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[PF₆⁻]^{1/2}CH₂Cl₂, 136379-20-9; [2c*][PF₆⁻], 136379-09-4; [2d*]-[PF₆⁻], 136379-11-8; [2e*][PF₆⁻], 136379-13-0; [2f*][PF₆⁻], 136379-15-2; [2g*][PF₆⁻], 136458-36-1; [2h*][PF₆⁻], 136379-17-4; [2i*][PF₆⁻], 136379-19-6; PhSH, 108-98-5; [PNO₂C₆H₄S]₂, 100-32-3; ^pTolSH, 106-45-6; ^pAnSH, 696-63-9; MesSH, 1541-10-2; C₆F₅SH, 771-62-0; EtSH, 75-08-1; ⁱPrSH, 75-33-2; ^tBuSH, 75-66-1; (η⁵-C₅H₅)(CO)₂Mn(THF), 12093-26-4; (η⁵-C₅H₄Me)(CO)₂Mn(THF), 51922-84-0; (η⁵-C₅Me₅)(CO)₂Mn(THF), 86155-78-4.

Supplementary Material Available: Tables of positional and thermal parameters as well as additional drawings of 1a*, 1f*, [2b*][PF₆⁻]^{1/2}CH₂Cl₂, [2i*][PF₆⁻], and [2h*][PF₆⁻] (15 pages); listings of observed and calculated structure factors (101 pages). Ordering information is given on any current masthead page.

Anionic (Nitrophenyl)palladium(II) Carbonyls. Crystal Structure of *cis*-[PPh₃(CH₂Ph)][Pd(C₆H₃Me-2,NO₂-6)Cl₂(CO)]

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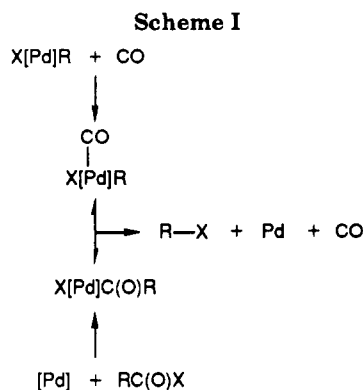
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Complexes [PPh₃(CH₂Ph)][Pd(R)Cl₂(CO)] [R = C₆H₃Me-2,NO₂-6 (1), C₆H₂(NO₂)₃-2,4,6 (2)] can be isolated by carbonylation, at room temperature and atmospheric pressure, of [PPh₃(CH₂Ph)]₂[Pd(R)Cl(μ-Cl)]₂. Complex 1 is the first example of an organocarbonylpalladium(II) complex characterized by an X-ray diffraction study. Crystals are triclinic, space group *P*1, with *Z* = 2 in a unit cell of dimensions *a* = 10.446 (5) Å, *b* = 12.538 (7) Å, *c* = 14.148 (6) Å, α = 65.40 (2)°, β = 74.17 (2)°, and γ = 72.83 (2)°. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 1274 observed reflections to *R* and *R*_w values of 0.0319 and 0.0440. In the anionic complex the Pd atom is in a square-planar arrangement with two Cl atoms in *cis* positions and the carbonyl group and the 2-methyl-6-nitrophenyl ligand *trans* to them. The Pd-CO bond [Pd-C = 1.853 (10) Å] is discussed on the basis of the IR and X-ray data.

