# Chemoselective methoxycarbonylation of terminal alkynes catalyzed by Pd(II)-TROPP complexes†

**Lorenzo Bettucci,[a] Claudio Bianchini,[a] Werner Oberhauser,*[a] Matthias Vogt[b] and Hansjörg Grützmacher[b]**

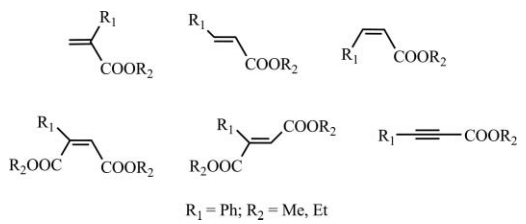
***Received 12th February 2010, Accepted 7th May 2010***
***First published as an Advance Article on the web 8th June 2010***
**DOI: 10.1039/c002976a**



The mono-phosphanes 5-(diphenyl)-phosphanyl-5*H*-dibenzo[a,d]cycloheptene (TROPP$^{Ph}$) and 5-((2-methoxy)phenyl)-phosphanyl-5*H*-dibenzo[a,d]cycloheptene (TROPP$^{(2\text{-MeOPh})}$) have been employed to coordinate $PdCl_2$, yielding [$PdCl_2$(TROPP$^{Ph}$)] (**1a**) and [$PdCl_2$(TROPP$^{(2\text{-MeOPh})}$)] (**1b**), respectively. The corresponding tosylate (OTs) complexes [$Pd(OTs)_2$(TROPP$^{Ph}$)] (**2a**) and [$Pd(OTs)_2$(TROPP$^{(2\text{-MeOPh})}$)] (**2b**) have been successfully applied in the *p*-benzoquinone (BQ)-assisted methoxycarbonylation of terminal alkynes to give chemoselectively the corresponding alkynylcarboxylic acid methyl ester with high TOF (up to 980 $h^{-1}$). Unlike **2a**/**b**, the Pd$^{II}$-(tosylate)-diphosphane complexes [Pd(OTs)($H_2O$)(dppp)](OTs) **2c** (dppp = 1,3-bis-di(phenylphosphanyl)propane and [$Pd(H_2O)_2$(MeO-dppp)](OTs)$_2$ **2d** (MeO-dppp = 1,3-bis(di(2-methoxyphenyl)phosphanyl)propane) preferentially catalyzed a double alkyne insertion. The "*in situ*" spectroscopic observation of the Pd-methoxycarbonyl compound [Pd(COOMe)(TROPP$^{Ph}$)](OTs) (**3a**) in conjunction with the evidence of the fast β-hydride elimination reaction of TROPP-based Pd-catalysts in the dimerization reaction of ethene are indicative for a strongly electrophilic metal centre. The X-ray crystal structures of **1a**·0.5$C_2H_4Cl_2$ and of the neutral and cationic Pd-alkyl complexes [Pd(Me)(Cl)(TROPP$^{Ph}$) (**7a**·0.5$CH_2Cl_2$) and [Pd($CH_2CH_2$COMe)-(TROPP$^{Ph}$)]($PF_6$) (**10a**·0.5$C_6H_6$), respectively, confirm unambiguously the bidentate coordination mode of TROPP-ligands to Pd$^{II}$, that persists even in the presence of CO pressure.

## Introduction

The transition metal-catalyzed carbonylation of alkenes and alkynes has been known since the 1930s.[1] Alkoxycarbonylation reactions of terminal alkynes are of particular interest as they lead to the formation of useful building blocks, such as α,β-unsaturated esters (*i.e.* mono-and di-carbonylated products)[2] and alkynylcarboxylic esters.[3] In particular, the latter esters are important intermediates in the synthesis of carbapenems, that are known for their broad spectrum of antibacterial properties.[4] Several different products obtained from the same terminal alkyne ($R_1C_2H$) by oxidative carbonylation reaction carried out in an alcohol (ROH) are depicted in Scheme 1.




**Scheme 1**

The selectivity towards different carbonylation products largely depends on the reaction conditions and on the nature of the catalyst employed. Significant examples for the carbonylation reaction of terminal alkynes are: (i) The Drent's methoxycarbonylation of propene,[5] chemoselectively yielding methyl methacrylate, which is a large scale chemical intermediate for the production of homopolymers and copolymers and (ii) the Tsuji's Pd/Cu-catalyzed oxidative alkoxycarbonylation of terminal alkynes yielding the corresponding alkynylcarboxylic acid ester.[3a] Unfortunately, the latter catalytic reaction is chemoselective only when carried out at a high palladium-substrate ratio, otherwise, 1,4-disubstituted-1,3-diynes are obtained by a rapid Cu-catalyzed alkyne coupling.[3a,b,e,f,g]

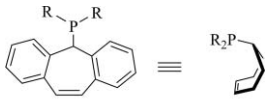
Since Pd$^{II}$ is reduced to Pd$^0$ in the course of the catalytic carbonylation reaction the metal re-oxidation is fundamental for a successful catalysis and a ligand capable of stabilizing low metal oxidation states would be important to stabilize Pd$^0$ single species, avoiding the formation of palladium black.

To this purpose, our attention was attracted by the TROPP ligands.[6] These ligands are known for their particular shape which consists of a boat conformation providing a concave rigid bidentate binding site composed of a σ-donor (*i.e.* phosphorus) and a π-acceptor moiety (*i.e.* C–C double bond). It has been established that the electronic property of TROPP ligands are remarkable to stabilize unusual oxidation states, as reported for rhodium[7a,b] and iridium.[7b,c]

Herein, we describe the synthesis and characterization of neutral and cationic Pd$^{II}$-complexes with TROPP ligands (Scheme 2). The corresponding palladium-tosylate complexes have been successfully employed as precursors for the oxidative methoxycarbonylation of terminal alkynes.

[a]*Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Area di Ricerca CNR di Firenze, via Madonna del Piano 10, 50019, Sesto Fiorentino, Italy. E-mail: werner.oberhauser@iccom.cnr.it; Fax: +39-055-5225203*
[b]*ETH Zürich, Laboratorium für Anorganische Chemie, HCI-H131, Wolfgang-Pauli-Str. 10, CH-8093, Zürich, Switzerland*

† CCDC reference numbers 696684, 696685 and 739871. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c002976a



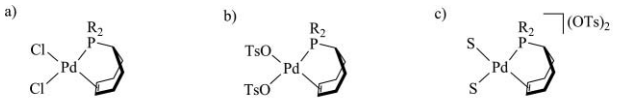

R = Ph (TROPP$^{Ph}$)
R = 2-MeOPh (TROPP$^{(2\text{-MeOPh})}$)

**Scheme 2**

## Results and discussion

### Synthesis of palladium complexes

The reaction of [PdCl$_2$(η$^4$-COD)] with (TROPP$^{Ph}$)[6] and (TROPP$^{(2\text{-MeOPh})}$) in dichloromethane gave the neutral complexes [PdCl$_2$(TROPP$^{Ph}$)] (**1a**) and [PdCl$_2$(TROPP$^{(2\text{-MeOPh})}$)] (**1b**) as yellow micro-crystalline compounds in 93 and 90% yield, respectively (Scheme 3(a)).




R = Ph (**1a**)
R = 2-MeOPh (**1b**)

R = Ph (**2a**)
R = 2-MeOPh (**2b**)

R = Ph (**2a'**)
R = 2-MeOPh (**2b'**)
S = solvent, fortuitous water

**Scheme 3**

The treatment of either complex with silver tosylate in dichloromethane gave the corresponding Pd-bis(tosylate) complexes of the formulae [Pd(OTs)$_2$(TROPP$^{Ph}$)] (**2a**) and [Pd(OTs)$_2$(TROPP$^{(2\text{-MeOPh})}$)] (**2b**) (Scheme 3(b)).

The neutral palladium complexes have been characterized in solution by multinuclear-NMR spectroscopy and in the solid state by elemental analysis. Additionally, **1a**·0.5C$_2$H$_4$Cl$_2$ has been identified by a single crystal structure analysis (*vide infra*). The $^{31}$P{$^1$H} NMR spectra of **1a/b** in CD$_2$Cl$_2$ exhibited a singlet centred at 107.40 and 112.80 ppm, while the corresponding $^{13}$C{$^1$H} NMR spectra showed, for the metal-coordinating sp$^2$-carbon atoms, a singlet centred at 100.00 ppm, that is significantly high-field shifted compared to the corresponding free ligand (*i.e.* 132.70 ppm).[6,7]

The $^{31}$P{$^1$H} NMR spectra of CD$_2$Cl$_2$ solutions of **2a/b** showed a singlet centred at 126.00 and 130.80 ppm, respectively, while the $^{13}$C{$^1$H} NMR spectra acquired in the same solvent showed a singlet at 97.30 ppm for the cycloheptene C=C$_{trop}$ double bond. The high-frequency shift of the $^{31}$P{$^1$H} NMR signal and the low-frequency shift of the $^{13}$C{$^1$H} NMR signal of **2a/b**, as compared to **1a/b** reflect the stronger *trans* influence of the tosylate *vs.* the chloride ligand.[8] Importantly, only one $^1$H NMR singlet for the chemically inequivalent tosylate methyl groups in **2a/b** was observed, even at low temperature (*i.e.* −60° C). This experimental evidence is in accordance with a OTs-exchange process at palladium, that is too fast to be observed on the NMR time scale.

