# Tripodal Oxygen Ligand Supported Palladium(II) Complexes: Alkylation, Carboxymethylation, and CO Insertion Reactions – X-ray Crystal Structure Determination of $[PdL_2]$, $L^- = [(C_5H_5)Co\{P(O)(OMe)_2\}_3]^-$, a Novel Homoleptic Oxygen Ligand Palladium Complex

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*Dedicated to Prof. Dr. H. Werner on the occasion of his 65th birthday*

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The reaction of $[PdCl_2(CH_3CN)_2]$ with the silver salt of the tripodal oxygen ligand $L^- = [(C_5H_5)Co\{P(O)(OMe)_2\}_3]^-$ yields the homoleptic oxygen ligand complex $[PdL_2]$ (**1**). The molecular structure of **1** was determined by single-crystal X-ray diffraction: monoclinic space group $P2_1/n$; $a$ = 8.515(1), $b$ = 13.627(2), $c$ = 15.828(2) Å; β = 92.44(1)°; $V$ = 1834.9(7) Å$^3$; $Z$ = 2. The complexes $[Pd(PPh_3)XL]$ [X = Cl (**2a**), Br (**2b**), I (**2c**)] have been prepared starting from **1**. Complex **2a** reacts with $PPh_3$ to form $[Pd(PPh_3)_2L]Cl$ (**3a**) and $[Pd(PPh_3)_2L]L$ (**3b**). Treatment of **2a** with CO in MeOH yields the carboxymethyl complex $[\{(PPh_3)(COOMe)Pd(\mu\text{-}Cl)\}_2]$ (**4**) and the protonated ligand HL. The carboxymethyl complex **4** shows some catalytic activity for the copolymerization of CO and ethene. Complex **4** reacts with AgL to yield $[Pd(PPh_3)(COOMe)L]$ (**6**). Alkylation of **2a** with $Me_4Sn$ leads to the methyl complexes $[Pd(PPh_3)MeL]$ (**7**) and $[Me_2ClSnL]$ (**8**). CO insertion in the palladium–carbon bond of **7** gives the stable acetyl complex $[Pd(PPh_3)\{C(O)Me\}L]$ (**10**). The palladium(II) complexes **1**, **2**, **3**, **6**, **7**, and **10** of the tripodal oxygen ligand L are all fluxional molecules that have been studied by temperature-dependent $^1$H- and $^{31}$P-NMR spectroscopy.

## Introduction

Palladium coordination chemistry is dominated by phosphorus and nitrogen donor ligands. Due to their backbonding ability, phosphorus donor ligands stabilize not only palladium in the oxidation state II but also zero-valent palladium.[1] Stable palladium(IV) complexes of phosphorus donor ligands are rarely described in the literature.[2][3] Nitrogen donor ligands usually stabilize palladium in the oxidation state II. Organometallic palladium(IV) complexes with nitrogen ligands were reported by Byers et al. in 1986.[4] Until recently, the organometallic chemistry of palladium with oxygen donor ligands was limited to palladium(II). In 1993 we reported the first organopalladium(IV) complex with oxygen donor ligands.[5] The oxygen ligands used are the mono-anionic half-sandwich complexes $[(C_5H_5)Co\{P(O)R_2\}_3]^-$ (short: $L_R^-$),[6] which can coordinate by means of three P=O units (Figure 1). The steric and electronic properties of $L_R^-$ are adjustable through different substituents R (R = −alkyl, −O−alkyl, −O−phenyl). The electronic properties of this class of ligands are similar to those of fluoride and oxide ions, which makes them a useful model for metal oxide surfaces.

We became interested in the question whether palladium complexes of $L_R^-$ are catalytically active. Reactions which involve a change of the palladium oxidation state from II to IV have been discussed recently.[7,8,9] The previously-described palladium(II) chemistry of $L_R^-$ is limited to a few allyl−[10][11] and aryl−palladium complexes that are catalytically inactive.[12] We now report the preparation of new organopalladium(II) complexes of the tripodal oxygen ligand $L_{OMe}^-$, stereochemically nonrigid, methyl, acetyl, and carboxymethyl complexes and their possible role in catalytic reactions.

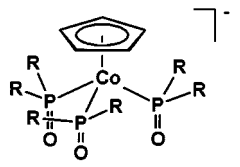


Figure 1. Schematic representation of the tripodal oxygen ligand $L^-$

## Results and Discussion

### $[PdL_2]$ (1), a Novel Homoleptic Palladium Complex

According to the HSAB concept, the palladium(II) ion is a soft metal ion.[13] Consequently, it prefers softer ligands to harder ones on complex formation. From this point of view, it makes sense that homoleptic palladium(II) complexes with hard oxygen donors are rarely observed. Known examples for homoleptic oxygen donor ligand Pd complexes are the palladium tetraaqua ion,[14] palladium carboxylate,[15] and palladium acetylacetonate.[16] All of these

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complexes feature labile oxygen palladium bonds and this explains the popularity of such complexes as starting material for new palladium complexes, as catalysts or catalyst precursors.

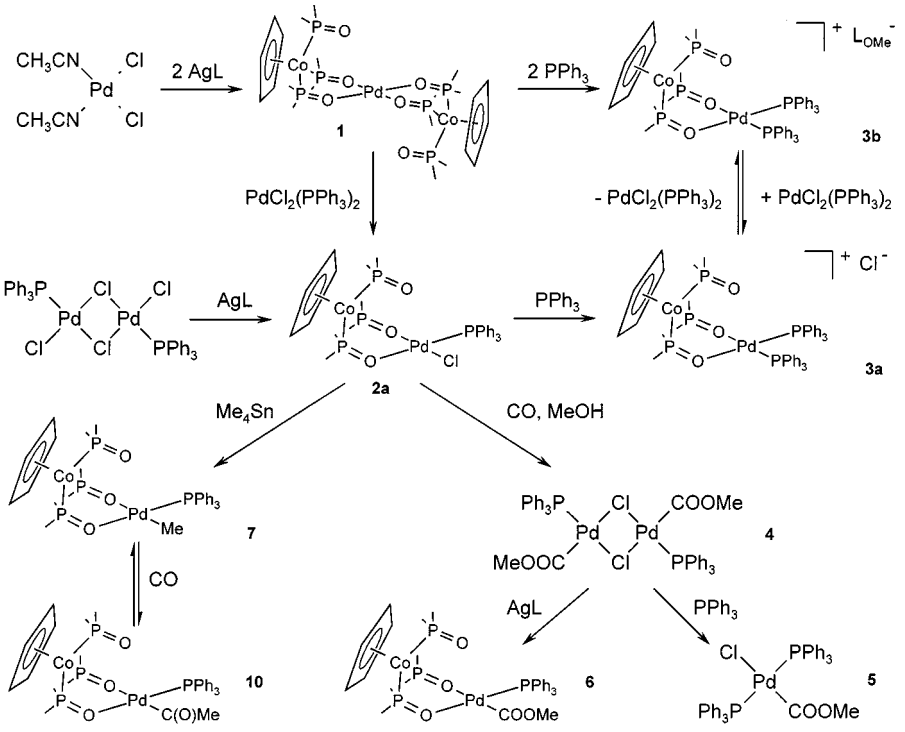
We have synthesized the new homoleptic Pd complex $[PdL_2]$ (**1**) (L = $[(C_5H_5)Co\{P(O)(OMe)_2\}_3]$) from $[PdCl_2(CH_3CN)_2]$ and AgL in dichloromethane (Scheme 1). Recrystallization from acetonitrile yielded dark red crystals of **1**. $^1H$- and $^{31}P\{^1H\}$-NMR spectra of **1** in solution indicated that it was a fluxional molecule on the NMR time scale. The $^{31}P\{^1H\}$-NMR spectrum at room temperature (Figure 2) revealed a broad singlet for the three phosphorus atoms of each of the two ligands. Due to rapid site exchange reactions, all six phosphorus atoms appear equivalent. Upon cooling of the sample to 193 K a splitting of the signal into two $AM_2$ systems was observed, which gave evidence for the presence of two isomers. The observed spin system revealed that the tridentate ligands coordinate in these isomers only with two of the three donor groups. Based on the NMR data only, it is not possible to determine the exact underlying configuration. One can think of a "*cis*" and "*trans*" isomer in which the non-coordinating P=O units are positioned on either the same or on opposite sides of the palladium coordination plane (Figure 3).