Introduction

Palladium compounds have been used as catalysts in carbonylation and decarbonylation reactions.¹ In these processes the organic compounds are assumed to be obtained on the basis of the unstability of some carbonyl intermediates (Scheme I). Under this assumption it is easy to justify the low number of organocarbonylpalladium(II) complexes reported.² This difficulty adds to the general tendency of palladium(II) compounds to be reduced to palladium(I) or -(0) complexes by carbon monoxide^{2a} and also to the lability of the Pd-CO bond.^{2,3} Owing to all these factors, structural studies on palladi-



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um(II) carbonyls are based on spectroscopic (mainly IR) data. Only very recently the first crystal structures of two such compounds, [PdX₃(CO)]⁻ (X = Cl, Br), have been reported.^{3d}

Calderazzo³ and Uson^{2b} have suggested a negligible π back-bonding contribution to the Pd(II)-CO bond on the basis of thermodynamic and spectroscopic data. Herein we report the preparation and IR data of two new carbo-

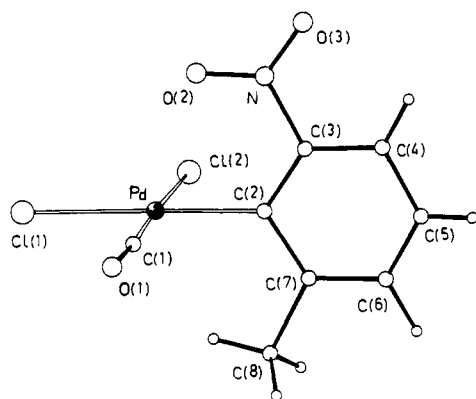


Figure 1. View of the molecular structure of the complex *cis*-[PPh₃(CH₂Ph)][Pd(C₆H₃Me-2,NO₂-6)Cl₂(CO)] (1) together with the atomic numbering scheme.

nylpalladium(II) complexes and the crystal structure of one of them with the aim of contributing to a better knowledge of this family of compounds and of the Pd-CO bond.

Results and Discussion

Synthesis. Complexes [PPh₃(CH₂Ph)][Pd(R)Cl₂(CO)] [R = C₆H₃Me-2,NO₂-6 (1), C₆H₂(NO₂)₃-2,4,6 (2)] can be obtained by bridge splitting with carbon monoxide of complexes [PPh₃(CH₂Ph)]₂[Pd(R)Cl(μ-Cl)]₂.⁴ The reaction takes place under very mild conditions (room temperature, atmospheric pressure) after a few minutes of bubbling CO through dichloromethane suspensions of the dimeric complexes. Both complexes are fairly stable in the solid state at room temperature, but they lose CO in solution giving the starting complexes. As far as we are aware, they are the first anionic organocarbonylpalladium(II) complexes and the most stable of all carbonyl derivatives of Pd(II) described so far.

IR and NMR Spectroscopic Data. Both complexes exhibit ν(CO) bands at frequencies [2100 (1), 2115 cm⁻¹ (2) in dichloromethane solution] lower than the aryl-cationic [Pd(C₆F₅)(CO)L₂]⁺ (2132–2163 cm⁻¹)⁵ or neutral [Pd(C₆F₅)₂(CO)₂] (2152–2186 cm⁻¹)^{2b} complexes or even lower than ν(CO) in carbonyl complexes of elements in low oxidation state, such as [Ni(CO)₄] (2123 cm⁻¹).⁶ All these data indicate that, in our complexes, the classical π back-bonding contribution to the Pd-CO bond is present. The effect of substitution of the aryl ligands in 1 or 2 by one chloro ligand to give [PdCl₃(CO)]⁻ causes an increase in both ν(CO) bands (2132 cm⁻¹).^{3d,7} We interpret this change as a consequence of the greater electronegativity of the chloro with respect to the aryl ligands. This forces the Pd atom to be a worse π-donor toward CO in [PdCl₃(CO)]⁻ than in complexes 1 or 2.