Conductivity measurements of **2a/b** carried out in CH$_2$Cl$_2$ and MeOH (*i.e.* reaction medium for the carbonylation reactions), showed that the latter compounds behave in CH$_2$Cl$_2$ as non-electrolyte, whereas in MeOH they behave as 1 : 2 electrolyte, which is consistent with the chemical formulae [Pd(TROPP$^{Ph}$)(S)$_2$](OTs)$_2$ (**2a′**) and [Pd(TROPP$^{(2\text{-MeOPh})}$)(S)$_2$](OTs)$_2$ (**2b′**) (S = MeOH or adventitious water) (Scheme 3(c)). The $^{31}$P{$^1$H} NMR spectra of **2a′/b′** in CD$_3$OD showed a broad singlet centred at 129.00 and 130.80 ppm, that became narrower at low temperature. The replacement of coordinating anions such as tosylate or triflate to palladium by MeOH is rather common for Pd(II) complexes.[8,9]

**Table 1** Selected bond lengths (Å) and angles (°) for **1a**·0.5C$_2$H$_4$Cl$_2$, **7a**·0.5CH$_2$Cl$_2$ and **10a**·0.5C$_6$H$_6$

| | **1a**·0.5C$_2$H$_4$Cl$_2$ | **7a**·0.5CH$_2$Cl$_2$ | **10a**·0.5C$_6$H$_6$ |
|---|---|---|---|
| Pd(1)–P(1) | 2.233(1) | 2.208(2) | 2.1981(8) |
| Pd(1)–Cl(1) | 2.353(1) | 2.383(3) | |
| Pd(1)–Cl(2) | 2.319(1) | | |
| Pd(1)–O(1) | | | 2.127(2) |
| Pd(1)–C(8) | 2.249(4) | 2.373(10) | 2.318(4) |
| Pd(1)–C(9) | 2.234(4) | 2.346(9) | 2.333(3) |
| Pd(1)–C(28) | | 2.102(9) | 2.042(3) |
| Pd(1)–C(ct) | 2.136(7) | 2.314(27) | 2.213(9) |
| C(8)–C(9) | 1.391(6) | 1.373(13) | 1.363(5) |
| C(30)–O(1) | | | 1.239(4) |
| Cl(1)–Pd(1)–Cl(2) | 92.62(4) | | |
| Cl(1)–Pd(1)–C(28) | | 91.80(30) | |
| P(1)–Pd(1)–C(8) | 90.89(11) | 92.60(20) | 94.95(9) |
| P(1)–Pd(1)–C(9) | 92.23(12) | 92.30(20) | 91.58(9) |
| P(1)–Pd(1)–C(28) | | 86.20(30) | 89.77(10) |
| P(1)–Pd(1)–C(ct) | 91.69(20) | 92.78(41) | 93.55(22) |
| O(1)–Pd(1)–C(28) | | | 82.14(13) |

ct (centroid of the C(8)=C(9) bond).

Suitable crystals of **1a**·0.5C$_2$H$_4$Cl$_2$ for a single crystal X-ray structure analysis were obtained by slow diffusion of toluene into a solution of **1a** in dichloroethane at room temperature. An ORTEP diagram of the latter compound is shown in Fig. 1, while selected bond distances and angles are reported in Table 1.

In the crystal structure of **1a**·0.5C$_2$H$_4$Cl$_2$ the 1,2-dichloroethane molecule lies about an inversion centre so that only one half of the molecule is in the asymmetric unit. The palladium atom exhibits a planar coordination geometry, built up by two *cis*-coordinating chloride atoms, a phosphorus atom and the centroid (ct) of the coordinating C=C$_{trop}$ bond (*i.e.* ct of C(8)=C(9) bond). The palladium atom is located in the best coordination plane defined by the atoms P(1), Cl(1), Cl(2), and ct. Both olefinic carbon atoms, C(8) and C(9) deviate symmetrically from the latter plane by 0.6926(29) and −0.6965(31) Å, respectively. The coordinating C=C$_{trop}$ bond (1.391(6) Å) is significantly elongated when compared to that of the free ligand (1.328(4) Å)[6] being almost identical to that found for the related palladium dichloride complex bearing the related dibenzo[a,d]cycloheptenyl dibenzophosphole[10] as ligand. The coordinating C=C$_{trop}$ bond axis is almost perpendicular (87.9(2)°) oriented with respect to the best coordination plane. The overall conformation of the coordinating TROPP$^{Ph}$ ligand is defined by the parameters $\alpha$ (52.40°) and $\beta$ (24.7°) as shown in Scheme 4 ($\alpha$ = 47.80° and $\beta$ = 24.40° for the free TROPP$^{Ph}$ ligand).

### Catalytic methoxycarbonylation of terminal alkynes

Compounds **2a/b** were tested as catalyst precursors for the methoxycarbonylation of terminal alkynes (*i.e.* phenylacetylene, 4-tolylacetylene and 4-bromo-phenylacetylene) in the presence of *p*-benzoquinone (BQ). For a comparative purpose, analogous reactions, catalyzed by the Pd-diphosphane

**Table 2** Methoxycarbonylation of terminal alkynes (R–$C_2$H) catalyzed by the precursors **2a–d**[a]

| Entry | Precatalyst/mmol | Substrate (R) | *t*/h | Conv. (%) | TOF[b] | Sel. A (%) | Sel. B (%) | Sel. C (%) |
|---|---|---|---|---|---|---|---|---|
| 1[c] | **2a** (0.02) | Ph | 1 | 2 | 2 | 75 | 25 | — |
| 2[d] | **2a** (0.02) | Ph | 1 | 9 | 9 | 81 | 19 | — |
| 3 | **2a** (0.02) | Ph | 1 | 93 | 93 | — | — | 100 |
| 4[e] | **2a** (0.02) | Ph | 1 | 40 | 40 | — | — | 100 |
| 5[f] | **2a** (0.02) | Ph | 1 | 65 | 65 | — | — | 100 |
| 6 | **2a** (0.001) | Ph | 1 | 27 | 540 | — | — | 100 |
| 7 | **2a** (0.001) | Ph | 2 | 51 | 510 | — | — | 100 |
| 8 | **2a** (0.02) | 4-Tolyl | 0.5 | 90 | 180 | — | — | 100 |
| 9 | **2a** (0.001) | 4-Tolyl | 0.5 | 24 | 960 | — | — | 100 |
| 10 | **2a** (0.001) | 4-Tolyl | 1 | 46 | 920 | — | — | 100 |
| 11 | **2a** (0.001) | 4-BrPh | 1 | 21 | 420 | — | — | 100 |
| 12[c] | **2b** (0.02) | Ph | 1 | 3 | 3 | 65 | 35 | — |
| 13[d] | **2b** (0.02) | Ph | 1 | 57 | 57 | 60 | 40 | — |
| 14 | **2b** (0.02) | Ph | 1 | 95 | 95 | — | — | 100 |
| 15 | **2b** (0.001) | Ph | 1 | 26 | 520 | — | — | 100 |
| 16 | **2b** (0.02) | 4-Tolyl | 0.5 | 93 | 186 | — | — | 100 |
| 17 | **2b** (0.001) | 4-Tolyl | 0.5 | 23 | 920 | — | — | 100 |
| 18 | **2b** (0.001) | 4-Tolyl | 1 | 44 | 880 | — | — | 100 |
| 19[g] | **2b** (0.001) | 4-Tolyl | 0.5 | 22 | 880 | — | — | 100 |
| 20 | **2b** (0.001) | 4-BrPh | 1 | 20 | 400 | — | — | 100 |
| 21[c] | **2c** (0.02) | Ph | 1 | 47 | 47 | 68.0 | 32.0 | — |
| 22 | **2c** (0.02) | Ph | 1 | 89 | 89 | — | — | 11 |
| 23 | **2c** (0.02) | 4-Tolyl | 0.5 | 85 | 170 | — | — | 16 |
| 24 | **2c** (0.02) | 4-BrPh | 1 | trace | — | — | — | nd. |
| 25[c] | **2d** (0.02) | Ph | 1 | 15 | 15 | 58.0 | 42.0 | — |
| 26 | **2d** (0.02) | Ph | 1 | 42 | 42 | — | — | 15 |
| 27 | **2d** (0.02) | 4-Tolyl | 0.5 | 68 | 136 | — | — | 12 |
| 28 | **2d** (0.02) | 4-BrPh | 1 | trace | — | — | — | nd. |
| 29[h] | **$PdCl_2$/$CuCl_2$** | Ph | 1 | 87 | 87 | — | — | 3 |

[a] Catalytic conditions: MeOH, 25 mL; substrate, 2.00 mmol; BQ, 2.40 mmol; *p*(CO), 7 bar; temperature, 70 °C; stirring rate, 800 rpm. [b] Turn over frequency expressed as mmol (alkyne) converted × (mmol (Pd) × h)$^{-1}$. [c] Without BQ. [d] TsOH, 0.60 mmol. [e] BQ, 1.20 mmol. [f] *p*(CO), 28 bar. [g] Reaction in 2-propanol. [h] $PdCl_2$, 0.02 mmol, $CuCl_2$, 2.40 mmol, NaOAc, 2.40 mmol.