Due to the rapid rearrangement process and hence equivalence of all methyl groups, the room-temperature $^1H$-NMR spectrum (Figure 4) showed a poorly-resolved "virtual quadruplet" at $\delta$ = 3.8. On cooling to 193 K, the molecular symmetry changed from $C_{3V}$ to $C_S$. The resulting $A[MX_3(Y_3)_2]_2$ spin system (A, M = $^{31}P$; X, Y = $^1H$) gave rise to one doublet and two "virtual triplets". The presence of two isomers that did not interconvert at low temperature was again shown by the doubling of signals. In the $^1H$-NMR spectrum, two doublets ($^3J_{HP}$ = 11 Hz) could be clearly distinguished while the expected four "virtual triplets" superimposed in a way that left only two distinguishable multiplets. The two cyclopentadienyl signals at around $\delta$ = 5.1 indicated that the two isomers were formed in nearly equal amounts.

The stereochemical non-rigidity can be regarded as a fast nucleophilic substitution of a non-coordinating P=O unit for a coordinating one. Numerous investigations showed that the nucleophilic substitution at palladium(II) complexes[17] and other square planar $d^8$-complexes[18] follows an associative mechanism through a five coordinate transition state. It has been shown that this associative mechanism is also operative in the water exchange reaction at the palladium tetraaqua ion.[19][20] The rearrangement process of the ligands in **1** probably occurs via a five-coordinate transition state too. The alternative dissociative mechanism would feature a three-coordinated transition state with one mono-coordinated ligand. A coordination number of three is highly unlikely for a palladium(II) centre with hard ligands.

## X-ray Crystal Structure of $[PdL_2]$ (1)

Complex $[PdL_2]$ (**1**) crystallized in the monoclinic space group $P2_1/n$ with $a$ = 851.5(1), $b$ = 1362.7(2), $c$ = 1582.8(2) pm, $\beta$ = 92.44(1)°. Data collection parameters, selected bond lengths and angles are listed in Tables 1−3. The palladium atom in **1** is coordinated by four oxygen atoms in a square planar fashion. The two tripodal ligands each use




Scheme 1. Synthesis and reactions of tripodal oxygen ligand supported palladium(II) complexes

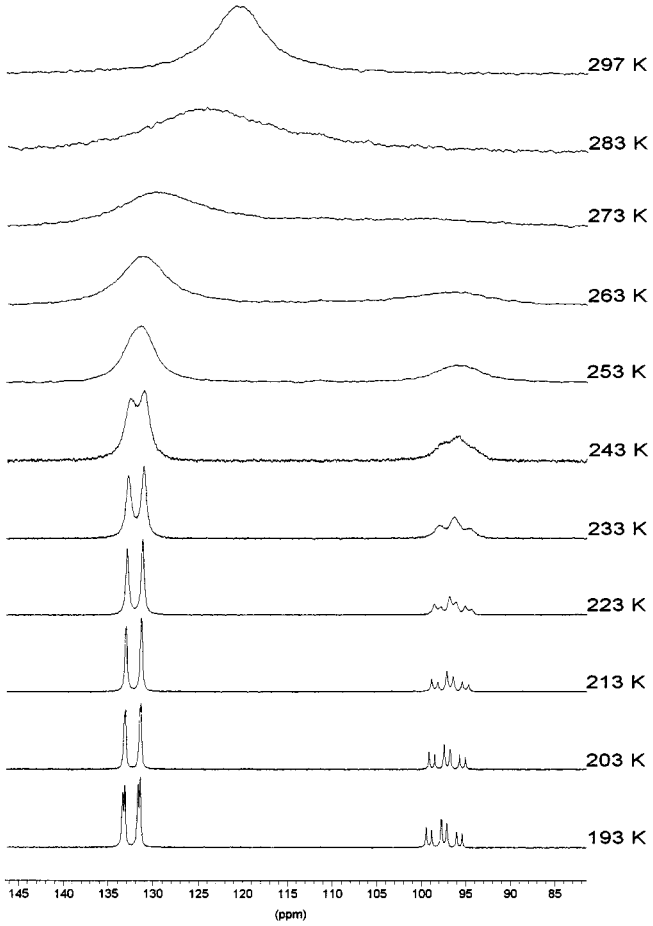



Figure 2. $^{31}P\{^{1}H\}$-NMR spectrum of **1** in $CD_2Cl_2$ at various temperatures