The ν(PdCl) trans to R band appears in 1 at lower wavenumber (285 cm⁻¹) than ν(PdCl) trans to CO (315 cm⁻¹) because the trans influence of an aryl ligand is greater than that of CO. That value is 15 cm⁻¹ lower than the corresponding one in *trans*-[Pd(R)Cl(PPh₃)₂],^{4a} which is a consequence of the neutral nature of this complex,

Table I. Important Interatomic Distances (Å) and Angles (deg) for Complex 1

Pd-Cl(1)	2.393 (2)	C(4)-C(5)	1.375 (11)
Pd-Cl(2)	2.312 (3)	C(5)-C(6)	1.376 (12)
Pd-C(1)	1.853 (10)	C(6)-C(7)	1.390 (9)
Pd-C(2)	2.000 (5)	C(2)-C(7)	1.404 (8)
C(1)-O(1)	1.138 (13)	C(7)-C(8)	1.520 (11)
C(2)-C(3)	1.389 (8)	P(1)-C(9)	1.795 (8)
C(3)-C(4)	1.397 (9)	P(1)-C(15)	1.780 (5)
N-C(3)	1.473 (8)	P(1)-C(21)	1.802 (7)
N-O(2)	1.222 (7)	P(1)-C(27)	1.816 (6)
N-O(3)	1.208 (9)		
Cl(1)-Pd-Cl(2)	94.2 (1)	C(4)-C(3)-N	114.8 (7)
Cl(1)-Pd-C(1)	87.2 (2)	C(3)-C(4)-C(5)	117.3 (8)
C(1)-Pd-C(2)	88.9 (3)	C(4)-C(5)-C(6)	120.6 (8)
C(2)-Pd-Cl(2)	89.6 (2)	C(5)-C(6)-C(7)	121.1 (8)
Pd-C(1)-O(1)	175.4 (7)	C(6)-C(7)-C(2)	120.6 (8)
Pd-C(2)-C(3)	124.0 (4)	C(6)-C(7)-C(8)	118.5 (7)
Pd-C(2)-C(7)	120.1 (6)	C(2)-C(7)-C(8)	120.9 (7)
C(3)-C(2)-C(7)	115.9 (6)	C(3)-N-O(2)	120.0 (7)
C(2)-C(3)-C(4)	124.4 (7)	C(3)-N-O(3)	118.3 (7)
C(2)-C(3)-N	120.7 (6)	O(2)-N-O(3)	121.7 (7)

which increases the π-donor ability of the chloro ligand. We have already observed a similar relationship between charge of a complex and the frequency of the ν(M-Cl) mode.⁸ Complex 2 shows two bands in the 400–200-cm⁻¹ region. The one at 335 cm⁻¹ can be assigned to ν(PdCl) trans to CO, but the corresponding one of ν(PdCl) trans to R appears as a very broad band (290–250 cm⁻¹). The ν(PdCl) trans to CO and ν(CO) frequencies in complex 2 are 20 and 15 cm⁻¹ higher than the corresponding ones in complex 1. This could be interpreted as a consequence of R in 2 being of greater electronegativity than R in 1 due to the presence of the three electron-withdrawing nitro substituents.

¹H NMR data show the expected resonances due to the Me group in 1, to the phenyl groups, and to the cation in both complexes (see Experimental Section).

Description of the Crystal Structure of *cis*-[PPh₃(CH₂Ph)][Pd(C₆H₃Me-2,NO₂-6)Cl₂(CO)] (1). The crystals of 1 consist of [PPh₃(CH₂Ph)]⁺ cations and of [Pd(C₆H₃Me-2,NO₂-6)Cl₂(CO)]⁻ anions. The structure of the anion is represented in Figure 1 together with the atomic numbering system; selected bond distances and angles are given in Table I. In the anionic complex the Pd atom is coordinated in a square-planar fashion by two Cl atoms in *cis* position [Pd-Cl(1) = 2.393 (2) and Pd-Cl(2) = 2.312 (3) Å], by the carbon atom C(1) from a terminal carbonyl group [Pd-C(1) = 1.853 (10) Å, Pd-C(1)-O(1) = 175.4 (7)°], and by the C(2) atom from the 2-methyl-6-nitrophenyl ligand [Pd-C(2) = 2.000 (5) Å]. The square-planar coordination is only slightly distorted, as the Cl(1), Cl(2), C(1), and C(2) atoms deviate by 0.002 (3), -0.002 (3), -0.026 (8), and 0.020 (7) Å, respectively, from the mean plane through the coordinated atoms with the Pd atom out of the plane by 0.015 (2) Å.