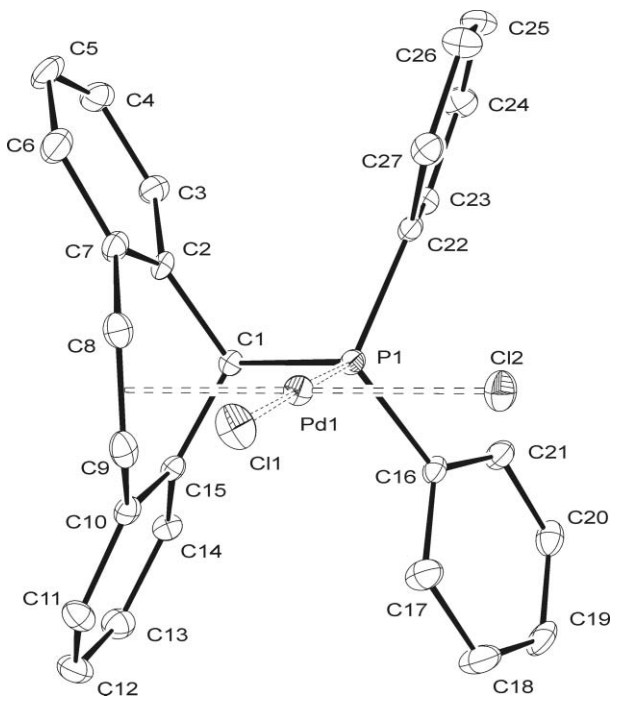
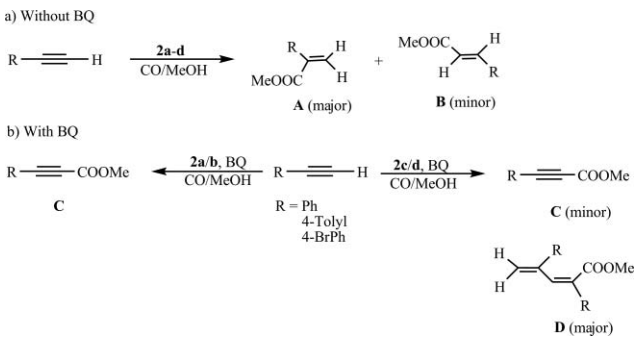



**Fig. 1** ORTEP diagram of **1a**·0.5$C_2H_4Cl_2$ with 30% probability ellipsoids. Hydrogen atoms and the solvent molecule are omitted for clarity.

complexes [Pd(OTs)($H_2$0)(dppp)](OTs) (**2c**)[11] (dppp = 1,3-bis(diphenylphosphanyl)propane) and [Pd($H_2O$)$_2$(MeO-dppp)](OTs)$_2$ (**2d**)[8a] (MeO-dppp = 1,3-bis(di(2-methoxyphenyl)-phosphanyl)propane) that share with **2a**/**b** a similar ligand bite angle of *ca.* 90°, were carried out. The result of this comparative catalytic study is shown in Table 2.


**Scheme 4**

Regardless of the precatalyst employed, catalytic methoxycarbonylation reactions of terminal alkynes carried out in the absence of BQ yielded the unsaturated monoesters **A** and **B** (Scheme 5(a)) with the branched ester **A** as the major product.




**Scheme 5**

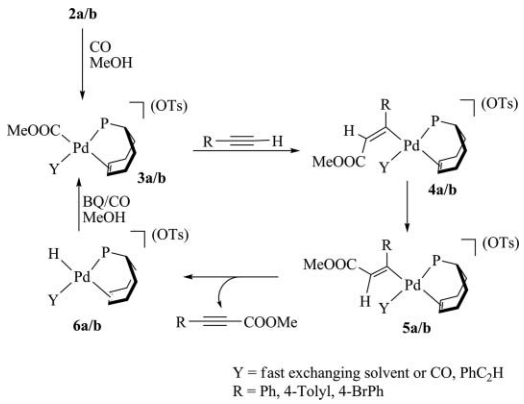
Under the latter catalytic conditions, **2a/b** were almost inactive (entries 1 and 12, Table 2), whereas upon addition of HOTs, an increased catalytic conversion was observed with the branched ester **A** as the major product (entries 2/13 *vs.* 1/12, Table 2). The diphosphane complexes **2c/d** showed a good catalytic activity also in the absence of a Brønsted acid, with a slight chemoselectivity in favour of the branched ester of 68.0 and 58.0%, respectively (entries 21 and 25, Table 2).

Catalytic methoxycarbonylation reactions of terminal alkynes promoted with **2a/b** in the presence of BQ exclusively yielded the corresponding alkynylcarboxylic acid methyl ester **C** in high yield (*i.e.* TOF up to 960 $h^{-1}$). In contrast, **2c/d** gave under identical catalytic conditions a mixture of **C** and the 2,4-di-substituted 2,4-pentadienylcarboxylic acid methyl ester **D**[2d] (Scheme 5(b)) as the major compound (Table 2). This finding clearly indicates that, unlike **2a/b**, **2c/d** preferentially undergo a double 1,2-alkyne insertion. The highest substrate conversion into **C** was found to be obtained in the CO pressure range from 7 to 21 bar. Importantly, even at CO pressures higher than 21 bar, the diesters formed upon a double methoxycarbonylation reaction were not obtained. A strong dependence of the catalytic activity on the amount of BQ present in the reaction mixture was observed (entry 3 *vs.* 4, Table 2), indicating a BQ-promoted oxidation of $Pd^0$ to $Pd^{II}$ in the course of the catalytic cycle. Furthermore, decreasing the amount of precatalyst from 0.02 to 0.001 mmol while keeping the amount of substrate constant at 2 mmol, remarkably increased the TOF of the catalytic reactions. We interpret this result due to a reduced Pd black formation at lower Pd concentrations.

The substitution of BQ by $CuCl_2$ in the **2a/b**-catalyzed methoxycarbonylation reactions chemoselectively gave the corresponding 1,4-di-substituted 1,3-butadiyne, which is typically obtained as a major side-product in the Pd/Cu-based carbonylation reactions of terminal alkynes.[3a] As a matter of fact, the catalytic system comprising $PdCl_2/CuCl_2$/NaOAc gave under the present catalytic conditions **C** in 3% yield, while the corresponding 1,4-di-substituted-1,3-butadiyne was the major product (entry 29, Table 2).

The substitution of methanol by 2-propanol as carbonylation reaction medium had no effect neither on the chemoselectivity nor on the catalytic activity (entry 19 *vs.* 17, Table 2).

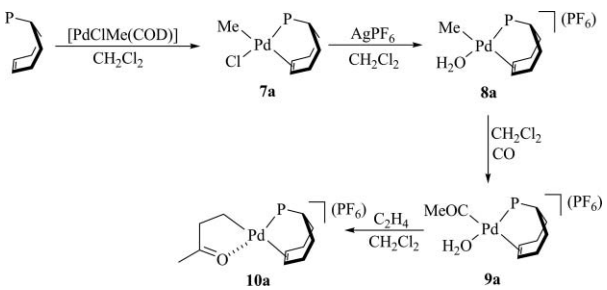
For the chemoselective **2a/b**-catalyzed oxidative methoxycarbonylation reaction of terminal alkynes we propose the catalytic cycle shown in Scheme 6.




**Scheme 6**

The catalytic cycle comprises the transformation of the precatalyst **2a/b** (Scheme 6) into the Pd-alkoxycarbonyl species **3a/b**, that undergoes a *cis*-2,1-insertion in the presence of the terminal alkyne, yielding the Pd-alkenyl intermediate **4a/b**.[3d] The latter compound is proposed to undergo an isomerization reaction into **5a/b** enabling a β-hydride elimination reaction.[3d] A fast β-hydride elimination reaction generates the Pd-hydride **6a/b** with the concomitant release of the corresponding alkynylcarboxylic acid ester. Finally, the BQ-assisted conversion of **6a/b** into **3a/b** closes the catalytic cycle.[12] The following experimental evidence corroborates the proposed catalytic cycle:

(i) The Pd-methoxycarbonyl compound [Pd(COOMe)-($CD_3OD$)(TROPP$^{Ph}$)](OTs) (**3a′**) (Scheme 6) was observed spectroscopically by bubbling $^{13}CO$ through a solution of **2a** in $CD_3OD$.[13] The latter compound could not be isolated due to its rapid CO-de-insertion reaction in the absence of CO but it was unambiguously identified. The $^{13}C\{^1H\}$ NMR spectrum of **3a′** revealed a doublet centred at 175.00 ppm with a $^2J_{PC}$ of 16.3 Hz for the carboxyl C-atom, which is consistent with a *cis*-coordination of the methoxycarbonyl moiety with respect to the phosphorus atom of the ligand.[13a] The related Pd-acyl model compound of the formula [Pd(COMe)($H_2O$)(TROPP$^{Ph}$)]($PF_6$) (**9a**) (Scheme 7), shows also a *cis*-stereochemistry of the palladium coordinating acyl moiety with respect of the phosphorus donor atom. As a consequence, its $^1H$ NMR spectrum, acquired in $CD_2Cl_2$, exhibited a doublet at 1.89 ppm ($^4J_{PH}$ of 1.5 Hz) for $COCH_3$, while the corresponding $^{13}C\{^1H\}$ NMR spectrum showed a singlet at 118.70 ppm for the palladium coordinating $sp^2$-hybridized carbon atoms. It is important to stress, that CO neither coordinates to **3a/a′** and **9a** nor displaces the coordinating C=$C_{trop}$ bond from palladium, even at high CO pressure (*i.e.* 20 bar). This finding is in agreement with a strong electrophilic palladium centre.[14]



