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Catalytic Properties of [Pd(COOMe)$_n$X$_{2-n}$(PPh$_3$)$_2$] (n = 0, 1, 2; X = Cl, NO$_2$, ONO$_2$, OAc and OTs) in the Oxidative Carbonylation of MeOH

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cis-[Pd(ONO$_2$)$_2$(PPh$_3$)$_2$] (**1**) reacts under mild conditions with CO in methanol (MeOH) in the presence of pyridine (py), yielding *trans*-[Pd(COOMe)(ONO$_2$)(PPh$_3$)$_2$] (**1a**). The use of NEt$_3$ instead of py leads to a mixture of **1a**, *trans*-[Pd(COOMe)$_2$(PPh$_3$)$_2$] (**2**), and [Pd(CO)(PPh$_3$)$_3$]. Pure **2** was prepared by reacting *cis*-[Pd(OTs)$_2$(PPh$_3$)$_2$] with CO in MeOH and subsequently adding NEt$_3$. The nitro complex *trans*-[Pd(COOMe)(NO$_2$)(PPh$_3$)$_2$] (**3a**) was prepared by reacting *trans*-[Pd(COOMe)Cl(PPh$_3$)$_2$] with AgNO$_2$ or with AgOTs and NaNO$_2$. New syntheses for **1** and *trans*-[Pd(NO$_2$)$_2$(PPh$_3$)$_2$] (**3**) are also reported. All complexes have been characterized by IR and ^{1}H and ^{31}P{^{1}H} NMR spectroscopies. Complexes **1** and **2** exchange irreversibly and quantitatively one nitrato with one carbomethoxy ligand, yielding **1a**. **2** in CD$_2$Cl$_2$ at 40 °C decomposes with the formation of dimethyl carbonate (DMC), whereas under 4 atm of CO, DMC and dimethyl oxalate (DMO) are formed, ca. 12% each; in the presence of PPh$_3$ and in the absence of CO, decomposition occurs at 60 °C with the formation of DMC only, suggesting that decarbonylation involves a five-coordinate intermediate or predissociation of a PPh$_3$ ligand. The oxidative carbonylation of MeOH does not occur when using NaNO$_2$ or NaNO$_3$ as the oxidant and **1**, **1a**, **3**, or **3a** as the catalyst precursor. On the contrary, when using benzoquinone (BQ) as the oxidant, these complexes, **2**, or [Pd(COOMe)$_{2-n}$X$_n$(PPh$_3$)$_2$] (X = Cl, OAc, OTs; n = 1, 2) promote selective catalysis to DMO. After catalysis the precursors are transformed into [Pd(BQ)(PPh$_3$)$_2$]$_2$·H$_2$BQ, [Pd(CO)(PPh$_3$)]$_3$ and [Pd(CO)(PPh$_3$)$_3$]. Also the last with BQ gives selective catalysis to DMO. The solid-state structures of **1**·CH$_2$Cl$_2$ and **1a** have been determined by means of single-crystal X-ray diffraction.

Introduction

Palladium(II) carboalkoxy complexes are intermediates in several important catalytic carbonylation reactions carried out in the presence of an alkanol, such as, for example, the alkene−CO copolymerization to polyketones[1] and the oxidative carbonylation of alkenes to unsaturated esters or diesters[3] or of alkanols to carbonates and oxalates.[2m,3] They have been proposed as intermediates also in the catalytic hydrocarboalkoxylation of alkenes to monoesters.[4]

The interaction of CO with an alkanol on the metal center provides the most direct method of synthesis.[5] Other methods include the oxidative addition of chloro or cyano formate or of phenylcarbonate to palladium(0) complexes,[6] the decarbonylation of alkoxalyl complexes,[7] and exchange with HgCl(COOMe).[8]

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It has been reported that $PdCl_2$[9] and $Pd(OAc)_2$[10] promote the noncatalytic carbonylation of ethanol (EtOH) or methanol (MeOH) to diethyl carbonate or dimethyl oxalate (DMO), respectively, with concomitant reduction to palladium metal. The formation of these products occurs through the intermediacy of PdCOOR species. The presence of PPh_3 prevents the formation of palladium black, yielding instead palladium(0) complexes such as $[Pd(CO)(PPh_3)]_3$ and $[Pd(CO)(PPh_3)_3]$.[5o,p,10] In order to be catalytic in palladium, some other oxidants, such as oxygen, Cu^{2+}, Fe^{3+}, benzoquinone (BQ), or an organic nitrite or a combination of them, must be used.[3]

With the aim of finding whether a NO_3^- or a NO_2^- ligand could act as the oxidant in the oxidative carbonylation of MeOH, we took into consideration the use of complexes of the type *trans*-$[Pd(COOMe)_{2-n}X_n(PPh_3)_2]$ ($X = ONO_2$, NO_2; $n = 0, 1, 2$). Here, we report their synthesis, reactivity, and catalytic activity in the oxidative carbonylation of MeOH. The X-ray diffraction structures of *trans*-$[Pd(COOMe)(ONO_2)(PPh_3)_2]$ and *cis*-$[Pd(ONO_2)_2(PPh_3)_2]\cdot CH_2Cl_2$ are also reported.

Experimental Section

Instrumentation and Materials. IR spectra were recorded in a Nujol mull or in KBr on a Nicolet Fourier transform infrared (FTIR) instrument model Nexus (the IR frequencies reported below, when not indicated, refer to spectra taken in a Nujol mull). ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AMX 300 spectrometer equipped with a BB multinuclear probe operating in the FT mode at 300 and 121.442 MHz for ^1H and $^{31}P\{^1H\}$, respectively. ^1H and $^{31}P\{^1H\}$ chemical shifts are reported in ppm downfield of the deuterated solvent used as the internal standard or of externally referenced to 85% H_3PO_4, respectively. Gas chromatography (GC) analysis was performed using a Hewlett-Packard model 6890 chromatograph fitted with a HP5, 30 m × 0.32 μm × 0.25 μm column [detector, flame ionization; carrier gas, N_2, 0.7 mL/min; oven, 40 (3.5 min) to 250 °C at 15 °C/min]. For detection of methyl formate, a 80/120 Carbowax 20M, 6 ft × $^1/_4$ in. o.d., 2 mm i.d. glass column was used (temperature, 50−170 °C, 5 °C/min; detector, FID; carrier gas, N_2, 20 mL/min. For the detection of formaldehyde by the EPA 8315A method, http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/8315a.pdf, an Agilent HPLC−UV/vis instrument was used (wavelength, 360 nm), equipped with a Zorbax ODS column 5 μm, 4.6 × 250 mm, at 30 °C.