Noteworthy is the remarkable difference in the Pd-Cl bonds, the one trans to the C(2) atom of the phenyl ring being much longer than the one trans to the carbonyl group, which is reflected in its IR spectrum (see above). The Pd-Cl bond trans to a carbon atom from 2,4,6-trinitrophenyl (R) ligand has been found shorter in the anionic complex *cis*-[Pd(R)Cl₂[S(O)Me₂]]⁻, 2.365 (1) Å,^{4b} and in the neutral [Pd(R)Cl(AsPh₃)₂], 2.329 (5) Å.¹³ All these data about Pd-Cl distances allow us to propose the following trans influence scale: C₆H₃Me-2,NO₂-6 > C₆H₂(N-

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O₂)₃-2,4,6 > CO. The Pd–Cl bond opposite the carbonyl group is slightly longer than that found in the anionic complex [PdCl₃(CO)]⁻, 2.284 (2) Å.^{3d} This difference accounts for the higher energy of the ν(PdCl) trans to CO mode (332 cm⁻¹)⁷ in this complex than in 1 (315 cm⁻¹).

The values of the Pd–C(1) and C(1)–O(1) bonds, 1.853 (10) and 1.138 (13) Å, are comparable to those found in the anionic complex [PdCl₃(CO)]⁻, 1.87 (1) and 1.11 (1) Å,^{3d} and are in agreement with a π back-bonding character in the Pd–CO bond. Thus, the Pd–C(1) bond distance is shorter not only than the Pd–aryl bond [Pd–C(2) = 2.000 (5) Å] but also than other Pd–C_{sp} bonds like in *trans*-[Pd(CN)₂IP(CH₂Ph)₃]₂ [1.998 (5) Å]⁹ or in *trans*-[Pd(C₂C₆H₄C₂H-2)(NCS)(PEt₃)₂] [1.952 (7) Å]¹⁰ or in [Pd(CNMe)₄]²⁺ [1.975 (7), 1.993 (7) Å].¹¹ In addition, the C–O bond distance is as expected for a “classical” terminal carbonyl (mean value: 1.145 (20) Å from 10 022 values).¹²

The Pd–C(2) bond with the 2-methyl-6-nitrophenyl ligand, 2.000 (5) Å, is comparable to that reported for the Pd–C bond involving the 2,4,6-trinitrophenyl (R) ligand in [Pd(R)Cl(AsPh₃)₂], 1.97 (2) Å,¹³ or in *cis*-[Pd(R)Cl₂(S(O)Me₂)]⁻, 1.994 (4) Å,^{4b} but it is slightly longer than that reported for [Pd(R′)Cl(μ-Cl)]₂²⁻ [1.958 (8) Å] (R′ = C₆H₃Me-2,NO₂-6)^{4a} certainly due to the different nature of the Pd–Cl bond trans to the aryl ligand. Comparing the values of the Pd–C(2) bond distance with those found in other arylpalladium(II) complexes [mean value: 1.981 (32) Å from 28 values],¹² it can be concluded that the fact that it does not insert CO in the Pd–aryl bond is not due to an unusual stability of such bond. Probably, the presence of the two ortho substituents in 1 and 2 gives account of their inertness. The phenyl ring is strictly planar with the C(8) and N atoms of the substituents and the Pd atom practically coplanar [they deviate by 0.005 (11), -0.016 (7), and -0.005 (2) Å, respectively, from the mean plane passing through the phenyl ring] and forms an angle of 90.8 (2)° with the mean coordination plane. The almost perpendicular disposition of this ligand with respect to the coordination plane determines approximate axial positions for the O(2) atom of the nitro group [Pd...O(2) = 2.755 (6) Å] and for one hydrogen atom of the methyl group [Pd...H(81) = 2.56 Å]. Short axial Pd...O and Pd...H contacts are common features in square-planar Pd complexes with nitro and methyl-supporting ligands, even if it is not easy to attribute them to weak bonding interactions.^{13,14} The Pd...O(2) contact in 1 is significantly shorter than that found in its starting complex [Pd(R)Cl(μ-Cl)]₂²⁻ [2.893 (6) Å].^{4a} The nitro group, in which the N–O bonds are of 1.222 (7) and 1.208 (9) Å, is also strictly planar and tilted by 7.2 (3)° with respect to the phenyl ring.