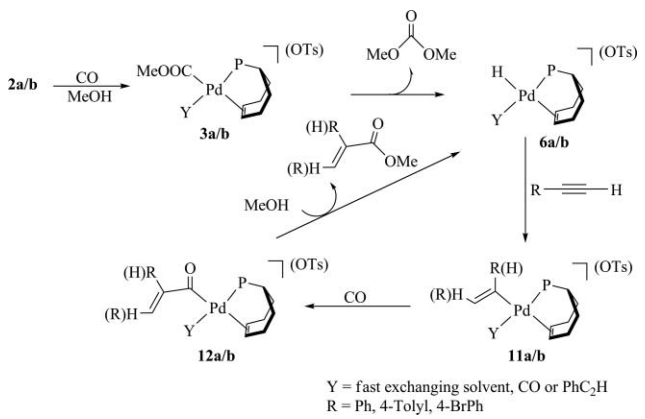

**Scheme 7**

(ii) The catalytic activity has been found to be independent of the type of alcohol employed as reaction medium (entry 19 *vs.* 17, Table 2). This evidence rules out a methanolysis reaction path (*i.e.* reaction of methanol with a palladium acyl species) as termination reaction.[15] Instead, the palladium β-hydride elimination, which is fostered by an electrophilic metal centre, is favoured.[16] In order to experimentally prove the rapid β-hydride elimination activity of the TROPP-based Pd-catalyst, the model compound [PdMe($H_2O$)(TROPP$^{Ph}$)]($PF_6$) (**8a**) (Scheme 7) was used to catalyze the oligomerization reaction of ethene in toluene at 50° C. As a result, a stoichiometric amount of propene (*i.e.* with respect to the amount of the precursor) and a 1 : 18 mixture of 1- and *cis*/*trans* 2-butenes with a TOF of $160^{-h}$ was obtained.

**Table 3** Crystallographic data for **1a**·0.5$C_2H_4Cl_2$, **7a**·0.5$CH_2Cl_2$ and **10a**·0.5$C_6H_6$

| | **1a**·0.5$C_2H_4Cl_2$ | **7a**·0.5$CH_2Cl_2$ | **10a**·0.5$C_6H_6$ |
|---|---|---|---|
| Empirical formula | $C_{28}H_{23}Cl_3PPd$ | $C_{28.5}H_{25}Cl_2PPd$ | $C_{34}H_{31}F_6OP_2Pd$ |
| Formula weight | 603.18 | 575.76 | 737.93 |
| $T$/K | 170.0(2) | 293.2(2) | 180.2(2) |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ |
| $a$/Å | 8.6468(6) | 8.907(5) | 17.9962(5) |
| $b$/Å | 14.0728(8) | 19.718(5) | 8.9054(2) |
| $c$/Å | 20.6612(12) | 15.161(5) | 21.4435(5) |
| $\beta$/° | 95.573(6) | 92.175(5) | 110.763(3) |
| $V$/Å$^3$ | 2502.3(3) | 2660.8(2) | 3213.42(14) |
| $Z$ | 4 | 4 | 4 |
| $D_c$/mg m$^{-3}$ | 1.601 | 1.437 | 1.525 |
| $\mu$/mm$^{-1}$ | 1.141 | 0.973 | 0.738 |
| $F$(000) | 1212 | 1164 | 1492 |
| Crystal size/mm | 0.20 × 0.20 × 0.10 | 0.30 × 0.20 × 0.20 | 0.40 × 0.30 × 0.20 |
| Absorption correction | MULTI-SCAN | PSI-SCAN | MULTI-SCAN |
| Reflections collected | 6900 | 4654 | 10 409 |
| $\theta$ range for data collection/° | 3.81–30.67 | 2.51–24.98 | 3.72–32.48 |
| Refinement method | Full-matrix least-squares on $F^2$ | | |
| Data/restraints/parameter | 3929/0/298 | 2463/3/293 | 6560/2/383 |
| Goodness-of-fit on $F^2$ | 0.923 | 1.029 | 1.039 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0572$ | $R_1 = 0.0686$ | $R_1 = 0.0509$ |
| | w$R_2 = 0.0919$ | w$R_2 = 0.1659$ | w$R_2 = 0.1371$ |
| $R$ indices (all data) | $R_1 = 0.1153$ | $R_1 = 0.1759$ | $R_1 = 0.0890$ |
| | w$R_2 = 0.1008$ | w$R_2 = 0.2076$ | w$R_2 = 0.1615$ |
| Largest diff. peak, hole/e Å$^{-3}$ | 1.257, –0.934 | 0.881, –0.480 | 1.57, –0.846 |




**Scheme 8**

(iii) The **2a/b**-catalyzed carbonylation reactions of terminal alkynes carried out in the absence of BQ led to the selective formation of the monoesters **A** and **B** (Scheme 5(a)). The proposed catalytic cycle for their formation (Scheme 8) comprises a 1,2- and 2,1-insertion of the terminal alkyne into the Pd–H bond of the intermediates **6a/b** (Scheme 8), yielding the Pd-alkenyl isomers **11a/b**. Subsequent insertion of CO, followed by methanolysis releases the esters **A** and **B** and regenerates **6a/b** (Scheme 5(a)). Notably, the first Pd-hydride that enters the catalytic cycle stems from the methanolysis of intermediates **3a/b**), releasing a stoichiometric amount of dimethyl carbonate that was actually detected by a GC-MS analysis of the catalytic reaction mixture.

In order to prove the *trans*-coordination of the alkenyl moiety in the intermediates **4a/b** and **5a/b** (Scheme 6) with respect to the C=$C_{trop}$ unit of the ligand, neutral and mono-cationic Pd-alkyl compounds of the formulae [PdMeCl(TROPP$^{Ph}$)] (**7a**), [PdMe($H_2O$)(TROPP$^{Ph}$)]($PF_6$) (**8a**) and [Pd($CH_2CH_2COMe$)-(TROPP$^{Ph}$)]($PF_6$) (**10a**) were synthesized (Scheme 7). The $^1$H and $^{13}C\{^1H\}$ NMR spectra of the latter Pd-alkyl compounds are consistent with a *trans*-coordination of the alkyl moiety with respect to *meta* coordinating C=$C_{trop}$ bond of the ligand. Due to the higher *trans*-influence of the alkyl moieties *vs.* chloride or tosylate, the $^{13}$C resonances of the C=$C_{trop}$ double bond were shifted to higher frequencies by 12–19 ppm compared to **1a** and **2a**.

Single crystal X-ray structure analyses of **7a**·0.5$CH_2Cl_2$ and **10a**·0.5$C_6H_6$ confirmed the relative stereochemistry observed in solution. Suitable crystals for an X-ray diffraction experiment of **7a**·0.5$CH_2Cl_2$ and **10a**·0.5$C_6H_6$ were obtained by a slow diffusion of toluene into a $CH_2Cl_2$ solution of the corresponding compound. Benzene has been found to be present as an impurity (<0.5%) in toluene used for crystallization. ORTEP diagrams of **7a**·0.5$CH_2Cl_2$ and **10a**·0.5$C_6H_6$ are shown in Fig. 2 and 3, respectively, while selected bond lengths and angles as well as crystallographic data are reported in Tables 1 and 3, respectively.

The crystal structure of **7a**·0.5$CH_2Cl_2$ shows the expected planar coordination sphere for the palladium atom. The metal centre deviates from the best coordination plane, defined by the atoms P(1), Cl(1), ct (*i.e.* centroid of the C(8)=C(9) bond) and C(28) by 0.020(3) Å in the direction of C(8). The methyl group (C(28)) is located *trans* to the C=$C_{trop}$ bond of the cycloheptene moiety, showing a Pd–C bond length of 2.102(9) Å, which is in the range of previously reported Pd-methyl bond length.[17] Apparently, the higher *trans*-influence of the methyl group *vs.* chloride is responsible for a shortening of the coordinating cycloheptene C–C double bond to 1.373(13) Å, as compared to **1a**·0.5$C_2H_4Cl_2$ (1.391(6) Å). Nevertheless, a significant elongation of the latter double bond with respect to the free TROPP$^{Ph}$ ligand (1.328(4) Å) is observed.[6] The bite angle of the ligand in **7a**·0.5$CH_2Cl_2$ may be described by the P(1)–Pd(1)–ct angle of 92.78(41)°. The two inter-planar angles $\alpha$ and $\beta$, defined as shown in Scheme 4,[5a] show

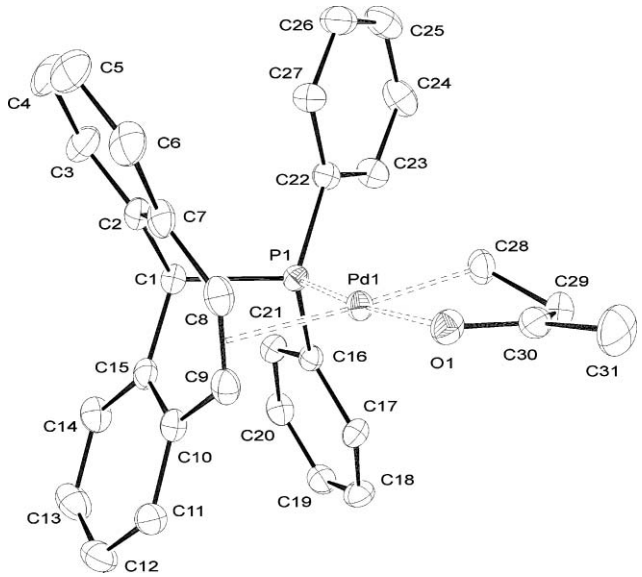



**Fig. 2** ORTEP diagram of **7a**·0.5$CH_2Cl_2$ with 30% probability ellipsoids. The solvent molecule and hydrogen atoms are omitted for clarity.