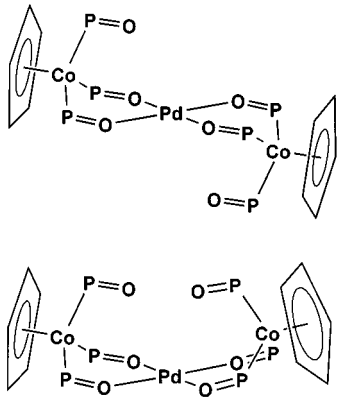



Figure 3. Possible configurations of **1** in solution at low temperature

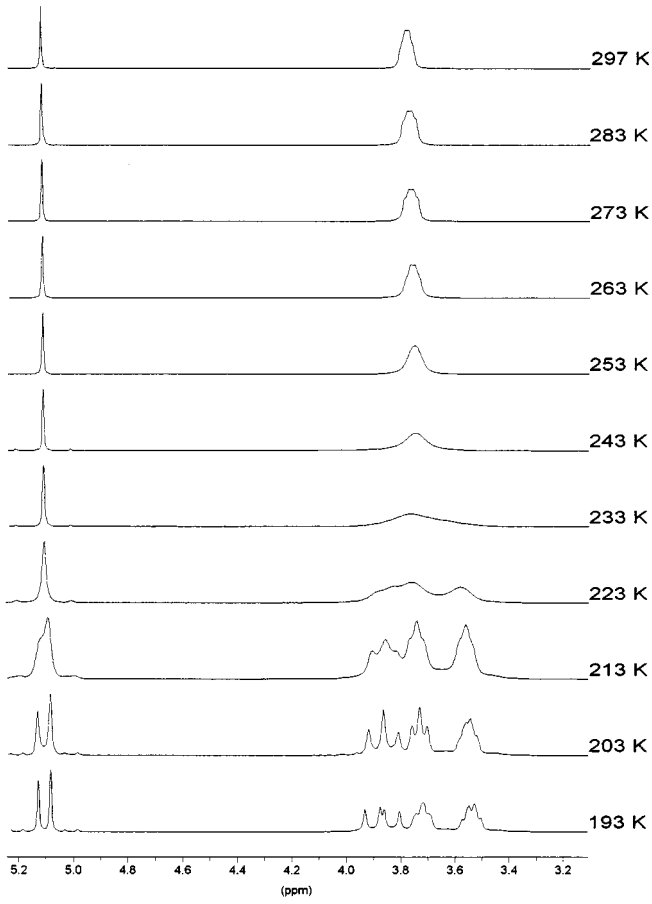



Figure 4. $^{1}H$-NMR spectrum of **1** in $CD_2Cl_2$ at various temperatures

only two donor groups to coordinate the $Pd^{II}$ ion (Figure 5). The measured O1−Pd−O4 chelate angle of 92.6(1)° deviates only slightly from the ideal value (90°) for a square planar geometry. The observed palladium−oxygen bond lengths are equal within experimental error [Pd−O 199.6(3), 199.4(3) pm] and fall in the expected range.[22] The distances are similar to the reported Pd−O contacts in palladium acetate (197.3−201.4 pm)[15] and are slightly longer than the corresponding bonds in $[Pd(acac)_2]$ (196(1) pm).[16]

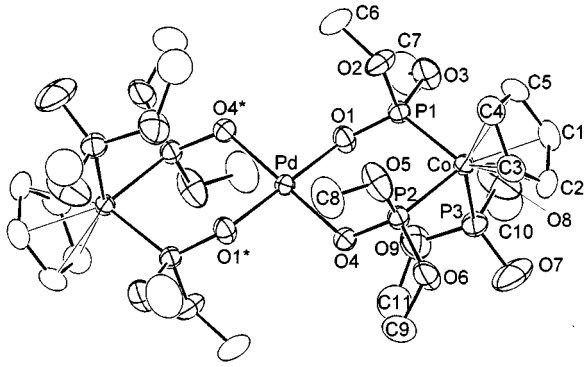



Figure 5. ORTEP plot of **1** showing 50% probability ellipsoids and the atomic numbering scheme; starred atoms represent transformed coordinates of the type $1 - x$, $1 - y$, $1 - z$

Due to the bidentate coordination mode of the tripodal ligand $L^-$ the bond lengths and angles differ slightly in each of the $P(O)(OMe)_2$ groups. The coordinating P=O units show longer phosphorus−oxygen bond lengths [P−O 151.5(3), 151.7(3) pm] than the non-coordinating one [P=O 145.9(4) pm], which corresponds to a partial loss of double bond character of the phosphoryl units. In the solid state, the non-coordinating P=O units are twisted away

Table 1. Selected bond lengths for **1**

| atom 1 | atom 2 | distance [pm] | atom 1 | atom 2 | distance [pm] |
|---|---|---|---|---|---|
| Pd | O1 | 199.6(3) | Co | C4 | 209.1(4) |
| Pd | O4 | 199.4(3) | Co | C5 | 209.1(4) |
| Co | P1 | 215.2(1) | P1 | O1 | 151.5(3) |
| Co | P2 | 214.4(1) | P1 | O2 | 159.7(3) |
| Co | P3 | 220.4(1) | P1 | O3 | 159.4(3) |
| Co | C1 | 207.8(4) | P2 | O4 | 151.7(3) |
| Co | C2 | 207.4(4) | P2 | O5 | 158.8(3) |
| Co | C3 | 207.6(4) | P2 | O6 | 158.3(3) |
| | | | P3 | O7 | 145.9(4) |
| | | | P3 | O8 | 160.6(4) |
| | | | P3 | O9 | 158.7(3) |

Table 2. Selected bond angles for **1**

| | | | angle [°] | | | | angle [°] |
|---|---|---|---|---|---|---|---|
| O1 | Pd | O1* | 180.(0) | O4 | P2 | O5 | 108.4(2) |
| O1 | Pd | O4 | 92.6(1) | O4 | P2 | O6 | 104.5(2) |
| O1 | Pd | O4* | 87.4(1) | O5 | P2 | O6 | 104.8(2) |
| P1 | Co | P2 | 91.75(4) | Co | P3 | O7 | 116.4(2) |
| P1 | Co | P3 | 93.62(5) | Co | P3 | O8 | 103.0(1) |
| P2 | Co | P3 | 94.20(5) | Co | P3 | O9 | 114.8(1) |
| Co | P1 | O1 | 121.5(1) | O7 | P3 | O8 | 111.6(3) |
| Co | P1 | O2 | 106.2(1) | O7 | P3 | O9 | 111.1(2) |
| Co | P1 | O3 | 111.7(1) | O8 | P3 | O9 | 97.9(2) |
| O1 | P1 | O2 | 108.7(2) | Pd | O1 | P1 | 124.9(2) |
| O1 | P1 | O3 | 104.9(2) | P1 | O2 | C6 | 118.2(3) |
| O2 | P1 | O3 | 102.1(2) | P1 | O3 | C7 | 123.9(3) |
| Co | P2 | O4 | 122.0(1) | Pd | O4 | P2 | 122.6(2) |
| Co | P2 | O5 | 106.0(1) | P2 | O5 | C8 | 122.8(3) |
| Co | P2 | O6 | 110.1(1) | P2 | O6 | C9 | 126.4(3) |
| | | | | P3 | O8 | C10 | 120.7(4) |
| | | | | P3 | O9 | C11 | 120.8(4) |

from the palladium centre. A similar orientation was observed in the analogous trispyrazolylborate complex $[Pd\{HB(pz)_3\}_2]$,[21] where the two tripodal ligands also bind with two donor groups only.

## Reaction of $PdL_2$ with $[PdCl_2(PPh_3)_2]$

Complex **1** undergoes a metathesis reaction with $[PdCl_2(PPh_3)_2]$ to form the new chloro complex $[Pd(PPh_3)ClL]$ (**2a**) that was isolated as air-stable red crystals (Scheme 1). Reaction of $[\{(PPh_3)ClPd(\mu\text{-}Cl)\}_2]$ with the silver salt AgL (Scheme 1) was an alternative route to **2a**. The homologous, dark brown iodo complex $[Pd(PPh_3)IL]$ (**2c**) is similarly available from $PdI_2$ in acetonitrile with $PPh_3$ and subsequent addition of AgL. The deep red bromo complex $[Pd(PPh_3)BrL]$ (**2b**) was prepared by halide exchange from **2a** with silver triflate and $[NBu_4]Br$.

Room-temperature 500 MHz $^{31}P\{^1H\}$-NMR spectra of **2a**–**c** showed local $C_{3v}$ symmetry for the tripodal oxygen ligands L which corroborated the fluxionality of these molecules. Below 223 K the singlet was split into a triplet and a singlet, a fact that can be explained by two different exchange rates of the two coordinated $P(O)(OMe)_2$ groups with the non-coordinated $P(O)(OMe)_2$ group. The triplet is assigned to the $P(O)(OMe)_2$ group in a *trans* position to the chloride ligand that exerts a much weaker *trans* effect than triphenylphosphane. At 173 K, the rearrangement process of **2a** became so slow on the NMR time scale that the $^{31}P\{^1H\}$-NMR spectrum revealed one broad signal for each of the three phosphorus atoms which was consistent with the expected $C_1$ symmetry.