Conclusions

Although the π back-bonding in the Pd–CO bond can be considered as negligible or unimportant in neutral or cationic complexes, all data we report here about the first two organo-carbonyl anionic complexes of palladium can be interpreted by using the classical σ-donor–π-acceptor

Table II. Experimental Data for the X-ray Diffraction Study on Complex 1

mol formula	C ₃₃ H ₂₈ Cl ₂ NO ₃ PPd
mol wt	694.87
cryst system	triclinic
space group	P1
radiatn (λ, Å)	Ni-filtered Cu Kα (1.54178)
a, Å	10.446 (5)
b, Å	12.538 (7)
c, Å	14.148 (6)
α, deg	65.40 (2)
β, deg	74.17 (2)
γ, deg	72.83 (2)
V, Å ³	1586 (1)
Z	2
D _{calcd} , g cm ⁻³	1.455
F(000)	704
cryst dimens, mm	0.20 × 0.23 × 0.30
μ(Cu Kα), cm ⁻¹	71.75
2θ range, deg	6–140
reflens measd	±h, ±k, l
no. of unique tot. data	6035
no. of unique obsd data	4505 [I > 2σ(I)]
R	0.0502
R _w	0.0670

ability of carbon monoxide. More synthetic and structural work on this area could give a better understanding of the bonding in carbonylpalladium(II) complexes. Crystal structures of some neutral and/or cationic carbonylpalladium(II) complexes would be very important to gain a better insight into the Pd–CO bond.

Experimental Section

Recording of infrared spectra, the C, H, and N analyses, conductance measurements, melting point determinations, and ¹H NMR spectra were performed as described elsewhere.¹⁵ Reactions were carried out at room temperature with magnetic stirring and without special precautions against light or atmospheric moisture.

Preparation of the Complexes [PPh₃(CH₂Ph)]₂[Pd(R)Cl₂(CO)] [R = C₆H₃Me-2,NO₂-6 (1), R = C₆H₂(NO₂)₃-2,4,6 (2)]. Into a suspension of [PPh₃(CH₂Ph)]₂[Pd(R)Cl(μ-Cl)]₂ (ca. 0.1 mmol) in dichloromethane (15 mL) was bubbled a stream of CO during a few minutes at atmospheric pressure until a yellow solution was obtained. This solution was stirred under CO for 2 h and filtered, and to the resulting solution, diethyl ether (45 mL) was added to give 1 or 2 as yellow solids in 60–65% yield. Anal. Calcd for C₃₃H₂₈Cl₂NO₃PPd (1): C, 57.04; H, 4.06; N, 2.01. Found: C, 56.98; H, 4.07; N, 1.91. Calcd for C₃₂H₂₄Cl₂N₃O₇PPd (2): C, 49.86; H, 3.14; N, 5.45. Found: C, 50.02; H, 3.55; N, 5.46. Mp (°C): 183 (1); 123 dec (2). Molar conductivity (Ω⁻¹ cm² mol⁻¹): 97 (1); 101 (2). ¹H NMR spectra (200 MHz, CDCl₃): (1) δ 2.77 (s, 3 H, Me), 4.95 [d, CH₂ of the cation, ²J(HP) = 13 Hz], 6–8 [unresolved multiplets, Ph of the cation + H(3) + H(4) + H(5) of R]; (2) δ 4.81 [d, CH₂ of the cation, ²J(HP) = 14 Hz], 8.82 [s, H(3) + H(5) of R].