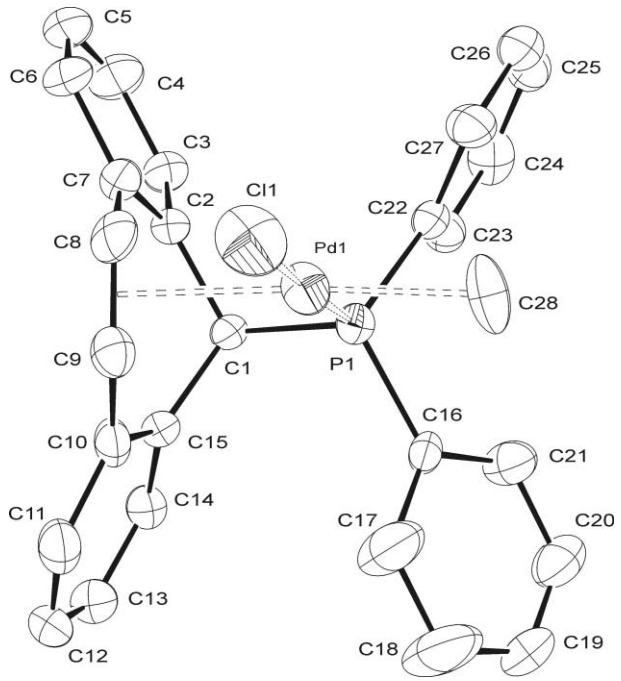



**Fig. 3** ORTEP diagram of **10a**·0.5$C_6H_6$ with 30% probability ellipsoids. Hydrogen atoms, the counter-anion and the solvent molecule are omitted for clarity.

a value of 51.8(5)° and 25.1(6)°, respectively, that is comparable to the value found for **1a**·0.5$C_2H_4Cl_2$ (*vide supra*).

The crystal structure of **10a**·0.5$C_6H_6$ (Fig. 3) reveals one molecule of **10a** and a molecule of benzene in the asymmetric unit with an occupancy factor of 0.5.

The planar coordination sphere around the palladium centre consists of one phosphorus donor atom, the centroid ct of the C(8)=C(9) bond of the cycloheptene moiety, the carbonyl oxygen atom (O(1)) and the $sp^3$-hybridized carbon atom (C(28)). The two latter atoms belong to a palladium-β-keto-chelate ring.[13b,18] The palladium atom deviates by 0.047(3) Å from the least-square coordination plane, defined by the atoms O(1), C(28), P(1), and ct. The carbon atom C(28) coordinates *trans* to the C–C double bond of the ligand and the C(8)=C(9) bonding distance of 1.363(5) Å is almost identical to that found for **7a**·0.5$CH_2Cl_2$. The Pd(1)–O(1) bonding distance of 2.127(2) Å is in the range of the bond lengths reported for related palladium-β-keto-chelate complexes.[13b,18a] Importantly, this latter bond persists also in solution. In fact, an IR spectrum of **10a** acquired in $CH_2Cl_2$ exhibited a $\nu$(CO) of 1632 $cm^{-1}$. The corresponding $^{13}C\{^1H\}$ NMR spectrum acquired in $CD_2Cl_2$, showed for the carbonyl carbon resonances a singlet centred at 235.81 ppm. The overall concave conformation of $TROPP^{Ph}$ in **10a**·0.5$C_6H_6$ (*i.e.* $\alpha = 50.3(2)$ and $\beta = 24.1(2)°$) is comparable to that of **1a**·0.5$C_2H_4Cl_2$ and **7a**·0.5$CH_2Cl_2$ (*vide supra*).

## Conclusions

Neutral and cationic TROPP-modified $Pd^{II}$ complexes have been synthesized and characterized. NMR spectroscopic analysis and crystal structure data confirm the bidentate coordination mode of TROPP ligands to a palladium(II) centre. Even in CO-pressurized solutions a de-coordination of the $C{=}C_{trop}$ double bond from the palladium centre was not observed.

The cationic Pd-tosylate complexes **2a/b** have been successfully applied in the BQ-assisted methoxycarbonylation of terminal alkynes to give chemoselectively the corresponding alkynylcarboxylic acid methyl ester in high yield (TOF up to 980 $h^{-1}$). This catalytic activity strongly contrasts with the one obtained from analogous reactions promoted by Pd/Cu-based or Pd-diphosphane precatalysts. These systems lead either to alkyne-coupling products or double alkyne insertion products as major by-products.

The "*in situ*" spectroscopic detection of the Pd-methoxycarbonyl species **3a′**, combined with the experimental evidence of the exclusive dimerization reaction of ethene, catalyzed by the cationic Pd–Me model compound **8a**, corroborates the presence of a strongly electrophilic metal centre in TROPP-modified $Pd^{II}$-catalysts.

## Experimental

### Materials and physical measurements

All reactions and manipulations were carried out under a nitrogen atmosphere by using the standard Schlenk-type techniques. The solvents were dried by passing them through columns of suitable molecular sieves under nitrogen. The reagents were used as purchased from Aldrich or Fluka, unless stated otherwise. [$PdCl_2(\eta^4$-COD)],[19] [PdClMe($\eta^4$-COD)],[20] **2c**,[11] **2d**,[8a] $TROPP^{Ph}$ **6**, 5-chloro-5*H*-dibenzo[a,d]cycloheptene[21] and di(2-methoxyphenyl)phosphane[22] were prepared according to literature methods. Carbonylation reactions were performed in a 320 mL stainless steel autoclave, constructed at ICCOM-CNR (Florence, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. GC analyses were performed on a Shimadzu GC-14 A 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.

GC-MS analyses were performed with a Shimadzu QP2100S apparatus equipped with a column identical with that used for GC analysis. Deuterated solvents for routine NMR measurements were dried over activated molecular sieves. $^{1}H$, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectra were obtained on either a Bruker Avance II DRX 300 spectrometer at 300.13, 75.49, 121.49 MHz, respectively, or on a Bruker Avance DRX-400 spectrometer at 400.13, 100.62 and 161.98 MHz, respectively. Chemical shifts ($\delta$) are reported in ppm relative to TMS, referenced to the chemical shifts of residual solvents resonances ($^{1}H$ and $^{13}C$ NMR) or 85% $H_3PO_4$. High-pressure NMR (HPNMR) experiments were carried out on a Bruker ACP 200 spectrometer operating at 200.13 and 81.01 MHz for $^{1}H$ and $^{31}P\{^{1}H\}$, respectively, using a 10 mm sapphire NMR tube (Saphikon, Milford, NH) equipped with titanium high-pressure charging head constructed at the ICCOM-CNR (Florence, Italy).[23] Conductivity measurement were carried out with an Orion model 101 conductivity meter with $10^{-3}$ M solutions.[24] Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded on a FT-IR Perkin-Elmer BX spectrometer.

## Preparations

**Synthesis of TROPP$^{(2\text{-MeOPh})}$.** A solution of di(2-methoxyphenyl)phosphine[22] (246.1 mg, 1.00 mmol) was added to a deaerated solution of 5-chloro-5*H*-dibenzo[a,d]cycloheptene[21] (226.6 mg, 1.00 mmol) in toluene (30 mL) under vigorous stirring. After a reaction time of 10 min the corresponding hydrochloride compound started to precipitate. The suspension was than refluxed for 10 min, followed by its cooling to room temperature. At the latter temperature a deaerated solution of sodium carbonate in water (15 mL) (10%, w/w) was added and the suspension was again refluxed under vigorous stirring, obtaining two clear phase, that were separated at room temperature. The water phase was again extracted with toluene (15 mL) and then the combined toluene phases were dried over $Na_2SO_4$. The inorganic salt was then separated by filtration, the solvent removed and the residue recrystallized from acetonitrile. Yield: 65.0% (283.7 mg, 0.650 mmol). $C_{29}H_{25}O_2P$ (436.49): calc. C, 79.80; H, 5.72; found: C, 79.74; H, 5.68%. $^{1}H$ NMR ($CDCl_3$, 300.13 MHz, ppm): $\delta$ 3.51 (s, 6H, $OCH_3$), 5.14 (d, $^{2}J_{PH}$ = 4.2 Hz, 1H, PC*H*), 6.58–7.45 (m, 18H, Ar–*H* + C*H*=C*H*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.49 MHz, ppm): $\delta$ 54.20 (d, $^{1}J_{PC}$ = 21.6 Hz, P*C*H), 55.00 (s, O*C*H$_3$), 109.80–161.90 (Ar–*C* + *C*H=*C*H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.49 MHz, ppm): $\delta$ –36.00 (s).

**Synthesis of [PdCl$_2$(L)] (L = TROPP$^{Ph}$, 1a; TROPP$^{(2\text{-MeOPh})}$, 1b).** An appropriate amount of ligand (0.420 mmol) was added to a deaerated solution of [PdCl$_2$($\eta^4$-COD)] (120.0 mg, 0.420 mmol) in $CH_2Cl_2$ (10 mL). The resulting yellow suspension was allowed to stir for 20 min, followed by its concentration to a small volume (5 mL). The addition of diethyl ether to the latter solution caused the precipitation of the product as microcrystalline yellow powder, that was successively separated by filtration, washed with diethyl ether (2 × 5 mL) and dried in a stream of nitrogen.