Again we have no direct evidence for the mechanism of the ligand rearrangement process. We can exclude dissociation of the triphenylphosphane ligand since the triphenylphosphane phosphorus nucleus in **2a**–**c** showed coupling to the phosphorus nuclei of the ligand L. We assumed a transition state with coordination number five at the palladium centre to explain the dynamic NMR behaviour of complex **1.** The coalescence temperature for **2a** was significantly lower than for **1**. A possible explanation for this observation is the presence of a triphenylphosphane ligand in **2a**. Square planar $d^8$-metal complexes with soft ligands are more likely to form five-coordinate species than compounds with hard donors.[23] Consequently it would be easier for the palladium centre in **2a** to form a five-coordinate complex which in turn would decrease the energy barrier for the observed interconversion.

## Reaction of $[Pd(PPh_3)ClL]$ (2a) with Triphenylphosphane

The reaction of **2a** with one equivalent of $PPh_3$ was complex. The first step was chloride ligand displacement and formation of the complex $[Pd(PPh_3)_2L]Cl$ (**3a**). Complex **3a** dismutated partly to form $[Pd(PPh_3)_2L]L$ (**3b**) and $[PdCl_2(PPh_3)_2]$ (Scheme 1). The same equilibrium mixture was obtained when we treat **3b** with one equivalent $[PdCl_2(PPh_3)_2]$. Compounds **3a**, **b** were identified by their $^{31}P$-NMR spectrum. The formation of an ionic compound were followed by conductivity measurements during the reaction of **2a** with $PPh_3$. The molar conductivity of a dichloromethane solution of **2a** ($c$ = 0.001 mol·l$^{-1}$) increased upon the addition of one equivalent $PPh_3$ from 0.2 to 49 $\mu\Omega^{-1}\cdot cm^{-2}\cdot mol^{-1}$.

The analogous reaction of the cyclopentadienyl complex $[Pd(PEt_3)BrCp]$ with triphenylphosphane has been reported to yield the ionic complex $[Pd(PEt_3)(PPh_3)Cp]Br$.[24] According to this observation, only the formation of **3a** would have been expected. The fact that we observed the formation of **3a** and **3b** demonstrates the much lower affinity of palladium(II) towards the oxygen ligand L than towards the carbon ligand Cp.

## Reactivity of $[Pd(PPh_3)ClL]$ (2a) towards Carbon Monoxide and Ethene in Methanol

Alkoxycarbonyl palladium complexes are an interesting class of compounds. They are discussed as important intermediates during the synthesis of oxalic acid esters from carbon monoxide and alcohols.[25] Furthermore they are assumed to form as intermediates during the ester forming

hydrocarboxylation of olefins and the copolymerization of olefins with carbon monoxide to yield polyketones.[26–28]

We have therefore looked at the reactivity of the tripodal oxygen ligand palladium complex **2a** toward carbon monoxide, ethene, and methanol. Compound **2a** is stable in methanol. However, under carbon monoxide at 40 bar, the methoxycarbonyl complex $[\{(PPh_3)(COOMe)Pd(\mu\text{-}Cl)\}_2]$ (**4**) (Equation 1) was formed. The oxygen ligand took up the proton and was displaced as HL. According to our knowledge, **4** is the first halide-bridged methoxycarbonyl palladium complex. Its IR spectrum showed strong C=O and C–O–C valence vibrations that are characteristic of methoxycarbonyl complexes.[25] From the $^{31}P\{^1H\}$-NMR spectrum one must conclude that the dinuclear complex **4** exists as a *cis*/*trans* isomer mixture in solution.[29] The analogous reaction of $[Pd(PPh_3)Cl(acac)]$ with CO in methanol also led to the methoxycarbonyl palladium complex **4** (Equation 2). $PPh_3$ cleaved the chloride bridge in **4** and yielded the mononuclear complex $[PdCl(COOMe)(PPh_3)_2]$ (**5**), which was identified by comparison of its IR- and NMR data with the values reported in the literature.[25]

$$[Pd(PPh_3)ClL]\ (\mathbf{2a}) + CO + MeOH \rightarrow [\{(PPh_3)(COOMe)Pd(\mu\text{-}Cl)\}_2]\ (\mathbf{4}) + 2\ HL \quad (1)$$

$$[Pd(PPh_3)Cl(acac)] + CO + MeOH \rightarrow [\{(PPh_3)(COOMe)Pd(\mu\text{-}Cl)\}_2]\ (\mathbf{4}) + 2\ Hacac \quad (2)$$

## Synthesis of $[Pd(PPh_3)(COOMe)L]$ (6)

We wondered whether the loss of the oxygen ligand–palladium bond during the formation of the methoxycarbonyl group meant that a complex with both the ligand L and a methoxycarbonyl group coordinated to palladium was unstable. We found that this type of compound was perfectly stable. It could be obtained in a clean reaction starting from the chloride bridged methoxycarbonyl complex **4** and AgL (Scheme 1). The product $[Pd(PPh_3)(COOMe)L]$ (**6**) is a yellow crystalline material, stable in moist air and soluble in polar solvents. It showed the same non-rigidity as the chloride complex **2a**, i.e. it exhibited the same type of dynamic NMR behaviour. Apart from the signal of the methoxycarbonyl group, the NMR spectra of the complexes **6** and **2** are identical. However, down to 203 K it was not possible to reach the slow exchange limit. Absorption bands at 1672 $cm^{-1}$ [ν(C=O)] and 1078 $cm^{-1}$ [ν(O–C–O)], characteristic of methoxycarbonyl complexes, were visible in the IR spectrum of **6**.[25]

The palladium complex **2a** is a catalyst precursor for the copolymerization of carbon monoxide with ethene. The reaction in methanol at 80°C under 25 bar each of ethene and CO produced a perfectly alternating polyketone. Under these reaction conditions, complex **2a** was transformed into the methoxycarbonyl complex **4**. We do not know whether **4** was the catalytically active compound or just another catalyst precursor. The system was not stable towards formation of metallic palladium and the polyketone yields were low.