CD_2Cl_2 and the solvents (Aldrich) for the preparation of the complexes were used as received. $Pd(OAc)_2$, AgTsO, $AgNO_3$, $AgNO_2$, PPh_3, *p*-toluensulfonic acid, NEt_3, and BQ were also Aldrich products; only BQ was purified before use (from ethyl ether). CO (purity higher than 99%) was supplied by SIAD Spa (Italy). The complexes *trans*-$[Pd(COOMe)(OTs)(PPh_3)_2]$,[5a] *trans*-$[Pd(COOMe)Cl(PPh_3)_2]$,[5k] *trans*-$[PdCl_2(PPh_3)_2]$,[11] *trans*-$[PdOAc)_2(PPh_3)_2]$,[12] and *cis*-$[Pd(OTs)_2(PPh_3)_2]$[13] were prepared according to methods reported in the literature.

The reactivity tests under CO pressures higher than 2 atm were carried out using a stainless autoclave of ca. 60 mL, into which a glass bottle containing the solvent and reagents was introduced. The autoclave was first flushed several times with CO and then taken to the desired pressure and temperature. The solution was stirred with a magnetic bar. After 1 h of reaction, the autoclave was rapidly cooled to 0 °C and then slowly depressurized. The content was analyzed by GC and IR and NMR spectroscopies.

Preparation of the Complexes. **Synthesis of *cis*-$[Pd(ONO_2)_2(PPh_3)_2]$ (1).** Several procedures for preparing this complex have already been reported in the literature.[14−16]

We followed a more direct procedure. To a solution of 0.4 mmol of $Pd(AcO)_2$ in 4 mL of acetone was added at room temperature under stirring 0.91 mmol of PPh_3. A yellow precipitate formed in a few seconds. To this suspension was added dropwise at room temperature 160 mg of 65% HNO_3. The mixture was stirred for 30 min, after which the yellow precipitate was filtered off, washed with ether, and dried under vacuum. Yield: 93%. Anal. Calcd for $C_{36}H_{30}N_2O_6P_2Pd$: C, 57.27; H, 4.01; N, 3.71. Found: C, 57.65; H, 3.92; N, 3.87. IR data are reported in ref 14. ^1H NMR in CD_2Cl_2 (δ): 7.69−7.63 (c m, 30H, PPh_3). $^{31}P\{^1H\}$ NMR in CD_2Cl_2 (δ): 33.61 (s).

Synthesis of *trans*-$[Pd(COOMe)(ONO_2)(PPh_3)_2]$ (1a). A total of 5 mL of MeOH containing 0.1 mmol of **1**, together with 0.1 mmol of PPh_3 and 0.12 mmol of pyridine, was added to a glass bottle introduced into a 60 mL autoclave. After washing with CO at room temperature, the autoclave was heated at 50 °C for 2 h under 5 atm of CO. After filtration, 20 mL of diethyl ether was added under stirring. The suspension that formed after a few minutes was allowed to stir for about 30 min, after which the white precipitate was filtered off, washed with ether, and dried under vacuum. Yield: 77%. Anal. Calcd for $C_{38}H_{33}NO_5P_2Pd$: C, 60.69; H, 4.42; N, 1.86. Found: C, 60.21; H, 4.70; N, 1.78. IR

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(Nujol): 1670 s (ν_{CO}), 1655 w (ν_{CO}), 1465 s (in KBr, $\nu_{asym\ NO_2}$), 1385 s (in KBr), 1284 s ($\nu_{sym\ NO_2}$), 1076 br (ν_{COC}), 1018 w (ν_{NO}), 804 w (δ_{ONO}) cm^{-1}. ^{1}H NMR in CD_2Cl_2 (δ): 7.65−7.42 (c m, 30H, PPh_3), 2.58 (s, 3H, $COOCH_3$). ^{31}P{^{1}H} NMR in CD_2Cl_2 (δ): 18.55 (s).

In a different procedure, 0.1 mmol of *trans*-[Pd(COOMe)Cl(PPh_3)$_2$], suspended in 2 mL of MeOH, was treated with a slight excess of $AgNO_3$ in 4 mL of CH_2Cl_2 under stirring at room temperature. The white precipitate that formed after a few minutes was filtered off and washed with CH_2Cl_2. To the solution were added under stirring 70 mL of diethyl ether/petroleum ether (2:5). After a few minutes, a white precipitate formed. The suspension was stirred for a further 30 min and filtered, and the solid was washed with a mixture of the two ethers and dried under vacuum. Yield: 92%. The product was recrystallized from CH_2Cl_2/petroleum ether.

In another procedure, 0.25 mmol of $LiNO_3$ dissolved in 10 mL of water was added to 0.1 mmol of *trans*-[Pd(COOMe)(OTs)(PPh_3)$_2$] dissolved in 2 mL of MeOH at ambient temperature under stirring. A white precipitate formed immediately. The suspension was stirred for 30 min and then filtered off. The solid was washed with diethyl ether and dried under vacuum. Yield: 93%.

Synthesis of *trans*-[Pd(COOMe)$_2$(PPh$_3$)$_2$] (2). A procedure for preparing this complex has been reported.[5p] Following the procedure for the preparation of **1**, but using NEt_3 in place of pyridine after 2 h under 5 atm of CO at room temperature, **2** precipitated in a mixture with **1a**, [Pd(CO)(PPh_3)$_3$],[17] and minor amounts of unreacted **1**.

Pure complex **2** has been synthesized by treating *cis*-[Pd(OTs)$_2$(PPh_3)$_2$] (0.1 mmol), dissolved in 2 mL of MeOH, with CO (2 atm) at 0 °C for 10 min under stirring, during which time the solution turned from brownish to yellowish. NEt_3 (0.8 mmol) was then added with stirring for a further 10 min. The light-brown solid that formed was collected on a filter, washed with MeOH and Et_2O, and dried under vacuum. Yield: 87%. Anal. Calcd for $C_{40}H_{36}O_4P_2Pd$: C, 64.14; H, 4.84. Found: C, 63.78; H, 4.94. IR (Nujol): 1631 s (ν_{CO}), 1014 br (ν_{COC}) cm^{-1}. ^{1}H NMR in CD_2Cl_2 (δ): 7.68−7.37 (c m, 30H, PPh_3), 2.55 (s, 6H, $COOCH_3$). ^{31}P{^{1}H} NMR in CD_2Cl_2 (δ): 21.76 (s).

Synthesis of [Pd(NO$_2$)$_2$(PPh$_3$)$_2$] (3). For this complex also, several procedures have already been reported.[15,18−21]

We followed a simpler procedure. A total of 0.1 mmol of $Pd(OAc)_2$ was stirred in 5 mL of acetonitrile at room temperature for 10 min, after which 0.22 mmol of $AgNO_2$ was added and stirred for a further 30 min. The white precipitate that formed was filtered off. To the solution was added with stirring for another 0.5 h 0.2 mmol of PPh_3 dissolved in 10 mL of diethyl ether. The resulting suspension was filtered. The white-ivory solid was washed with ether and dried under vacuum. Yield: 89%. $NaNO_2$ dissolved in water can be used in place of $AgNO_2$. Yield: 81%. Anal. Calcd for $C_{36}H_{30}N_2O_4P_2Pd$: C, 59.80; H, 4.18; N, 3.87. Found: C, 60.21; H, 4.24; N 3.57. IR data are reported in ref 15. ^{1}H NMR in CD_2Cl_2 (δ): 7.69−7.47 (c m, 30H, PPh_3). ^{31}P{^{1}H} NMR in CD_2Cl_2 (δ): 16,41 (s).

