05. Found: C, 55.28; H, 4.98. **6**: yield 99.0 mg (85%). Anal. Calcd (found) for $C_{40}H_{42}O_8P_2S_2Pd$: C, 54.42; H, 4.76. Found: C, 54.38; H, 4.60.

Catalytic Reactions. A homemade stainless steel autoclave (80.0 mL) was charged with the catalyst precursor (0.01 mmol Pd), before it was sealed and evacuated by a vacuum pump. Afterward a deaerated solution of the terminal alkyne (1.00 mmol) in MeOH (10.0 mL) and *n*-decane (100.0 μL) was introduced into the autoclave by suction, followed by pressurizing the autoclave with CO (45 psi) and heating it to 70 °C by means of an oil bath. Once the reaction temperature was reached, the CO pressure was adjusted to 150 psi, followed by charging the autoclave with H_2 (150 psi) when needed. After the desired reaction time, the autoclave was cooled to room temperature by means of an ice/water bath, the gas pressure released, and the catalytic solution analyzed by GC and GC-MS.

Theoretical Calculations. Structural optimizations were carried out at the hybrid density functional theory (DFT) level using the Gaussian03 suite of programs.[21] Both B97-D[16] and the Becke three-parameter hybrid exchange-correlation function,[22] containing the nonlocal gradient correction of Lee, Yang, and Parr (B3LYP)[23] were used for the pro-branched and pro-linear models of the phenyl and hexyl precursors. In the case of conformers **8a,b** only the calculations at the B97-D level were reported. Single-point energies for the optimized models were recalculated also in methanol by using the conductor-like polarizable continuum model (CPCM).[24] Calculations of the frequencies were performed to validate the nature of the optimized stationary points. The negative frequencies found in the calculations tried to break the imposed constraint on the cyclobutane rings. The Stuttgart/Dresden effective core potential was used for metals.[25] The basis set used for the remaining atomic species was 6-31G(d,p).[26]

ASSOCIATED CONTENT

Supporting Information

Figures, tables, text, and CIF files giving NMR characterization of **1**−**6**, *operando* high-pressure ^{31}P{^{1}H} NMR spectroscopic studies with **1** and **6**, and single crystal X-ray structure analyses of **2**·4DMF, **4**·CH_2Cl_2, **5**, **6**, and theoretical model compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: werner.oberhauser@iccom.cnr.it (W.O.); Peter.Brueggeller@uibk.ac.at (P.B.).

Notes

The authors declare no competing financial interest.

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