## Alkylation Reaction of 2a with $Me_4Sn$

The treatment of palladium halide complexes with organotin reagents is a standard procedure to form palladium–carbon bonds.[31] The attempted alkylation of the palladium chloride compound **2a** with $Me_4Sn$ turned out to be a complex reaction. The reaction yielded the expected methyl palladium compound $[Pd(PPh_3)MeL]$ (**7**) together with the oxygen ligand tin complex $[Me_2ClSnL]$ (**8**) and the dinuclear palladium complex $[\{(PPh_3)MePd(\mu\text{-}Cl)\}_2]$ (**9**). Complex **9** is a known compound. It has been prepared form [PdMeCl(cod)] with one equivalent of $PPh_3$[30] and by alkylation of $[\{(PPh_3)ClPd(\mu\text{-}Cl)\}_2]$ with tetramethyltin.[32] The oxygen ligand tin complex **8** can be synthesized from $Me_2SnCl_2$ and the sodium salt of the ligand NaL (Equation 3).

$$Me_2SnCl_2 + NaL \rightarrow [Me_2ClSnL]\ (\mathbf{8}) \quad (3)$$

At room temperature, compound **8** exhibited fluxional behaviour in the $^1H$-NMR spectrum: The tripodal ligand shows local $C_{3v}$ symmetry. The tin methyl groups appeared as expected as a singlet with the typical $^2J_{HSn}$ satellites due to their coupling with the tin isotopes $^{117}Sn$ (72 Hz) and $^{119}Sn$ (75 Hz). These coupling constants were similar to reported values for analogous trispyrazolylborate complexes like $[SnMe_2ClTp]$ ($^2J_{119Sn\text{-}H}$ = 66 Hz)[33] and $[SnMe_2ClTp^{Me,Me}]$ ($^2J_{117Sn\text{-}H}$ = 67 Hz, $^2J_{119Sn\text{-}H}$ = 72 Hz).[34] It is possible to slow down the exchange process on cooling the sample to 203 K. The proton NMR signals of L revealed the expected lowering of symmetry from $C_{3v}$ to $C_s$ and the $^{31}P\{^1H\}$-NMR spectrum accordingly displayed an $AM_2$-spin system at the slow exchange limit. In the $^{119}Sn\{^1H\}$-NMR spectrum of **8** the slow exchange limit was already reached at 253 K. The quadruplet signal observed at room temperature ($^2J_{Sn\text{-}P}$ = 88±1 Hz) was split into a multiplet that could be interpreted as the A-part of an $AXY_2$-spin system.

## Insertion of Carbon Monoxide in $[Pd(PPh_3)MeL]$ (7)

We were interested to see whether the methylpalladium complex **7** catalyzed the formation of polyketones. Our experiments show that **7** was able to reversibly insert carbon monoxide to yield the acetyl palladium complex $[Pd(PPh_3)\{C(O)Me\}L]$ (**10**). However, the acetyl palladium complex did not react further under an ethene atmosphere. The acetyl complex **10** possessed remarkable stability. Heating in high boiling solvents under vacuum led to deinsertion of carbon monoxide and to the formation of the methyl complex **7** in a clean reaction. A dichloromethane or acetonitrile solution of **10** could be stored for several weeks without decomposition. Analogous acetyl complexes of palladium with acetylacetonate as oxygen ligand decomposed easily in solution with the formation of metallic palladium. The $^1H$-, $^{13}C$-, and $^{31}P$-NMR data of the $[Pd(PPh_3)L]$ part of **10** were similar to the ones of the complexes discussed above. The proton NMR signal of the acetyl group was

observed at δ = 2.18. A characteristic $^{13}C$-signature was given by the carbonyl carbon atom, which appeared as a doublet at δ = 226 ($^2J_{C\text{-}P}$ = 2 Hz). The ν(C=O) IR-absorption occurred at 1703 $cm^{-1}$.

## Concluding Remarks

The tripodal oxygen ligand L seemed to be more efficient than most other oxygen ligands in stabilizing organopalladium fragments. The reactions of the complexes that we have observed are probably reasonable models of reactions that occur or have been postulated to occur at palladium−metal oxide surface species. The pronounced non-rigid behaviour of the palladium complexes described here has its equivalent in the high mobility of Pd on silica and alumina surfaces.

## Experimental Section

**General:** All reactions were carried out under nitrogen using standard Schlenk techniques. Filtration was done with 1-μm membrane filters (regenerated cellulose, Schleicher & Schuell). Acetonitrile was used as purchased (p.a. quality); all other solvents were dried by standard methods and distilled prior to use. − NMR spectra were recorded with a Bruker DRX 200 spectrometer, chemical shifts are given in ppm using the solvent signal as reference. Signal multiplicity is indicated by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quadruplet, vq = "virtual quadruplet". − IR spectra were taken with a Bruker IFS 66 FT spectrometer. − Elemental analyses were performed in the Institut für Pharmazeutische Chemie, Universität Düsseldorf, using a Perkin−Elmer CHN-2400/II elemental analyzer.

**[PdL$_2$] (1):** To a suspension of [$PdCl_2(CH_3CN)_2$] (0.43 g, 1.7 mmol) in dichloromethane (30 mL) was added slowly at −30°C a solution of AgL[35] (2.2 g, 3.9 mmol) in $CH_2Cl_2$ (20 mL). The reaction mixture was warmed slowly to room temperature and heated at reflux for 1 h. Filtration of the black suspension through a membrane yielded a clear yellow solution. Removal of the solvent and recrystallization from a small amount of acetonitrile gave 1.20 g of yellow crystals (69%). − $^1H$ NMR ($CDCl_3$): δ = 3.80 (vq, $^3J_{HP}$ = 10 Hz, 18 H, OC$H_3$), 5.12 (s, 5 H, $C_5H_5$). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 126 (br. s, $P_{ligand}$). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 52.6 (s, O$CH_3$), 90.6 (s, $C_5H_5$). − IR (KBr): $\tilde{\nu}$ = 2992 $cm^{-1}$ (w), 2944 (m), 2839 (w), 1423 (m), 1165 (s, P=O), 1117 (vs), 1067 (vs), 1007 (vs), 828 (m), 777 (s), 750 (s), 724 (s), 563 (m, P=O). − $C_{22}H_{46}Co_2O_{18}P_6Pd$ (1008.7): found C 26.42, H 4.42, Pd 10.73; calcd. C 26.20 H 4.60 Pd 10.52. − FAB-MS: positive ions: *m/z* (%) = 1031.7 (15) [M + Na]$^+$, 1009.7 (88) [M + 2]$^+$, 510.2 (100) [CoL$^+$]; negative ions: *m/z* = 1008.3 (11) [M$^-$], 451.1 (100) [L$^-$].

**[Pd(PPh$_3$)ClL] (2a):** $PdCl_2$ (1.41 g, 7.95 mmol) and $PPh_3$ (2.09 g, 7.95 mmol) were suspended in acetonitrile (100 mL) and heated at reflux for 2 h. The solvent was removed in vacuo and the orange precipitate of [$PdCl_2(PPh_3)]_2$ was dissolved in of dichloromethane (80 mL). A solution of AgL (4.45 g, 7.95 mmol) in dichloromethane (40 mL) was added slowly at −50°C. The reaction mixture was allowed to warm to −30°C when the mixture turned black. The suspension was stirred for an additional 2 h at room temperature and filtered through a membrane to give a red solution. The solvent was removed in vacuo and the residue was recrystallized from acetonitrile (ca. 200 mL) to yield 4.85 g of red crystals (72%). − $^1H$ NMR ($CDCl_3$): δ = 3.59 (vq, $^3J_{HP}$ = 11 Hz, 18 H, OC$H_3$), 5.09 (s, 5 H, $C_5H_5$), 7.3−7.7 [m, 15 H, P($C_6H_5$)$_3$]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 115 (s, $P_{ligand}$), 26.7 [q, $^3J_{PP}$ = 5 Hz, $P(C_6H_5)_3$]. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 52.4 (s, O$CH_3$), 90.3 (s, $C_5H_5$), 128.7 [d, $J_{CP}$ = 12 Hz, P($C_6H_5$)$_3$], 128.9 [d, $J_{CP}$ = 58 Hz, P($C_6H_5$)$_3$], 131.5 [s, P($C_6H_5$)$_3$], 135.2 [d, $J_{CP}$ = 11 Hz, P($C_6H_5$)$_3$]. − IR (nujol): $\tilde{\nu}$ = 1462 $cm^{-1}$ (vs), 1436 (m), 1175 (sh), 1154 (s, P=O), 1089 (s), 1041 (vs), 1008 (vs), 771 (m), 712 (s), 562 (m, P=O). − $C_{29}H_{38}ClCoO_9P_4Pd$ (855.3): found C 40.55, H 4.69; calcd. C 40.72, H 4.48. − MS (EI); *m/z* (%): 961 (10.8) [Co(L)$_2$]$^+$, 856 (3.7) [M$^+$ + 2], 262 (100) [$PPh_3^+$], 183 (60.3) [$PPh_2^+$ − 2], 108 (26.5) [$PPh^+$].