The dinitro complex can also be prepared by using 0.1 mmol of $PdCl_2$ dissolved in 0.2 mL of acetic acid in place of $Pd(OAc)_2$, following the procedure just reported. Yield: 72%.

Synthesis of *trans*-[Pd(COOMe)(NO$_2$)(PPh$_3$)$_2$] (3a). Several attempts to prepare this complex by the direct carbonylation of the corresponding dinitro complex in MeOH, as reported for **1a**, gave unsatisfactory results.

Complex **3a** was prepared from a preformed palladium carbomethoxy complex. To 0.14 mmol of *trans*-[Pd(COOMe)Cl(PPh_3)$_2$] dissolved in 3 mL of MeOH was added at room temperature under stirring for 30 min 0.16 mmol of AgTsO. After filtration, 0.4 mmol of $NaNO_2$ in 10 mL of water was added. The white precipitate was collected on a filter, washed with water and diethyl ether, and dried under vacuum. Yield: 89%. Anal. Calcd for $C_{38}H_{33}NO_4P_2Pd$: C, 62.01; H, 4.52; N, 1.86. Found: C, 62.33; H, 4.69; N, 1.90. IR (Nujol): 1657 s (ν_{CO}), 1413 s ($\nu_{asym\ NO_2}$), 1331 s ($\nu_{sym\ NO_2}$), 1055 br (ν_{COC}), 821 w (δ_{ONO}), 600−550 w ($\rho_{w\ ONO}$) cm^{-1}. ^{1}H NMR in CD_2Cl_2 (δ): 7.63−7.37 (c m, 30H, PPh_3), 2.50 (s, 3H, $COOCH_3$). ^{31}P{^{1}H} NMR in CD_2Cl_2 (δ): 18.82 (s).

In a procedure different from that of 0.1 mmol of *trans*-[Pd(COOMe)Cl(PPh_3)$_2$], dissolved in 4 mL of acetonitrile/CH_2Cl_2 (1:3), 0.1 mmol of $AgNO_2$ was added at room temperature under stirring. The suspension that formed was filtered. After the white solid that precipitated upon the addition of diethyl ether and petroleum ether was collected on a filter and the usual workup, the yield was 82%.

Synthesis of *cis*-[Pd(C$_2$O$_4$)(PPh$_3$)$_2$] (4). This complex was prepared by treating with oxalic acid the carbonato complex [Pd(CO_3)(PPh_3)$_2$],[22] in turn prepared by bubbling a mixture of oxygen and carbon dioxide through a benzene solution of [Pd(PPh_3)$_4$].[23]

We followed a more direct procedure. A total of 0.1 mmol of *trans*-[Pd(OAc)$_2$(PPh_3)$_2$] in 50 mL of EtOH was treated with a slight excess of oxalic acid. After ca. 10 min, an ivory solid precipitated. The suspension was stirred for a further 2 h. After 50 mL of petroleum ether was added, the solid was collected on a filter, washed with EtOH and petroleum ether, and dried. Yield: 66%. Anal. Calcd for $C_{38}H_{30}O_4P_2Pd$: C, 63.48; H, 4.21. Found: C, 63.07; H, 3.95. ^{1}H NMR in CD_2Cl_2 (δ): 7.49−7.28 (c m, 30H, PPh_3). ^{31}P{^{1}H} NMR in CD_2Cl_2 (δ): 33.94 (s).

X-ray Structure Determinations. Crystals of both complexes **1** and **1a**, suitable for X-ray analysis, were obtained by slow recrystallization from CH_2Cl_2/*n*-hexane solutions. Complex **1** crystallizes with a dichlorometane molecule and is indicated hereafter as **1**·CH_2Cl_2. The selected specimens of both compounds were lodged into Lindemann glass capillaries and mounted on the goniometer head of a four-circle Philips PW1100 diffractometer made available by colleagues of the CMR-ICIS Institute of Padua, Padua, Italy. Raw diffraction data were collected at room temperature with the $\omega-2\theta$ technique, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Intensities were corrected for Lorentz and polarization effects, as well as for absorption (ψ scans).[24]

Unit cell parameters were determined by the least-squares refinement of 30 well-centered high-angle reflections. Three standard reflections were checked every 150 measurements to assess the crystal stability; no sign of decay was noticed. The structures were solved with a combination of direct methods and Fourier difference syntheses (*SIR* program)[25] and subsequently refined by standard full-matrix least squares based on F_o^2 with the *SHELXL-97*[26] and *SHELXTL-NT*[27] programs. In the last cycles of refinement, all non-hydrogen atoms were allowed to

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Table 1. Crystallographic Data of Complexes **1a** and **1**·CH_2Cl_2

	1a	**1**·CH_2Cl_2
empirical formula	$C_{38}H_{33}NO_5P_2Pd$	$C_{37}H_{32}N_2O_6P_2Cl_2Pd$
fw	751.99	839.89
cryst size (mm^3)	0.24 × 0.20 × 0.15	0.30 × 0.25 × 0.18
cryst syst	monoclinic	monoclinic
Space group	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)
a (Å)	11.011(3)	11.975(2)
b (Å)	19.446(3)	20.127(3)
c (Å)	16.276(3)	15.479(3)
β (deg)	91.85(3)	95.06(3)
volume (Å^3)	3483(1)	3716(1)
Z	4	4
T (K)	294	294
calcd density (Mg m^{-3})	1.434	1.501
abs coeff (cm^{-1})	6.68	7.77
$F(000)$	1536	1704
θ range (deg)	3.04−26.00	3.31−25.00
indep (unique) reflns/R_{int}	6803/0.0377	6487/0.0179
obsd reflns [$I > 2\sigma(I)$]	6306	5786
data/param	6803/849	6487/451
R indices [$I > 2\sigma(I)$]	$R1^b = 0.0447$; $wR2^c = 0.0980$	$R1^b = 0.0523$; $wR2^c = 0.1194$
R indices (all data)	$R1^b = 0.0522$; $wR2^c = 0.1050$	$R1^b = 0.0635$; $wR2^c = 0.1278$
GOF^a on F^2	1.190	1.245
largest difference peak and hole (e Å^{-3})	0.697 and −0.690	0.675 and −0.792

[a] $GOF = [\sum(w(F_o^2 - F_c^2)^2]/(N_{obsns} - N_{params})]^{1/2}$, based on all data. [b] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

vibrate anisotropically. Hydrogen atoms were introduced in calculated positions in their described geometries and refined as a "riding model", with fixed isotropic thermal parameters set at 1.2 times U_{equiv} of the appropriate carrier atom.