**1a.** Yield: 93.0% (216.2 mg, 0.390 mmol). $C_{27}H_{21}Cl_2PPd$ (553.59): calc. C, 58.58; H, 3.79; found C, 58.42; H, 3.61%. $^{1}H$ NMR ($CDCl_3$, 300.13 MHz, ppm): $\delta$ 5.15 (d, $^{2}J_{PH}$ = 21.2 Hz, 1H, PC*H*), 7.08–7.70 (m, 20H, Ar–*H* + C*H*=C*H*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.49 MHz, ppm): $\delta$ 55.19 (d, $^{1}J_{PC}$ = 21.0 Hz, P*C*H), 100.01 (s, *C*H=*C*H), 128.47–135.50 (Ar–*C*). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121.49 MHz, ppm): $\delta$ 107.38 (s).

**1b.** Yield: 90.0% (231.4 mg, 0.377 mmol). $C_{29}H_{25}Cl_2O_2PPd$ (613.59): calc. C, 56.77; H, 4.07; found: C, 56.69; H, 3.99%. $^{1}H$ NMR ($CDCl_3$, 400.13 MHz, ppm): $\delta$ 3.59 (s, 6H, O*CH*$_3$), 5.79 (d, $^{2}J_{PH}$ = 16.0 Hz, 1H, PC*H*), 6.32 (s, 2H, C*H*=C*H*), 6.73–7.75 (m, 16H, Ar–*H*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.62 MHz, ppm): $\delta$ 51.99 (d, $^{1}J_{PC}$ = 22.1 Hz, P*C*H), 55.57 (s, O*C*H$_3$), 100.01 (s, *C*H=*C*H), 100.22–160.13 (Ar–*C*). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 161.98 MHz, ppm): $\delta$ 112.84 (s).

**Synthesis of [Pd(OTs)$_2$(L)] (L = TROPP$^{Ph}$, 2a; TROPP$^{(2\text{-MeOPh})}$, 2b.** **1a/b** (0.200 mmol) were suspended in deaerated $CH_2Cl_2$ (10 mL), followed by the addition of silver tosylate (117.1 mg, 0.420 mmol). The obtained suspensions were allowed to stir for 4 h at room temperature, followed by their filtration through a small plug of Celite. The resulting yellow solutions were concentrated to a small volume (2 mL) and on addition of diethyl ether (20 mL) the products precipitated as yellow microcrystalline powders that were separated by filtration, washed with diethyl ether (10 mL) and then dried in a stream of nitrogen.

**2a.** Yield: 88% (145.2 mg, 0.176 mmol). $C_{41}H_{35}O_6PS_2Pd$ (824.92): calc. C, 59.70; H, 4.24; found: C, 59.59; H, 4.19%. $^{1}H$ NMR ($CD_2Cl_2$, 400.13 MHz, ppm): $\delta$ 2.35 (s, 6H, C*H*$_3$), 5.29 (d, $^{2}J_{PH}$ = 15.2 Hz, 1H, PC*H*), 7.09–7.87 (m, 28H, Ar–*H* + C*H*=C*H*). $^{13}C\{^{1}H\}$ NMR ($CD_2Cl_2$, 100.62 MHz, ppm): $\delta$ 21.09 (s, *C*H$_3$), 52.73 (d, $^{1}J_{PC}$ = 25.3 Hz, P*C*H), 97.33 (br s, *C*H=*C*H), 123.36–141.09 (Ar–*C*). $^{31}P\{^{1}H\}$ NMR ($CD_2Cl_2$, 161.98 MHz, ppm): $\delta$ 125.99 (br s).

**2b.** Yield: 80.0% (141.6 mg, 0.160 mmol). $C_{43}H_{39}O_8PS_2Pd$ (884.92): calc. C, 58.36; H, 4.41; found: C, 58.28; H, 4.35%. $^{1}H$ NMR ($CD_2Cl_2$, 400.13 MHz, ppm): $\delta$ 2.36 (s, 6H, C*H*$_3$), 3.64 (s, 6H, O*CH*$_3$), 5.58 (d, $^{2}J_{PH}$ = 16.0 Hz, 1H, PC*H*), 6.78–7.78 (m, 26H, Ar–*H* + C*H*=C*H*). $^{13}C\{^{1}H\}$ NMR ($CD_2Cl_2$, 100.62 MHz, ppm): $\delta$ 15.13 (s, *C*H$_3$), 51.66 (d, $^{1}J_{PC}$ = 27.2 Hz, P*C*H), 97.33 (br s, *C*H=*C*H), 111.11–160.57 (Ar–*C*). $^{31}P\{^{1}H\}$ NMR ($CD_2Cl_2$, 161.98 MHz, ppm): $\delta$ 130.76 (br s).

Dissolution of **2a/b** in $CD_3OD$ gave the cationic complexes [Pd(L)($CD_3OD$)$_2$](OTs)$_2$ (L = TROPP$^{Ph}$, **2a′**; TROPP$^{(2\text{-MeOPh})}$, **2b′**).

**2a′.** $^{1}H$ NMR ($CD_3OD$, 400.13 MHz, ppm): $\delta$ 2.35 (s, 6H, C*H*$_3$), 5.89 (d, $^{2}J_{PH}$ = 13.2 Hz, 1H, PC*H*), 7.20–7.93 (m, 28H, Ar–*H* + C*H*=C*H*). $^{13}C\{^{1}H\}$ NMR ($CD_3OD$, 100.62 MHz, ppm): $\delta$ 19.97 (s, *C*H$_3$), 51.62 (d, $^{1}J_{PC}$ = 26.1 Hz, P*C*H), 98.87 (br s, *C*H=*C*H), 125.66–141.20 (Ar–*C*). $^{31}P\{^{1}H\}$ NMR ($CD_3OD$, 161.98 MHz, ppm): $\delta$ 129.00 (br s). $\Lambda_M$ (MeOH, 21.0 °C): 130 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**2b′.** $^{1}H$ NMR ($CD_3OD$, 400.13 MHz, ppm: $\delta$ 2.34 (s, 6H, C*H*$_3$), 3.64 (s, 6H, O*CH*$_3$), 5.88 (d, $^{2}J_{PH}$ = 14.2 Hz, 1H, PC*H*), 7.02–7.98 (m, 26H, Ar–*H* + C*H*=C*H*). $^{13}C\{^{1}H\}$ NMR ($CD_3OD$, 100.62 MHz, ppm): $\delta$ 19.67 (s, *C*H$_3$), 51.42 (d, $^{1}J_{PC}$ = 26.2 Hz, P*C*H), 98.93 (br s, *C*H=*C*H), 110.11–161.57 (Ar–*C*). $^{31}P\{^{1}H\}$ NMR ($CD_3OD$, 161.98 MHz, ppm): $\delta$ 134.00 (br s). $\Lambda_M$ (MeOH, 21.0 °C): 129 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**"*In situ*" synthesis of [Pd(COOMe)($CD_3OD$)(TROPP$^{Ph}$)](OTs) (3a′) in $CD_3OD$.** **2a** (25.0 mg, 0.030 mmol) was dissolved in

deaerated $CD_3OD$ at room temperature. Then CO was bubbled through the latter solution for half a minute at room temperature. During this time the colour of the solution turned red. The red solution was then transferred into a 5 mm NMR tube in order to acquire NMR spectra.

Integrals of $^1H$ NMR signals are not reported due to the concomitant presence of TsOH in solution that rapidly exchanges the counter-anion with **3a′**. $^1H$ NMR ($CD_3OD$, 400.12 MHz, ppm): $\delta$ 2.38 (s, C$H_3$), 5.79 (d, $^2J_{PH}$ = 16.0 Hz, PC*H*), 7.08 (s, C*H*=C*H*), 7.35–7.77 (m, Ar–*H*). $^{13}C\{^1H\}$ NMR ($CD_3OD$, 100.62 MHz, ppm): $\delta$ 13.9 (s, *C*$H_3$), 54.80 (d, $^1J_{PC}$ = 24.5 Hz, P*C*H), 115.54 (s, *C*H=*C*H), 124.90–140.46 (Ar–*C*), 174.9 (d, $^2J_{PC}$ = 16.3 Hz, *C*OCD$_3$). $^{31}P\{^1H\}$ NMR ($CD_3OD$, 161.98 MHz, ppm): $\delta$ 68.35 (d, $^2J_{PC}$ = 16.3 Hz).

**Synthesis of [PdClMe(TROPP$^{Ph}$)] (7a).** [PdClMe($\eta^4$-COD)] (106.0 mg, 0.400 mmol) was dissolved in deaerated $CH_2Cl_2$ (10 mL) followed by the addition of TROPP$^{Ph}$ (150.9 mg, 0.400 mmol) at room temperature. The solution was allowed to stir for 20 min, followed by its concentration to a small volume (2 mL). After the addition of diethyl ether the product precipitated as white microcrystalline powder, that was separated by filtration, washed with diethyl ether and dried in a stream of nitrogen. Yield: 90.0% (191.9 mg, 0.360 mmol). $C_{28}H_{24}ClPPd$ (533.15): calc. C, 63.08; H, 4.50; found: C, 62.98; H, 4.41%. $^1H$ NMR ($CDCl_3$, 300.13 MHz, ppm): $\delta$ 0.92 (d, $^3J_{PH}$ = 2.9 Hz, 3H, PdC$H_3$), 5.16 (d, $^2J_{PH}$ = 15.1 Hz, 1H, PC*H*), 6.93–7.39 (m, 20H, Ar–*H* + C*H*=C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.49 MHz, ppm): $\delta$ 8.45 (s, Pd*C*$H_3$), 56.37 (d, $^1J_{PC}$ = 21.1 Hz, P*C*H), 113.49 (s, *C*H=*C*H), 127.27–134.63 (Ar–*C*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.49 MHz, ppm): $\delta$ 76.06 (s).