**[Pd(PPh$_3$)BrL] (2b):** Compound **2a** (0.31 g, 0.37 mmol) and AgOTf (0.11 g, 0.43 mmol) were dissolved in acetonitrile (10 mL) and stirred for 15 min. The AgCl precipitate was separated by membrane filtration and the clear solution was treated with [$NBu_4$]Br (0.12 g, 0.37 mmol). After about 60 minutes the red−brown precipitate was separated by filtration, dried, and recrystallized from a small amount of acetonitrile. Yield 0.10 g (30%). − $^1H$ NMR ($CDCl_3$): δ = 3.59 (vq, $^3J_{HP}$ = 11 Hz, 18 H, OC$H_3$), 5.10 (s, 5 H, $C_5H_5$), 7.3−7.9 [m, 15 H, P($C_6H_5$)$_3$]. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 114.4 (s, $P_{ligand}$), 28.5 [q, $^3J_{PP}$ = 5 Hz, $P(C_6H_5)_3$]. − IR (nujol): $\tilde{\nu}$ = 1463 $cm^{-1}$ (s), 1377 (m), 1161 (s, P=O), 1089 (vs), 1043 (vs), 1006 (vs), 770 (s), 560 (m, P=O). − $C_{29}H_{38}BrCoO_9P_4Pd$ (899.8): found C 38.39, H 4.23; calcd. C 38.71, H 4.26.

**[Pd(PPh$_3$)IL] (2c):** Prepared analogously to **2a** using $PdI_2$ (0.52 g, 1.4 mmol), $PPh_3$ (0.38 g, 1.4 mmol) and AgL (0.80 g, 1.4 mmol). Yield 1.10 g (80%). − $^1H$ NMR ($CDCl_3$): δ = 3.59 (vq, $^3J_{HP}$ = 11 Hz, 18 H, OC$H_3$), 5.10 (s, 5 H, $C_5H_5$), 7.4−7.9 (m, 15 H, P($C_6H_5$)$_3$). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 112.6 (s, $P_{ligand}$), 28.9 [q, $^3J_{PP}$ = 5 Hz, $P(C_6H_5)_3$]. − IR (nujol): $\tilde{\nu}$ = 1463 (s), 1377 (m), 1160 (s, P=O), 1089 (vs), 1043 (vs), 1005 (vs), 768 (s), 706 (s), 538 (s). − $C_{29}H_{38}CoIO_9P_4Pd$ (946.8): found C 36.68, H 3.74; calcd. C 36.79, H 4.05.

**[Pd(PPh$_3$)$_2$L]L (3b):** Compound **1** (0.10 g, 0.10 mmol) and $PPh_3$ (53 mg, 0.20 mmol) were dissolved in dichloromethane (10 mL). After 30 min, the solvent was removed in vacuo leaving a brown−red wax that could not be crystallized. − $^1H$ NMR ($CDCl_3$): δ = 3.27 (vq, $^3J_{HP}$ = 11 Hz, 18 H, OC$H_3$ of L$^-$), 3.67 {vq, $^3J_{HP}$ = 11 Hz, 18 H, OC$H_3$ of [Pd(PPh$_3$)$_2$L]$^+$}, 4.95 (s, 5 H, $C_5H_5$ of L$^-$), 5.14 {s, 5 H, $C_5H_5$ of [Pd(PPh$_3$)$_2$L]$^+$}, 7.1−7.6 [m, 30 H, P($C_6H_5$)$_3$], $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 117 {s, $P_{ligand}$ of [Pd(PPh$_3$)$_2$L]$^+$}, 105 (s, $P_{ligand}$ of L$^-$), 34.5 {q, $^3J_{PP}$ = 4 Hz, [Pd(*P*Ph$_3$)$_2$L]$^+$}. − IR (KBr): $\tilde{\nu}$ = 3052 $cm^{-1}$ (w), 2939 (w), 1436 (m), 1147 (s, P=O), 1076 (s), 1040 (vs), 1007 (vs), 834 (w), 748 (m), 706 (m), 562 (m, P=O).

**[{(PPh$_3$)(COOMe)Pd(μ-Cl)}$_2$] (4):** A solution of **2a** (0.35 g, 0.41 mmol) in methanol (5 mL) was placed in an autoclave and kept for 1 h under a CO pressure of 40 bar. The formation of a yellow solution and a white precipitate was observed. The white solid was separated by membrane filtration, washed with a small amount of methanol and dried in vacuo. Yield 0.11 g (58%). − $^1H$ NMR ($CD_2Cl_2$): δ = 3.14 (s, 3 H, COOC$H_3$), 7.5−7.8 [m, 15 H, P($C_6H_5$)$_3$]. − $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): δ = 27.6 [s, $P(C_6H_5)_3$], 26.8 [s, $P(C_6H_5)_3$]. − IR (KBr): $\tilde{\nu}$ = 2943 $cm^{-1}$ (w), 1672 (vs, C=O), 1479 (m), 1433 (s), 1417 (m), 1083 (vs, C−O−C), 750 (s), 697 (s), 533 (s).

**[PdCl(COOMe)(PPh$_3$)$_2$] (5):** Compound **4** (70 mg, 0.075 mmol) and $PPh_3$ (40 mg, 0.15 mmol) were dissolved in dichloromethane (10 mL). The mixture was stirred for 30 min and the solvent was removed in vacuo. The residue was treated with a little acetonitrile to give a white solid, which was filtered off and dried under vacuum. Yield 68 mg (60%). − $^1H$ NMR ($CD_2Cl_2$): δ = 2.50 (s, 3 H,

COOC$H_3$), 7.3−7.9 [m, 30 H, P($C_6H_5$)$_3$]. − $^{31}$P{$^1$H} NMR ($CD_2Cl_2$): δ = 20.4 [s, $P$($C_6H_5$)$_3$]. − IR (KBr): ṽ = 3051 cm$^{-1}$ (w), 1672 (vs, C=O), 1656 (s, C=O), 1433 (s), 1095 (m, C−O−C), 1064 (s), 693 (s), 519 (s). $C_{38}H_{33}ClO_2P_2Pd$ (725.5): found C 61.11, H 6.50; calcd. C 62.91, H 4.58.