For the structure of **1a**, the Flack parameter[28] has also been refined. The graphical representation of the two complexes have been obtained through the ORTEP module of the *WinGX* software.[29] A summary of the main crystallographic data is shown in Table 1 (see further for the selected bond lengths and angles). Full listings of the results of the crystallographic investigations for **1a** and **1**·CH_2Cl_2 are available as Supporting Information.

Results and Discussion

1. Synthesis, Characterization, and Reactivity of Complexes $[Pd(COOMe)_nX_{2-n}(PPh_3)_2]$ [X = (ONO_2), (NO_2); n = 1, 2].

1, suspended in MeOH in the presence of pyridine, reacts with CO under mild conditions, yielding **1a**. The formation of the complex occurs through interaction of CO with MeOH on the metal center with the release of one proton. Pyridine is necessary in order to neutralize the proton that would otherwise reverse the reaction. As a matter of fact, **1a**, suspended in MeOH containing HNO_3, gives back **1**.

$$\underset{\mathbf{1}}{cis\text{-}[Pd(ONO_2)_2L_2]} + CO + MeOH \xrightarrow{py} \underset{\mathbf{1a}}{trans\text{-}[Pd(COOMe)(ONO_2)L_2]} + pyH^+NO_3^- \qquad (1)$$

When NEt_3 is used in place of pyridine, the solid that is recovered after the reaction is a mixture of **1a**, the dicarbomethoxy complex **2**, $[Pd(CO)(PPh_3)]_3$,[17] and unreacted **1**.

Complex **2** does not form via disproportionation of **1a** to **1** and **2**, but rather the opposite occurs; i.e., **1** and **2** exchange a carbomethoxy ligand and a nitrate ligand, giving **1a**:

$$\underset{\mathbf{1}}{cis\text{-}[Pd(ONO_2)_2L_2]} + \underset{\mathbf{2}}{trans\text{-}[Pd(COOMe)_2L_2]} \rightarrow 2\underset{\mathbf{1a}}{trans\text{-}[Pd(COOMe)(ONO_2)L_2]} \qquad (2)$$

The reaction has been followed by NMR, by dissolving equimolar amounts of **1** and **2** in CD_2Cl_2 at −78 °C under argon (3 atm). The two $^{31}P\{^1H\}$ singlets at 33.73 and 21.40 ppm for **1** and **2**, respectively, that are still present at 0 °C disappear at 10 °C, to be replaced by one singlet at 18.53 ppm for complex **1a**. The transmetalation is irreversible (because upon cooling only this last signal remains present) and occurs with complete retention of the integrity of the carbomethoxy ligand, as proven by the ^1H NMR spectrum showing that the $H(PPh_3)$/H(COOMe) ratio is 60:6 before and after transmetalation. The transfer of an aryl or alkyl[30−33] group between palladium atoms is well-known, whereas to the best of our knowledge, the transfer of a carbomethoxy group from one palladium center to another has not been reported to date.

It was reported that the dinitrato complex **1** is reduced by CO in CH_2Cl_2 under ambient conditions, in the absence of any base, affording reasonably good yields (49%) of the corresponding dinitro complex **3** after just 1 h of reaction.[14] Thus, substitution of a NO_3 ligand of complex **1** with a COOMe one causes stabilization of the other NO_3 ligand toward reduction. That in the present case the product of reaction (1) is not the corresponding

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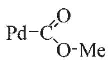
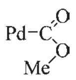
reduced nitro complex **3a** (or a nitrite complex *trans*-[Pd(COOMe)(ONO)(PPh$_3$)$_2$]) has been unambiguously proven by the fact that (i) the IR, ^{1}H MMR, and ^{31}P{^{1}H} NMR spectra of complex **1a** are identical with those of the carbomethoxy complex prepared by metathetical exchange of *trans*-[Pd(COOMe)Cl(PPh$_3$)$_2$] with AgNO$_3$ or by reaction of the cationic carbomethoxy complex *trans*-[Pd(COOMe)(OTs)(PPh$_3$)$_2$] with LiNO$_3$ and (ii) they differ from the spectra of the carbomethoxy−nitro complex **3a** prepared from *trans*-[Pd(COOMe)Cl(PPh$_3$)$_2$] and AgNO$_2$ or from *trans*-[Pd(COOMe)(OTs)(PPh$_3$)$_2$ and NaNO$_2$.

Compared to the IR of *trans*-[Pd(COOMe)Cl(PPh$_3$)$_2$],[5k] in complex **1a**, new absorptions are present, consistent with an O-coordinated monodentate nitrate [in the stretching region at 1465 ($\nu_{\mathrm{asym\ NO_2}}$), 1284 ($\nu_{\mathrm{sym\ NO_2}}$), and 1018 ($\nu_{\mathrm{NO}}$) cm^{-1} and in the deformation region at 803 cm^{-1} (δ_{ONO})][14,34] (see also the X-ray structure of **1a**). In addition, there is a band of strong intensity at 1385 cm^{-1}, characteristic of ionic nitrate.[35] This band is present in the spectra taken both in KBr and in a Nujol mull. Therefore, it cannot be due to the nitrate ligand displaced, even partially, from palladium(II) by Br$^-$ of KBr in the solid.

The ν_{CO} region of **1a** is characterized by a band of strong intensity at 1670 cm^{-1} and a band of weak intensity at 1655 cm^{-1}. At 1076 cm^{-1}, a rather broad band of strong intensity can be attributed to ν_{COC}. Also, the complex *trans*-[Pd(COOMe)Cl(PPh$_3$)$_2$] shows two absorptions in the ν_{CO} region, due to the possible presence of conformational isomers with cis and trans geometry.[5k]


cis

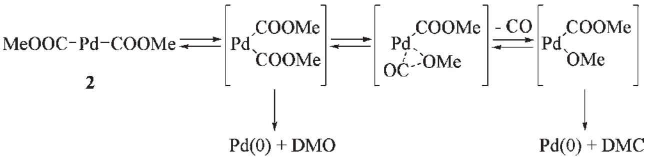

trans

Another explanation may be the following: In the X-ray crystal structure (see the structural characterization below for a detailed description), two independent, similar, but not identical, molecules are present in the asymmetric unit. The two molecules differ for the reciprocal orientation of the nitrate and COOMe ligands, as well as for the relative position of the COOMe moiety with respect to the PPh$_3$ ligands, and appear to be stabilized by a network of nonbonding contacts. If such arrangements coexist in the conditions under which the IR spectrum is taken, they might be the cause of the appearance of the two bands in the ν_{CO} region.