**Synthesis of [PdMe(H$_2$O)(TROPP$^{Ph}$)](PF$_6$) (8a). 7a** (106.6 mg, 0.20 mmol) was dissolved in deaerated $CH_2Cl_2$ (8 mL) at room temperature, followed by the addition of $AgPF_6$ (53.1 mg, 0.21 mmol). The resulting suspension was allowed to stir for 20 min at room temperature. AgCl was then removed upon filtration of the suspension through a plug of Celite. The yellow solution obtained was concentrated to dryness and the residue suspended in diethyl ether and stirred for 10 min at room temperature. Afterwards the yellow microcrystalline product was separated by filtration and dried in a stream of nitrogen. Yield: 80.0% (105.7 mg, 0.160 mmol). $C_{28}H_{26}F_6OP_2Pd$ (660.60): calc. C, 50.91; H, 3.93; found: C, 50.82; H, 3.79%. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz, ppm): $\delta$ 0.83 (s, 3H, PdC$H_3$), 4.11 (s, 2H, $H_2O$), 5.28 (d, $^2J_{PH}$ = 15.3 Hz, 1H, PC*H*), 7.02 (s, 2 H, C*H*=C*H*), 7.07–7.50 (m, 18H, Ar–*H*). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 75.49 MHz, ppm): $\delta$ 11.73 (s, Pd*C*$H_3$), 56.18 (d, $^1J_{PC}$ = 24.1 Hz, P*C*H), 113.56 (s, *C*H=H), 126.22–134.15 (Ar–*C*). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.49 MHz, ppm): $\delta$ 77.70 (s).

**"*In situ*" synthesis of [Pd(COMe)(H$_2$O)(TROPP$^{Ph}$)](PF$_6$) (9a).** **8a** (66.1 mg 0.100 mmol) was dissolved in deaerated $CD_2Cl_2$ (2 mL) at room temperature. The latter solution was then transferred into a 10 mm sapphire tube under nitrogen, followed by its pressurization with CO (75 psi) at room temperature. After a reaction time of 5 min the sapphire tube was depressurized and the solution transferred into a 5 mm NMR tube in order to acquire NMR spectra. An identical synthetic procedure was applied to obtain a $CH_2Cl_2$ solution of **9a** used for the acquisition of an IR spectrum. $^1H$ NMR ($CD_2Cl_2$, 300.13 MHz, ppm): $\delta$ 1.89 (d, $^4J_{PH}$ = 1.5 Hz, 3H, COC$H_3$), 5.25 (d, $^2J_{PH}$ = 16.2 Hz, 1H, PC*H*), 6.25 (br s, 2H, $H_2O$), 7.02–7.48 (m, 20H, Ar–*H* + C*H*=C*H*). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 75.49 MHz, ppm): $\delta$ 33.60 (d, $^3J_{PC}$ = 25.9 Hz, CO*C*$H_3$), 56.81 (d, $^1J_{PC}$ = 22.6 Hz, P*C*H), 118.75 (s, *C*H = *C*H), 126.71–134.53 (Ar–*C*), 223.24 (s, *C*OCH$_3$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 121.49 MHz, ppm): $\delta$ 48.21 (s). IR ($CH_2Cl_2$, $\nu$(CO)/cm$^{-1}$) 1716 (s).

**Synthesis of [Pd(CH$_2$CH$_2$COMe)(TROPP$^{Ph}$)](PF$_6$) (10a).** Ethene was bubbled for 5 min through a solution of **9a** (132.1 mg, 0.200 mmol) in deaerated $CH_2Cl_2$ (4 mL), that was obtained as described above, at room temperature. Afterwards the solution was concentrated to a small volume (2 mL) and diethyl ether was added, precipitating **10a** as yellow microcrystalline compound, that was separated by filtration, washed with diethyl ether (8 mL) and dried in a stream of nitrogen. Yield: 78.0% (109.0 mg, 0.156 mmol). $C_{31}H_{28}F_6OP_2Pd$ (698.63): calc. C, 53.29; H, 4.00; found: C, 53.19; H, 3.92%. $^1H$ NMR ($CD_2Cl_2$, 400.12 MHz, ppm): $\delta$ 1.86 (td, $^3J_{HH}$ = 6.1 Hz, $^3J_{PH}$ = 2.1 Hz, 2H, PdC$H_2$), 2.57 (s, 3H, COC$H_3$), 3.20 (t, $^3J_{HH}$ = 6.1 Hz, 2H, COC$H_2$), 5.35 (d, $^2J_{PH}$ = 16.4 Hz, 1H, PC*H*), 7.14–7.63 (m, 20H, Ar–*H* + C*H*=C*H*). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 100.62 MHz, ppm): $\delta$ 27.98 (s, CO*C*H$_3$), 32.76 (s, Pd*C*H$_2$), 51.49 (s, CO*C*H$_2$), 55.59 (d, $^1J_{PC}$ = 18.0 Hz, P*C*H), 112.40 (s, *C*H=*C*H), 112.40–134.38 (Ar–*C*), 235.81 (s, *C*OCH$_3$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 161.98 MHz, ppm): $\delta$ 73.74 (s). IR ($CH_2Cl_2$, $\nu$(CO)/cm$^{-1}$) 1632 (s).

**Methoxycarbonylation of terminal alkynes.** Typically, a solution of the substrate (2.00 mmol) in deaerated MeOH (20 mL) was introduced by suction into an autoclave (320 mL), previously evacuated by a vacuum pump, containing the desired amount of catalyst precursor and BQ or TsOH. The autoclave was then charged at room temperature with CO (1 bar), followed by its heating to 70 °C. Once the latter temperature had been reached the autoclave was charged with the desired CO pressure and stirring (800 rpm) was started. After the desired reaction time, the autoclave was successively cooled to 10 °C by means of an ice-water bath, unreacted CO released and *n*-decane (standard, 98.0 μL) added. The catalytic solution was then subjected to a GC and GC-MS analysis.

**Dimerization of ethene.** A solution of **8a** (13.2 mg, 0.02 mmol) in toluene (30 mL) was introduced by suction into an autoclave (320 mL), previously evacuated by a vacuum pump. The autoclave was then successively charged at room temperature with ethene (1 bar) and heated to 50 °C. Once the latter temperature had been reached stirring was started and the ethene pressure was adjusted to 21 bar, maintaining this latter pressure constant by continuously feeding the autoclave with ethene from a reservoir. After a reaction time of 2 h, the autoclave was cooled to 0 °C by means of an ice-acetone bath, the excess ethene was vented off slowly and the clear yellow reaction solution was subjected to a GC (standard, hexane (98.0 μL) and GC-MS analysis.

### X-Ray crystallographic data collection and refinement of the structures

The crystallographic data for **1a**·0.5$C_2H_4Cl_2$, **7a**·0.5$CH_2Cl_2$ and **10a**·0.5$C_6H_6$ are summarized in Table 3. The X-ray diffraction intensity data for **7a**·0.5$CH_2Cl_2$ were collected on a Enraf

Nonius CAD4 diffractometer, while those for **1a**·0.5$C_2H_4Cl_2$ and **10a**·0.5$C_6H_6$ were collected on an Oxford Diffraction CCD diffractometer (Xcalibur 3), applying graphite monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Absorption correction was carried out applying psi-scans (**7a**·0.5$CH_2Cl_2$) or SADABS[25a] (**1a**·0.5$C_2H_4Cl_2$, **10a**·0.5$C_6H_6$). All structure determination calculations were performed with the WINGX package[25b] that comprises SIR-97,[25c] SHELXL-97[25d] and ORTEP-3 programs.[25e] Final refinements based on $F^2$ were carried out with anisotropic thermal parameters for all non-hydrogen atoms, except those belonging to the solvent molecules (*i.e.* $CH_2Cl_2$ and $C_6H_6$). The occupancy factors for the solvents' carbon atoms were refined giving a value close to 0.5. As a consequence, the occupancy factor of the latter atoms was fixed to 0.5 in the last refinement cycle. The geometry of the solvent molecules was modeled applying DFIX restraints. Hydrogen atoms were included in the refinement using a riding model with isotropic $U$ values depending on the $U_{eq}$. CCDC reference number for **1a**·0.5$C_2H_4Cl_2$: 739871, **7a**·0.5$CH_2Cl_2$: 696685 and **10a**·0.5$C_6H_6$: 96684.

## Acknowledgements

The authors thank the European Commission for financing the project IDECAT (NoE contract no. NMP3-CT-2005-011730). Additional support by the Swiss National Science Foundation and the ETH Zürich is gratefully acknowledged.