**[Pd(PPh$_3$)Cl(acac)]:** [{(PPh$_3$)ClPd(μ-Cl)}$_2$] (1.0 g, 1.1 mmol) and [Ag(acac)] (0.47 g, 2.3 mmol) were stirred in acetonitrile (20 mL) for 1.5 h at room temperature. The reaction mixture was filtered through a membrane. The residue was extracted with dichloromethane. Both solutions were combined and the solvent was removed in vacuo. The yellow residue was recrystallized from acetone. Yield 0.72 g (63%). − $^1$H NMR ($CDCl_3$): δ = 1.60 (s, 3 H, C$H_3$), 2.14 (s, 3 H, C$H_3$), 5.35 (s, 1 H, C$H$), 7.4−7.9 [m, 15 H, P($C_6H_5$)$_3$]. − $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = 30.2 [s, $P$($C_6H_5$)$_3$]. − IR (KBr): ṽ = 1575 cm$^{-1}$ (s, C=O), 1565 (s, C=O), 1513 (s), 1434 (m), 1378 (m), 1097 (m), 691 (m), 536 (m), 515 (m), 497 (m). − $C_{23}H_{22}ClO_2PPd$ (503.7): found C 54.93, H 4.46; calcd. C 54.89, H 4.41.

**[{(PPh$_3$)(COOMe)Pd(μ-Cl)}$_2$] (4) from [Pd(PPh$_3$)Cl(acac)]:** [Pd(PPh$_3$)Cl(acac)] (0.30 g, 0.60 mmol) in methanol (5 mL) were treated for 60 min at room temperature with a CO pressure of 10 bar. Yield: 0.23 g (84%) grey-white precipitate, spectroscopic data as reported above.

**Copolymerization of CO/Ethene with [Pd(PPh$_3$)ClL$_{OMe}$] (2a) and [{(PPh$_3$)(COOMe)PdCl}$_2$] (4):** Compound **2a** (50 mg, 0.06 mmol) in methanol (20 mL) was pressurized in a 50-mL autoclave with 25 bar of CO and 25 bar of ethene at 80°C. Yield: 90 mg of polyketone as a grey precipitate. − TON = 16 g polyketone·(g Pd·h)$^{-1}$; IR (KBr): ṽ = 1692 cm$^{-1}$ [ṽ(C=O)]. An analogous experiment with **4** (27 mg, 0.03 mmol) yielded polyketone (0.11 g). − TON = 18 g polyketone·(g Pd·h)$^{-1}$.

**[Pd(PPh$_3$)(COOMe)L] (6):** Compound **4** (0.10 g, 0.11 mmol) and AgL (0.12 g, 0.22 mmol) were dissolved in dichloromethane (10 mL) and stirred for 2 h. The precipitated AgCl was filtered off and the solvent was removed in vacuo. The yellow residue was recrystallized with a little acetonitrile. Yield 0.13 g (66%). − $^1$H NMR ($CDCl_3$): δ = 3.15 (s, 3 H, COOC$H_3$), 3.59 (vq, 18 H, $^3J_{PH}$ = 11 Hz, OC$H_3$), 5.10 (s, 5 H, $C_5H_5$), 7.3−7.8 [m, 15 H, P($C_6H_5$)$_3$]. − $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = 112.7 (s, $P_{ligand}$), 27.3 [q, $^3J_{PP}$ = 4 Hz, $P$($C_6H_5$)$_3$]. − $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ = 51.9 (vq, O$C$H$_3$), 53.2 (s, COO$C$H$_3$), 90.1 (s, $C_5H_5$), 128.8 [d, $J_{CP}$ = 11 Hz, P($C_6H_5$)$_3$, 131.1 [d, $J_{CP}$ = 3 Hz, P($C_6H_5$)$_3$], 132.2 [d, $J_{CP}$ = 52 Hz, P($C_6H_5$)$_3$], 134.9 [d, $J_{CP}$ = 12 Hz, P($C_6H_5$)$_3$]. − IR (KBr): ṽ = 2935 cm$^{-1}$ (m), 2827 (w), 1672 (vs, C=O), 1437 (s), 1175 (vs, P=O), 1078 (vs, C−O−C), 1047 (vs), 1002 (vs), 833 (m), 695 (s), 575 (s, P=O). $C_{31}H_{41}CoO_{11}P_4Pd$ (878.9): found C 42.65, H 4.63; calcd. C 42.36, H 4.70.

**[Pd(PPh$_3$)MeL] (7):** Compound **2a** (1.0 g, 1.2 mmol) and $Me_4Sn$ (0.23 g, 1.3 mmol) were dissolved in dichloromethane (10 mL) and stirred for 4 h at room temperature. The reaction mixture became opaque and turned yellow almost instantly. The white precipitate formed [{(PPh$_3$)MePd(μ-Cl)}$_2$] (**9**) was isolated by centrifugation, washed with dichloromethane and dried. The yellow supernatant was reduced in volume and the residue was recrystallized twice from a small amount of acetonitrile. Yellow crystals of **7** were isolated and dried. The mother liquor was reduced in volume and stored at −20°C, which resulted in the formation of yellow crystals of [$Me_2$ClSnL] (**8**). Yields: 0.24 g of **9** (49%), 0.32 g of **7** (33%), and 0.14 g of **8** (22%). − Selected spectroscopic data for **7**: $^1$H NMR ($CDCl_3$): δ = 0.48 (d, $^3J_{HP}$ = 2 Hz, 3 H, PdC$H_3$), 3.61 (vq, $^3J_{HP}$ = 11 Hz, 18 H, OC$H_3$), 5.12 (s, 5 H, $C_5H_5$), 7.3−7.7 [m, 15 H, P($C_6H_5$)$_3$]. − $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = 112.2 (s, $P_{Ligand}$), 39.6 [q, $^3J_{PP}$ = 4 Hz, $P$($C_6H_5$)$_3$]. − For **8**: $^1$H NMR ($CDCl_3$): δ = 0.54 [s, $^2J_{HSn}$ = 74 Hz, 6 H, Sn(C$H_3$)$_2$], 3.72 (vq, $^3J_{HP}$ = 11 Hz, 18 H, OC$H_3$), 5.14 (s, 5 H, $C_5H_5$). − $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = 115.3 (s, $P_{ligand}$). − For **9**: $^1$H NMR ($CDCl_3$): δ = 0.67 (broad s, 3H, PdC$H_3$), 7.2−7.8 [m, 15H, P($C_6H_5$)$_3$]. − $C_{38}H_{36}Cl_2P_2Pd_2$ (838.4): found C 54.47, H 4.41; calcd. C 54.44, H 4.33. − IR (KBr): ṽ = 3072 cm$^{-1}$ (w, C−H), 3049 (w, C−H), 2977 (w, C−H), 2893 (w, C−H), 1479 (m, C−C), 1435 (s, C−C), 1097 (s), 743 (m, C−H), 705 (s, C−H), 538 (s), 525 (m), 511 (s), 493 (m).