If two conformational isomers are present in the solid state, they cannot be distinguished by NMR because the ^{1}H and ^{31}P{^{1}H} NMR spectra in CD$_2$Cl$_2$ show only one sharp singlet even at −78 °C, at 19.12 and 2.52 ppm, respectively (18.55 and 2.58 ppm at room temperature).

The IR spectrum of the analogous nitro−carbomethoxy complex **3a** presents bands of strong intensity at 1657 and 1055 cm^{-1} for ν_{CO} and ν_{COC}, respectively. The frequencies related to the NO$_2$ ligand appear at 1413 ($\nu_{\mathrm{asym\ NO_2}}$), 1331 ($\nu_{\mathrm{sym\ NO_2}}$), and 821 ($\delta_{\mathrm{ONO}}$) cm^{-1}; in the NO$_2$ wagging region (ρ_{w} 600−550 cm^{-1}), there are several bands of weak intensity that prevent an unambiguous assignment. Both $\nu_{\mathrm{asym\ NO_2}}$ and $\nu_{\mathrm{sym\ NO_2}}$ have been raised with respect to the free ion values (1328 and 1261 cm^{-1}).[36] Moreover, the band at 1331 cm^{-1} is characteristic of the nitrogen-bonded nitro group.[37] This leaves little doubt that the NO$_2$ ligand is coordinated through the nitrogen atom.

Scheme 1. Formation of DMC and DMO from **2**[a]



[a] For simplicity, the PPh$_3$ ligands are omitted.

The formation of **2** occurs even at −78 °C and has been followed by ^{31}P{^{1}H} NMR in CD$_2$Cl$_2$ (see the Supporting Information). Upon admission of CO, the signal at 37.91 ppm of *cis*-[Pd(OTs)$_2$(PPh$_3$)$_2$] is replaced by several signals, one of stronger intensity at 23.01 ppm, whose value suggests that it is relevant to a species having trans geometry (see later). Upon the addition of MeOH (10% with respect of CD$_2$Cl$_2$), these signals are immediately substituted by a signal at 19.04 ppm, related to *trans*-[Pd(OTs)(COOMe)(PPh$_3$)$_2$].[5a] Only upon the addition of NEt$_3$ (Pd:N = 1:10) is there formation of **2** (the signal at 20.91 ppm). The complex is stable up to room temperature.

Complex **2** is formed at −78 °C starting also from **1** or **1a**. In this case, **2** is stable up to 0 °C; however, at room temperature, one displaced nitrato ion reenters the coordination sphere of palladium(II), giving **1a**, at variance with what was observed when starting from *cis*-[Pd(OTs)$_2$(PPh$_3$)$_2$], probably because of the higher coordinating capacity of NO$_3$$^-$ compared to that TsO$^-$.

The stability of preformed **2** has also been studied in an NMR tube in CD$_2$Cl$_2$. In the absence of CO, **2** is stable at room temperature, but at 40 °C, it decomposes with the formation of DMC (ca. 10%), suggesting that decarbonylation of one carbomethoxy ligand occurs with the formation of a (methoxy)(carbomethoxy)palladium(II) species, leading to DMC. Under 4 atm of CO at 40 °C, decomposition occurs with the formation of DMC and DMO, ca. 12% for both. In Scheme 1, the products are formed via an intramolecular interaction in a species having the favorable cis geometry.[38]

Decarbonylation probably occurs through the available fifth coordination site of palladium(II) or via predissociation of a PPh$_3$ ligand, which makes another coordination site available. As a matter of fact, when the experiment is repeated in the presence of added PPh$_3$ (2 equiv) and in the absence of CO, decarbonylation occurs with the formation of only DMC (ca. 15%), but at 60 °C, probably because of the leaving CO competing

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with PPh_3 for the fifth coordination site or because the predissociation equilibrium is less favorable.

A comparison of ν_{CO} of **1a** and **3a** gives some insight into the nature of the *trans*-[Pd(COOMe)(NO_3)] and *trans*-[Pd(COOMe)(NO_2)] moieties. The nitrate ligand is coordinated through a Pd−O σ bond. The nitro ligand is coordinated through a nitrogen atom, the Pd−N bond has σ and π character, and it is known to exert a moderately strong trans effect.[39] The σ-donating effect should decrease the ν_{CO} stretching frequency, whereas the π-back-donation effect should increase this frequency. The fact that ν_{CO} of **1a** is higher than that of **3a** suggests that the σ effect prevails over the π effect.

A comparison of ν_{CO} of **3a** and **2** is also interesting. In the latter complex, ν_{CO} is significantly lower. This fact suggests that (i) the COOMe ligand displays a σ effect stronger than that of the NO_2 ligand and (ii) with the COOMe ligand also the σ effect prevails over the π effect.

A comparison of the NO_2 IR frequencies of **3** and **3a** gives some further insight. If **3** has a trans geometry, the fact that the frequencies differ little suggests that the COOMe and NO_2 ligands exert a similar effect on the NO_2 ligand in the trans position.

As to the geometry of the complexes, we have observed that those having trans or cis geometry, as was unambiguously established such as, for example, by X-ray diffraction or by IR studies, show the $^{31}P\{^1H\}$ NMR signal in the range 18−25 or 30−38 ppm, respectively (compare all of the complexes reported here and others; see, for example, ref 40). Moreover, the ^{31}P MMR spectrum of the oxalate complex [Pd(C_2O_4)(PPh_3)$_2$)], having cis geometry both in the solid and in solution, shows one singlet at 33.94 ppm. On the basis of these observations, we propose that **1a**, **1**·CH_2Cl_2, and **2**, having trans, cis, and trans geometry in the solid state, respectively, maintain the same geometry also in solution.

2. Catalytic Properties of Pd(COOMe)$_n$X$_{2-n}$(PPh$_3$)$_2$] (X = ONO$_2$, NO$_2$, Cl, OAc and OTs; *n* = 0, 1, 2). It was reported that *trans*-[Pd(OAc)$_2$(PPh_3)$_2$] in MeOH under 20−50 atm of CO at room temperature gives *trans*-[Pd(COOMe)(OAc)(PPh_3)$_2$], whereas at 50−80 °C, the formation of DMO, together with minor amounts of DMC, with concomitant reduction to palladium(0) complexes occurs.[5o,p] It was also reported that **2** at 50 °C under a CO atmosphere in MeOH decomposes, yielding oxalate and palladium(0) complexes.[5p] The formation of these products can be schematized as follows:

$$[Pd(OAc)_2L_2] \xrightarrow[-AcOH]{CO,\ MeOH} [Pd(COOMe)_n(OAc)_{2-n}L_2] \rightarrow DMO/DMC + Pd^0 \quad n = 1,2 \qquad (3)$$