## References

1 W. Reppe, *Ger. Pat.*, 855 110, 1939.
2 (*a*) G. Bartolo, G. Salerno and M. Costa in *Top. Organomet. Chem., Catalytic Carbonylation Reactions*, ed. M. Beller, Springer, Berlin, 2006, vol. 18, ch. 10, pp. 239–272; (*b*) C. Grosjean, K. Novakovic, S. K. Scott, A. Whiting, M. J. Willis and A. R. Wright, *J. Mol. Catal. A: Chem.*, 2008, **284**, 33–39; (*c*) D. Milstein, *Acc. Chem. Res.*, 1988, **21**, 428–434; (*d*) T. F. Murray and J. R. Norton, *J. Am. Chem. Soc.*, 1979, **101**, 4107–4119; (*e*) A. Scrivanti, V. Beghetto, E. Campagna, M. Zanato and U. Matteoli, *Organometallics*, 1998, **17**, 630–635; (*f*) D. Zargarian and H. Alper, *Organometallics*, 1993, **12**, 712–724; (*g*) B. E. Ali, J. Titani and A. M. El-Ghanam, *Tetrahedron Lett.*, 2001, **42**, 2385–2387; (*h*) M. Akao, S. Sugawara, K. Amino and Y. Inoue, *J. Mol. Catal. A: Chem.*, 2000, **157**, 117–122; (*i*) G. P. Chiusoli, M. Costa, P. Pergreffi, S. Riverberi and G. Salerno, *Gazz. Chim. Ital.*, 1985, **115**, 691–696; (*j*) D. Zargarian and H. Alper, *Organometallics*, 1991, **10**, 2914–2921.
3 (*a*) J. Tsuji, M. Takahashi and T. Takahashi, *Tetrahedron Lett.*, 1980, **21**, 849–850; (*b*) T. Kitamura, I. Mihara, H. Taniguchi and P. J. Stang, *J. Chem. Soc., Chem. Commun.*, 1990, 614–615; (*c*) Y. Sakurai, S. Sakaguchi and Y. Ishii, *Tetrahedron Lett.*, 1999, **40**, 1701–1704; (*d*) R. F. Heck, *J. Am. Chem. Soc.*, 1972, **94**, 2712–2716; (*e*) T. T. Zung, L. B. Bruk, O. N. Temkin and A. V. Malashkevich, *Mendeleev Commun.*, 1995, **5**, 3–4; (*f*) T. T. Zung, L. G. Bruk and O. N. Temkin, *Mendeleev Commun.*, 1994, **4**, 2–3; (*g*) L. G. Bruk and O. N. Temkin, *Inorg. Chim. Acta*, 1998, **280**, 202–210.
4 J. S. Prasad and L. S. Liebeskind, *Tetrahedron Lett.*, 1987, **28**, 1857–1860.
5 (*a*) E. Drent, P. Arnoldy and P. H. M. Budzelaar, *J. Organomet. Chem.*, 1993, **455**, 247–253; (*b*) E. Drent, P. Arnoldy and P. H. M. Budzelaar, *J. Organomet. Chem.*, 1994, **475**, 57–63; (*c*) S. Doherty, J. G. Knight and M. Betham, *Chem. Commun.*, 2006, 88–90; (*d*) A. Dervisi, P. G. Edwards, P. D. Newman, R. P. Tooze, S. J. Coles and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1999, 1113–1120.
6 J. Thomaier, S. Boulmaâz, H. Schönberg, H. Rüegger, A. Currao, H. Grützmacher, H. Hillebrecht and H. Pritzkow, *New J. Chem.*, 1998, **22**, 947–958.
7 (*a*) H. Schönberg, S. Boulmaâz, M. Wörle, L. Liesum, A. Schweiger and H. Grützmacher, *Angew. Chem., Int. Ed.*, 1998, **37**, 1423–1426; (*b*) F. Breher, H. Rüegger, M. Mlakar, M. Rudolph, S. Deblon, H. Schönberg, S. Boulmaâz, J. Thomaier and H. Grützmacher, *Chem.–Eur. J.*, 2004, **10**, 641–653; (*c*) S. Boulmaâz, M. Mlakar, S. Loss, H. Schönberg, S. Deblon, M. Wörle, R. Nesper and H. Grützmacher, *Chem. Commun.*, 1998, 2623–2624.
8 (*a*) C. Bianchini, A. Meli, W. Oberhauser, A. M. Segarra, C. Claver and E. J. Garcia Suarez, *J. Mol. Catal. A: Chem.*, 2007, **265**, 292–305; (*b*) C. Bianchini, A. Meli, W. Oberhauser, S. Parisel, E. Passaglia, F. Ciardelli, O. V. Gusev, A. M. Kal'sin and N. V. Vologdin, *Organometallics*, 2005, **24**, 1018–1030; (*c*) O. V. Gusev, A. M. Kalsin, M. G. Peterleitner, P. V. Petrovskii, K. A. Lyssenko, N. G. Akhmedov, C. Bianchini, A. Meli and W. Oberhauser, *Organometallics*, 2002, **21**, 3637–3649.
9 Z. Qin, M. C. Jennings and R. J. Puddephatt, *Inorg. Chem.*, 2001, **40**, 6220–6228.
10 C. Thoumazet, L. Ricard, H. Grützmacher and P. Le Floch, *Chem. Commun.*, 2005, 1592–1594.
11 F. Benetollo, R. Bertani, G. Bombieri and L. Toniolo, *Inorg. Chim. Acta*, 1995, **233**, 5–9.
12 (*a*) E. Drent and P. H. M. Budzelaar, *Chem. Rev.*, 1996, **96**, 663–681; (*b*) C. Bianchini, A. Meli and W. Oberhauser, *Dalton Trans.*, 2003, 2627–2635; (*c*) H. Grennberg, A. Gogoll and J.-E. Bäckvall, *Organometallics*, 1993, **12**, 1790–1793.
13 (*a*) J. Liu, B. T. Heaton, J. A. Iggo, R. Whyman, J. F. Bickley and A. Steiner, *Chem.–Eur. J.*, 2006, **12**, 4417–4430; (*b*) C. Bianchini, A. Meli, W. Oberhauser, P. W. N. M. van Leeuwen, M. A. Zuideveld, Z. Freixa, P. C. J. Kamer, A. L. Spek, O. V. Gusev and A. M. Kal'sin, *Organometallics*, 2003, **22**, 2409–2421; (*c*) O. V. Gusev, A. M. Kalsin, P. V. Petrovskii, K. A. Lyssenko, Y. F. Oprunenko, C. Bianchini, A. Meli and W. Oberhauser, *Organometallics*, 2003, **22**, 913–915.
14 D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chem.*, 1970, **9**, 1691–1694.
15 (*a*) T.-W. Lai and A. Sen, *Organometallics*, 1984, **3**, 866–870; (*b*) G. Cabinato and L. Toniolo, *J. Organomet. Chem.*, 1990, **398**, 187–195; (*c*) J. Liu, B. T. Heaton, J. A. Iggo and R. Whyman, *Chem. Commun.*, 2004, 1326–1327.
16 D. L. Thorn and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 2079–2090.
17 (*a*) B. R. Manzano, F. A. Jalón, F. Gómez-de la Torre, A. M. López-Agenjo, A. M. Rodríguez, K. Mereiter, W. Weissensteiner and T. Sturm, *Organometallics*, 2002, **21**, 789–802; (*b*) P. W. N. M. van Leeuwen, M. Zuideveld, B. H. G. Swennenhuis, Z. Freixa, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz and A. L. Spek, *J. Am. Chem. Soc.*, 2003, **125**, 5523–5539.
18 (*a*) P. Braunstein, J. Durand, M. Knorr and C. Strohmann, *Chem. Commun.*, 2001, 211–212; (*b*) K. Rajender Reddy, K. Surekha, G.-H. Lee, S.-M. Peng, J.-T. Chen and S.-T. Liu, *Organometallics*, 2001, **20**, 1292–1299; (*c*) M. Agostinho and P. Braunstein, *Chem. Commun.*, 2007, 58–60; (*d*) M. J. Green, G. J. P. Britovsek, K. J. Cavell, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 1563–1564; (*e*) S. Stoccoro, G. Minghetti, M. A. Cinellu, A. Zucca and M. Manassero, *Organometallics*, 2001, **20**, 4111–4113; (*f*) P. Braunstein, C. Frison and X. Morise, *Angew. Chem. Int. Ed*, 2000, **39**, 2867–2870.
19 D. Drew and J. R. Doyle, *Inorg. Chem*, 1972, **13**, 47–55.
20 R. E. Rülke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen and K. Vrieze, *Inorg. Chem.*, 1993, **32**, 5769–5778.
21 G. Berti, *J. Org. Chem.*, 1957, **22**, 230.
22 C. Bianchini, G. Lenoble, W. Oberhauser, S. Parisel and F. Zanobini, *Eur. J. Inorg. Chem.*, 2005, 4794–4800.
23 C. Bianchini, A. Meli and A. Traversi, *Ital. Pat.*, FI A,000,025, 1997.
24 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81–122.
25 (*a*) G. M. Sheldrick, *SADABS, Program for empirical absorption corrections*, University of Göttingen, Göttingen, Germany, 1986; (*b*) L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838; (*c*) A. Altomare, M. C. Burla, M. Cavalli, G. L. Cascarano, C. Giacovazzo, A. Gagliardi, G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115–119; (*d*) G. M. Sheldrick, *SHELX-97*, University of Göttingen, Germany, 1997; (*e*) M. N. Burnett and C. K. Johnson, *ORTEP-3*, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.