**[Me$_2$ClSnL] (8):** $Me_2SnCl_2$ (0.31 g, 1.4 mmol) and NaL (0.67 g, 1.4 mmol) were stirred in dichloromethane (10 mL). The yellow crystals of NaL dissolved slowly and a white precipitate was formed (NaCl). After 16 h, the mixture was filtered and the yellow filtrate was concentrated in vacuo to give a yellow powder (0.72 g, 81%) which was recrystallized from acetonitrile. Yield 0.49 g of yellow crystals (54%). − $^1$H NMR ($CDCl_3$): δ = 0.55 [s, $^2J_{H\text{-}119Sn}$ = 75 Hz, $^2J_{H117Sn}$ = 72 Hz, 6 H, Sn(C$H_3$)$_2$], 3.73 (vq, $^3J_{HP}$ = 11 Hz, 18 H, OC$H_3$), 5.14 (s, 5 H, $C_5H_5$). − $^1$H NMR ($CD_2Cl_2$, 203 K): δ = 0.38 [s, $^2J_{H\text{-}119Sn}$ = 74 Hz, $^2J_{H\text{-}117Sn}$ = 72 Hz, 6 H, Sn(C$H_3$)$_2$], 3.63 (d and vt superimposed, OC$H_3$), 3.70 (vt, $^3J_{HP}$ = 11 Hz, 18 H, OC$H_3$), 5.15 (s, 5 H, $C_5H_5$). − $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = 115.3 (s, $P_{ligand}$). − $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 203 K): $AB_2$-spin system, $\nu_A$ = 119.5, $\nu_B$ = 116.5, $J_{AB}$ = 146 Hz. − $^{119}$Sn{$^1$H} NMR ($CD_2Cl_2$): δ = −344.3 (q, $^2J_{P\text{-}119Sn}$ = 86±1 Hz). − $^{119}$Sn{$^1$H} NMR ($CD_2Cl_2$, 253 K): δ = −346.7 [dt ($AXY_2$-spin system), $^2J_{119SnP}$ ($J_{AX}$) = 107±1 Hz, $^2J_{119SnP}$ ($J_{AY}$) = 73±1 Hz]. − $C_{13}H_{29}ClCoO_9P_3Sn$ (635.4): found C 24.69, H 4.64; calcd. C 24.57, H 4.60. − IR (KBr): ṽ = 2988 cm$^{-1}$ (w), 2948 (m), 2912 (w), 2841 (w), 1459 (m), 1424 (m), 1175 (s), 1120 (vs) (P=O), 1029 (vs), 833 (m), 785 (s), 735 (m), 591 (vs, P=O). − MS (EI); *m/z* (%): 621 (100) [SnMeClL]$^+$, 601 (28) [SnMe$_2$L]$^+$, 571 (8) [SnL]$^+$, 497 (7), 480 (13), 418 (12).

**[Pd(PPh$_3$){C(O)Me}L] (10):** Carbon monoxide was bubbled for 30 min through a solution of **7** (0.19 g, 0.23 mmol) in dichloromethane (10 mL). The solvent was removed at room temperature in vacuo and the residue was recrystallized from acetonitrile. Yield: 0.12 g (61%). − $^1$H NMR ($CDCl_3$): δ = 2.18 [d, $^4J_{HP}$ = 1 Hz, 3 H, C(O)C$H_3$], 3.61 (vq, $^3J_{HP}$ = 11 Hz, 18 H, OC$H_3$), 5.10 (s, 5 H, $C_5H_5$). − $^{31}$P{$^1$H} NMR ($CDCl_3$): δ = 111.5 (s, $P_{ligand}$), 27.4 [q, $^3J_{PP}$ = 3 Hz, $P$($C_6H_5$)$_3$]. − $^{13}$C{$^1$H} NMR ($CDCl_3$): δ = 34.9 [s, C(O)$C$H$_3$], 51.9 ( vq, $^2J_{CP}$ = 9 Hz, O$C$H$_3$), 90.2 (s, $C_5H_5$), 128.8 [d, $J_{CP}$ = 11 Hz, P($C_6H_5$)$_3$], 130.9 [d, $J_{CP}$ not resolved, P($C_6H_5$)$_3$], 132.4 [d, $J_{CP}$ = 47 Hz, P($C_6H_5$)$_3$], 135.0 [d, $J_{CP}$ = 13 Hz, P($C_6H_5$)$_3$], 225.9 [d, $^2J_{CP}$ = 2 Hz, $C$(O)CH$_3$]. − IR (KBr): ṽ = 3048 cm$^{-1}$ (w), 2974 (w), 2936 (m), 2829 (w), 1703 (vs, C=O), 1439 (m), 1162 (vs, P=O), 1115 (s), 1034 (vs), 1006 (vs), 833 (w), 706 (s), 582 (m, P=O). − $C_{31}H_{41}CoO_{10}P_4Pd$ (862.9): found C 43.42, H 4.89; calcd. C 43.15, H 4.79.

**X-ray Crystal Structure Determination of [PdL$_2$] (1):** A suitable crystal of **1** was selected and mounted on an Enraf−Nonius CAD-4 diffractometer. Important crystal and data collection details are listed in Table 3. Data for **1** were collected at room temperature using ω-2Θ scans. Raw data were reduced to structure factors[36] (and their esd′s) by correcting for scan speed, Lorentz and polarization effects. No crystal decay was detected and no absorption corrections were applied at this stage. The systematically absent reflections showed the space group to be $P2_1/n$. The positional parameters for Pd and Co were obtained from a three-dimensional Patterson map. Positional parameters for all other non-hydrogen atoms were found in subsequent difference Fourier maps. The positional parameters for all non-hydrogen atoms were refined by using first isotropic, and later anisotropic thermal parameters. An em-

pirical absorption correction (DIFABS[37]) was applied after refinement of the positional parameters of all non-hydrogen atoms with isotropic thermal parameters. A difference Fourier map calculated after refinement of the positional parameters with anisotropic thermal parameters showed the positional parameters of almost all hydrogen atoms. However, hydrogen atoms were added to the structure model at calculated positions [$d$(C−H) = 95 pm][38] and are unrefined. The isotropic temperature factors for hydrogen atoms were fixed to be 1.3 times the $B_{eq}$ of the parent atom. All calculations were carried out with the MolEN[39] package. ORTEP[40] was used for molecular drawings. The Pd atoms reside on a crystallographic inversion centre. The asymmetric unit contains 1/2 molecule of **1**. Crystallographic data for the structure of **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118725. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Figure 5 shows one molecule of **1** (the contents of two asymmetric units) with the employed crystallographic numbering scheme.

Table 3. Crystal and data collection details for **1**

| | |
|---|---|
| Crystal size | 0.50 × 0.41 × 0.32 mm |
| Empirical formula | $C_{22}H_{46}Co_2O_{18}P_6Pd$ |
| Molecular mass | 1008.71 amu |
| $a$ | 8.515(1) Å |
| $b$ | 13.627(2) Å |
| $c$ | 15.828(2) Å |
| $\beta$ | 92.44(1)° |
| $V$ | 1834.9(7) Å$^3$ |
| Space group | $P2_1/n$ |
| $Z$ | 2 |
| $d_{calcd.}$ | 1.826 g/cm$^3$ |
| $d_{obsd.}$ | 1.83 g/cm$^3$ |
| μ | 1.70 mm$^{-1}$ |
| Data-coll. temp. | 298(2) K |
| 2Θ range | 2° to 45° |
| Measured intensities | 2694 |
| Unique data | 2386 |
| Observed data | 2188 |
| Observation criterion | $Fo^2 \geq 3\sigma(F_o^2)$ |
| Absorption correction | DIFABS |
| $R$ | 4.32% |
| $R_w$ | 6.00% |
| GOF | 1.431 |
| No. of variables | 224 |
| Resid. electr. dens. | 0.79/−0.97 e/Å$^3$ (near Pd) |

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