It has also been found that a Pd(OAc)$_2$/PPh_3 system (Pd:P = 1:3) can be made catalytic to DMO/DMC by the use of an oxidant, such as BQ, capable of reoxidizing palladium(0) to palladium(II), and that CH_3COOH has a beneficial effect of the catalytic activity.[3d] In principle, the $NO_{2,3}^-$ ligands of **1**, **1a**, **3**, and **3a** also can act as oxidants. As a matter of fact, the stoichiometric carboxylation of aromatic compounds promoted by Pd(OAc)$_2$ in CF_3COOH as the solvent, occurring with reduction to palladium metal, can be turned catalytic by the use of $NaNO_{2,3}$.[41]

Table 2. Oxidative Carbonylation of MeOH

entry	catalyst precursor	TOF_{DMO}, h^{-1}
1	**1**[a]	38
2	**1a**[a]	25
3	**2**[a]	19
4	**3**[a]	12
5	**3a**[a]	21
6	*trans*-[PdCl$_2$(PPh_3)$_2$][a]	34
7	*trans*-[PdCl(COOMe)(PPh_3)$_2$][a]	15
8	*trans*-[Pd(OAc)$_2$(PPh_3)$_2$][a]	33
9	*trans*-[Pd(COOMe)(OAc)(PPh_3)$_2$][a]	11
10	*cis*-[Pd(OTs)$_2$(PPh_3)$_2$][a]	44
11	*trans*-[Pd(COOMe)(OTs)(PPh_3)$_2$][a]	20
12	[Pd(CO)(PPh_3)$_3$][b]	38
13	[Pd(CO)(PPh_3)$_3$][b]	37
14	[Pd(CO)(PPh_3)$_3$][c]	19

[a] Run conditions: 10^{-2} mmol of Pd, Pd/PPh_3/NEt_3/BQ = 1:3:2:100, 5 mL of anhydrous MeOH, 65 atm of CO, 65 °C, 1 h. [b] Run conditions: Same as those in footnote a, but without added PPh_3 and with $HNEt_3^+X^-$ (X = Cl, AcO) in place of NEt_3. [c] Run conditions: Same as those in footnote a, but without added PPh_3.

We tested the reactivity of **1**, **1a**, **3**, and **3a** with MeOH under CO in order to check whether (i) these complexes will give DMC/DMO according to reaction (3) and (ii) the $NO_{2,3}^-$ ligands are able to reoxidize palladium(0) to palladium(II), so that more than 1 mol of DMC/DMO per palladium atom will form. We chose the conditions under which the particularly stable *trans*-[Pd(COOMe)Cl(PPh_3)$_2$] gives DMC/DMO and palladium(0).[5i] Upon heating of these complexes up to 90 °C in 2 mL of MeOH in the presence of PPh_3 and NEt_3 (Pd:P:N = 1:4:10), under 40 atm of CO for 1 h, there occurred the formation of [Pd(CO)(PPh_3)$_3$] (ca. 70%), $OPPh_3$ ($OPPh_3$: Pd = 0.5:1), and only trace amounts of the expected DMC/DMO, even with **1a** and **3a**, which have a preformed carbomethoxy ligand. The same results were obtained in the presence of added $NaNO_{2,3}$ (Pd:salt = 1:100). These attempts were repeated by warming of the autoclave up to 90 °C at a low rate, with the hope of increasing the possibility of spending enough time in the range of temperatures more favorable to the formation of DMO/DMC, albeit unsuccessfully. The addition of 20 equiv of CH_3COOH to the system **1**/PPh_3/$NaNO_{2,3}$ (1:1:100), under 60−70 atm of CO at 65 °C, led to decomposition to palladium metal without the formation of DMC or DMO.

In contrast, when **1**, **1a**, **2**, **3**, or **3a** was used with BQ, selective catalysis to DMO was observed, with no other carbonylation product being formed in detectable amounts. The reaction conditions (Table 2) were those experienced by Current except that in his case the concentration of the catalyst precursor was 12 times higher and NEt_3 was not used.[3d] The results obtained with other catalyst precursors are also reported. The comparison of their activity is not so straightforward because at the end of catalysis some decomposition to palladium metal occurred and the consumption of BQ was higher than that expected for the amount of DMO formed. Current

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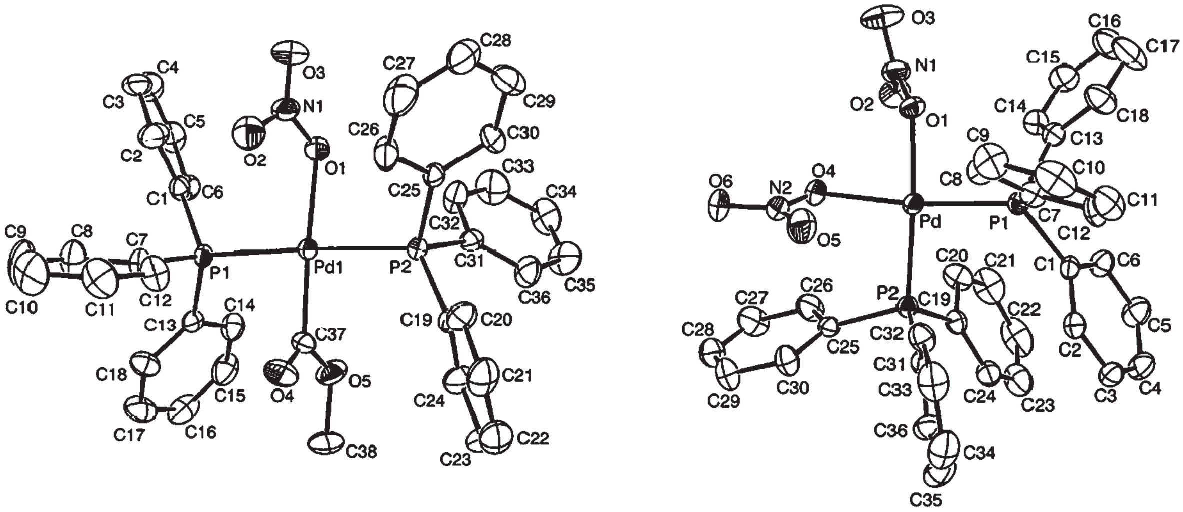

Figure 1. ORTEP representation of Mol 1 in complex **1a** (left) and of complex **1**·CH_2Cl_2 (right), with selected numbering schemes. Ellipsoids are at the 50% probability level; hydrogen atoms and the dichloromethane solvation molecule of **1**·CH_2Cl_2 have been omitted for clarity.

reported that an insoluble solid was produced by BQ polymerization promoted by a PPh_3-BQ adduct that formed in situ. He stated that "DMO yields could be variable, depending on the extent of these unrelated side reactions".[3d] Another BQ-consuming reaction could be the oxidation of MeOH to formaldehyde, which, in turn, can give rise to many derivatives (methyl hemiformaldehyde and diformaldehyde, formaldehyde oligomers, methyl formate, 4-hydroxyphenyl formate, pitches).[42] However, after the reaction, formaldehyde was present only in trace amounts, practically as much as when MeOH was used as the solvent, and no methyl formate nor trioxane was detected. We did not investigate these aspects any further because our main purpose was to establish whether $NO_{2,3}^-$ could act as stoichiometric oxidants. The results in Table 2 are only valid mainly as an indication that (i) **1**, **1a**, **3**, and **3a** can be effective catalyst precursors when used with BQ and (ii) when using them either as such or in the presence $NaNO_{2,3}$, catalysis does not occur because $NO_{2,3}^-$ fail to act as reoxidants.

It is interesting to observe that DMO forms selectively also when a preformed monocarbomethoxy precursor is used. This suggests that CO and MeOH interact with a monocarbomethoxy species to form a dicarbomethoxy one, which gives DMO, before any interaction of MeOH with any carbomethoxy species, which would give DMC. It suggests also that under relatively high pressure of CO the dicarbomethoxy intermediate does not undergo decarbonylation of one carbomethoxy ligand, which would lead to the formation of DMC, as shown in Scheme 1.

It is worth pointing out that also *trans*-[Pd(COOMe)Cl(PPh_3)$_2$] gives good results even though this complex is stable in the absence of BQ. As a matter of fact, it can be prepared in high yield by carbonylation of *trans*-[$PdCl_2$(PPh_3)$_2$] in MeOH in the presence of NEt_3 even at 70 °C.[5k] Therefore, BQ can also change the properties of the reaction center and, simultaneously, the mechanism and direction of the reaction.

In order to make the recovery of the precursor after catalysis easier, we carried out a reaction using a relatively large amount of **1** or **2** (0.1 mmol) with just 10 mmol of BQ, enough to ensure catalysis and, hopefully, not enough to cause coprecipitation of the solid mentioned by Current. After catalysis, the solid recovered by filtration was recognized by IR as a mixture of [Pd(CO)(PPh_3)$_3$] and [Pd(CO)(PPh_3)]$_3$.[17b] The $^{31}P\{^1H\}$ NMR spectrum of the filtered solution showed signals at 33.69 and 22.97 ppm assignable to [Pd(BQ)(PPh_3)$_2$]$_2$·H_2BQ and the PPh_3-BQ adduct, respectively.[5b] [Pd(CO)(PPh_3)$_3$] was reused as the precursor. In two experiments (entries 12 and 13), it was used in combination with 2 equiv of $HNEt_3^+X^-$ (X = Cl, AcO) in place of 2 equiv of NEt_3 and in the absence of 1 equiv of added PPh_3, which is related to the conditions of experiments 6 and 8 of Table 2. In another experiment (entry 14), the precursor was used in combination with NEt_3, again in the absence of 1 equiv of added PPh_3, which is related to the conditions of experiment 2. Again, selective catalysis to DMO was observed, with TOFs close to those of experiments 6, 8, and 2. These results, together with those of the attempted catalysis using $NaNO_{2,3}$, confirm that in the latter case catalysis does occur because these salts fail to reoxidize the palladium(0) species.

Experiments 3 and 14 prove that catalysis occurs even in the absence of any counteranion such as $NO_{3,2}^-$, Cl^-, AcO^-, or TsO^-. Therefore, these anions do not play a crucial role. A detailed investigation on elementary reactions relating to a putative catalytic cycle will be the subject of forthcoming studies.

3. Structural Characterization of 1a. A list of selected bond distances and angles for structurally characterized complexes is reported in Table 3. In **1a**, the palladium atom exhibits a nearly regular square-planar coordination and the reciprocal orientation of the two PPh_3 ligands is almost exactly staggered (Figure 1). The compound crystallizes with two independent molecules in the asymmetric unit (henceforth, Mol 1 and Mol 2), differing in the orientation of the nitrate and COOMe ligands. The arrangement is such that the nitrogen atom and the ester oxygen atom in one molecule are at opposite sides with respect to the coordination/basal plane, and their positions are reversed in the other molecule.

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A fitting of eight selected atoms of Mol 1 and Mol 2 made with the *Mercury* software[43] gives a root-mean-square (rms) value of 0.08 Å. An examination of the two overlapped molecules looking down the P1–Pd–P2 axis reveals that the mean planes Pd, P1, P2, O1, and C37 in Mol 1 and Mol 2 make an angle of about 35° with each other, so that the Pd–C37 bond nearly overlaps the P2–C19 link in Mol 1 and the P1–C13 one in Mol 2.

Among square-planar palladium complexes, –COOR ligands are scarce. In the CCDC database,[44] we found about 20 structural reports,[45] mostly *trans*-bis(phosphine) complexes. In this set, the average Pd–C distance and Pd–C–O and Pd–C–O angles are 1.985 Å, 126.3°, and 112.4°, compared with 1.948(8)/1.927(8) Å, 126.4(7)/129(1)°, and 111.9(7)/111(1)° in Mol 1 and Mol 2, respectively.

Compounds most closely resembling **1a** are $Pd(CO_2CH_3)(OCOCH_3)(PPh_3)_2$ (1.983 Å, 127.4°, and 110.7°),[45d] $PdCl(CO_2Ph)(PPh_3)_2$ (1.961 Å, 129.6°, and 109.6°),[45b] $Pd(CO_2CH_3)(OCOCH_3)(Ph_2Ppy)_2$ (py = pyridine; 1.967 Å, 127.9°, and 110.5°),[5e] and $PdCl[(CO_2C_2H_4CH_2(OH)](PN)$ [PN = 2-(*β*-diphenylphosphine)ethylpyridine-*N*,*P*; 1.964 Å, 124.5°, and 112.0°].[5c] In the same set, the shortest Pd–C distance is 1.909 Å in $PdCl[(CO_2CH_2CH(OH)C_2H_5)](PN)$;[5c] however, in this complex, the average Pd–C length (two independent molecules in the unit cell) is 1.964 Å. Not considering $PdCl[(CO_2CH_2CH(OH)C_2H_5)](PN)$, the Pd–C distances found in **1a** are, to the best of our knowledge, the shortest Pd–C distances so far reported in PdCOOR complexes.

The Pd–O(N) values in **1a** are close to those of complexes where the η^1-nitrate is trans to a *σ*-bonded carbon-donor atom, like in [(*S*)-9-[1-(dimethylamino)ethyl]-10-phenanthrenyl-*C*,*N*]-(7*R*-2,3-dimethyl-6-dimethylcarbamoyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-2-en-7-yl)-(nitrato-*O*)palladium(II) (2.150, 2.153, and 2.160 Å),[46a] $Pd(ONO_2)$(DMPP)(TMBA) [DMPP = 3,4-dimethyl-1-phenylphosphole; TMBA = (*S*)-(+)-*N*,*N*-dimethyl-α-methylbenzylamine; 2.159 Å],[46b] and (S_C,R_P)-[2-[1-(dimethylamino)ethyl]-3,6-dimethylphenyl](2,3-dimethyl-7-phenyl-6-(propionyl)-7-phosphabornene)(nitrato-*O*)palladium(II) (2.148 Å).[46c] The contacts for which the distance between interacting atoms is at least 0.1 shorter than the sum of the pertinent vdW radii are available as Supporting Information.

4. Structural Characterization of $1\cdot CH_2Cl_2$. In $1\cdot CH_2Cl_2$, the palladium environment is almost regular square-planar, with the two cis-disposed η^1-nitrate ligands at opposite sides with respect to the basal plane. The PPh_3 ligands are in a synclinal staggered conformation, and the C1 and C19 phenyl rings are engaged in a loose *π*–*π* stacking (centroid-to-centroid distance of 3.685 Å).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1a** (Mol 1 and Mol 2) and $1\cdot CH_2Cl_2$

	1a		
	Mol 1	Mol 2	$1\cdot CH_2Cl_2$
Pd–P1	2.349(3)	2.340(3)	2.272(1)
Pd–P2	2.364(3)	2.367(3)	2.255(1)
Pd–O1	2.150(6)	2.149(6)	2.088(3)
Pd–C37	1.948(8)	1.927(8)	
Pd–O4			2.111(4)
P–C	1.829(8)	1.822(8)	1.817(5)
	1.80(1)	1.819(9)	1.826(5)
	1.832(8)	1.846(8)	1.833(5)
	1.836(8)	1.844(8)	1.818(5)
	1.804(8)	1.812(9)	1.831(5)
	1.83(1)	1.83(1)	1.817(5)
P1–Pd–P2	176.8(1)	176.0(1)	96.2(1)
O1–Pd–P1	94.6(2)	88.1(2)	86.6(1)
O1–Pd–P2	88.6(2)	96.0(2)	175.2(1)
O1–Pd–C37	175.8(3)	177.7(5)	
P1–Pd–C37	86.8(2)	85.9(3)	
P2–Pd–C37	90.0(2)	90.1(3)	
O1–Pd–O4			86.2(1)
O4–Pd–P1			172.8(1)
O4–Pd–P2			91.0(1)

Only a few[47] nonchelating bis(triphenylphosphine)-palladium complexes are reported showing the cis disposition, either because of favorable nonbonding interactions or because of the lack of steric repulsions. The latter seems to be the case for $1\cdot CH_2Cl_2$.

Among known bis(nitrato)phosphine square-planar palladium complexes,[14,47] the average Pd–O and O–N distances and Pd–O–N angles are 2.092 Å, 1.297 Å, and 115.2°, compared with 2.088(3)/2.111(4) Å, 1.304(5)/1.302(7) Å, and 115.2(3)/111.8(4)° for N1 and N2 nitrates, respectively. Compounds in the overall better resembling $1\cdot CH_2Cl_2$ are $Pd(ONO_2)_2\{[CH_2[(C_6H_5)_2P]_2\}_2$ (2.103/2.114 Å, 1.292/1.289 Å, and 114.4/111.2°)[48a] and $Pd(ONO_2)_2(DMPP)_2$ (2.102/2.124 Å, 1.293/1.290 Å, and 115.6/113.0°).[48b]

The Pd–O distances in $1\cdot CH_2Cl_2$ are the shortest reported so far in bis(nitrato)bis(phosphine) complexes, after those of *trans*-$Pd(ONO_2)_2(OPPh_3)(PPh_3)$ (2.030/2.031 Å).[14] A comparison of the $Pd-ONO_2$ bond distances in **1a** and $1\cdot CH_2Cl_2$ indicates that the –COOMe ligand has a stronger trans influence than the PPh_3 one.

Longato et al.[49] recently reported the structure of the platinum analogue of $1\cdot CH_2Cl_2$. The platinum derivative is isostructural and isomorphous with $1\cdot CH_2Cl_2$, and a fitting of 11 selected atoms in the two complexes made with the *Mercury* software[43] gives a rms value of 0.05 Å.

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Other similar couples in CCDC are given by $Pd(ONO_2)_2\{[CH_2[(C_6H_5)_2P]_2\}_2$ and $Pt(ONO_2)_2\{[CH_2[(C_6H_5)_2P]_2\}_2$[50] and by $[Pd(ONO_2)_2(DMPP)_2]$ and $[Pt(ONO_2)_2(DMPP)_2]$.[48b] In all cases, the metal−P distances in platinum complexes are shorter, highlighting the better ability of platinum to establish π-back bonding with phosphorus.

The network of nonbonding interactions in **1**·CH_2Cl_2 is less extended than that in **1a**. The contacts for which the distance between interacting atoms is at least 0.1 Å shorter than the sum of the pertinent van der Waals radii are available as Supporting Information.

Conclusions

In summary, we have reported the synthesis and characterization of **1a** and **3a**, together with the new synthesis of **1**−**3** and the X-ray structures of **1a** and**1**·CH_2Cl_2 and the reactivity of all of them. **1** and **2** interchange a carbomethoxy ligand and a nitrate ligand, giving **1a** quantitatively and irreversibly. **2** forms even at −78 °C from *cis*-$[PdX_2(PPh_3)_2]$ (X = ONO_2, OTs) in CD_2Cl_2/MeOH, under CO, but only after the addition of NEt_3. **2** decomposes at 40 °C, giving DMC (ca. 10%), whereas under 4 atm of CO, it gives DMC and DMO (ca. 12% each). In the presence of PPh_3 and in the absence of CO, decomposition occurs at 60 °C with the formation of 15% of DMC only, suggesting that decarbonylation involves a five-coordinate intermediate or a predissociation of a PPh_3 ligand. Potential oxidants, such as $NaNO_2$ or $NaNO_3$, fail to give the oxidative carbonylation of MeOH when using **1**, **1a**, **3**, and **3a** as catalyst precursors. On the contrary, when using BQ as an oxidant, these complexes, **2**, or *trans*-$[Pd(COOMe)_{2-n}X_n(PPh_3)_2]$ (X = Cl, OTs, OAc; , n = 1, 2) promote selective catalysis to DMO. $[Pd(CO)(PPh_3)_3]$, $[Pd(CO)(PPh_3)]_3$, and $[Pd(BQ)(PPh_3)_2]_2 \cdot H_2B$ have been found after catalysis. $[Pd(CO)(PPh_3)_3]$ is also an effective precursor.

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Supporting Information Available: Crystallographic data for the structural analyses, a list of most relevant nonbonding contacts found in the solid state, as well as MNR spectra obtained in the synthesis of complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.