Single crystals of complex 1, suitable for the X-ray diffraction study, were obtained by slow diffusion of a saturated solution of CO in *n*-hexane into an acetone solution (saturated with CO) of complex 1 under a CO atmosphere.

X-ray Data Collection, Structure Determination, and Refinement for *cis*-[PPh₃(CH₂Ph)]₂[Pd(C₆H₃Me-2,NO₂-6)-Cl₂(CO)] (1). The crystallographic data are summarized in Table II. Unit cell parameters were determined from the θ values of 30 carefully centered reflections, having 22 < θ < 39°. Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using the nickel-filtered Cu Kα radiation and the θ/2θ scan type. The reflections were collected with a variable scan speed of 3–12° min⁻¹ and a scan width from (θ – 0.65)° to (θ + 0.65 + 0.142 tan θ)°. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed

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Table III. Fractional Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses for the Non-Hydrogen Atoms

	x	y	z
Pd	2409 (1)	2109 (1)	2769 (1)
Cl(1)	1941 (2)	3911 (2)	1281 (1)
Cl(2)	1423 (2)	1022 (2)	2293 (2)
P	-2565 (1)	5820 (1)	1771 (1)
O(1)	3582 (7)	3549 (6)	3423 (5)
O(2)	4988 (6)	827 (6)	2325 (4)
O(3)	6069 (7)	-909 (6)	3134 (6)
N	5102 (6)	-86 (6)	3110 (5)
C(1)	3161 (7)	2959 (7)	3203 (5)
C(2)	2852 (6)	663 (6)	4046 (4)
C(3)	4045 (7)	-205 (6)	4061 (5)
C(4)	4362 (9)	-1219 (7)	4948 (6)
C(5)	3429 (11)	-1357 (9)	5867 (7)
C(6)	2216 (9)	-540 (7)	5889 (6)
C(7)	1918 (7)	462 (7)	4996 (5)
C(8)	572 (9)	1342 (9)	5078 (7)
C(9)	-2757 (6)	4611 (5)	1490 (4)
C(10)	-1648 (6)	3671 (6)	1454 (5)
C(11)	-1777 (7)	2747 (6)	1206 (5)
C(12)	-2991 (7)	2763 (6)	1005 (5)
C(13)	-4108 (7)	3679 (6)	1070 (5)
C(14)	-3998 (6)	4602 (6)	1307 (5)
C(15)	-4026 (6)	7003 (5)	1540 (4)
C(16)	-4275 (6)	7660 (6)	515 (5)
C(17)	-5367 (7)	8605 (6)	310 (6)
C(18)	-6231 (7)	8915 (7)	1125 (6)
C(19)	-6026 (7)	8258 (7)	2152 (7)
C(20)	-4942 (6)	7313 (7)	2366 (5)
C(21)	-2376 (7)	5289 (6)	3131 (4)
C(22)	-2152 (8)	6077 (9)	3508 (6)
C(23)	-1972 (12)	5654 (13)	4546 (7)
C(24)	-2087 (15)	4498 (14)	5204 (8)
C(25)	-2300 (14)	3767 (12)	4827 (7)
C(26)	-2462 (11)	4140 (8)	3787 (6)
C(27)	-1076 (6)	6362 (6)	891 (5)
C(28)	-656 (6)	7266 (6)	1141 (4)
C(29)	-1394 (8)	8433 (7)	901 (7)
C(30)	-1024 (11)	9194 (9)	1203 (10)
C(31)	47 (11)	8853 (9)	1702 (8)
C(32)	819 (10)	7696 (9)	1907 (7)
C(33)	460 (8)	6894 (8)	1633 (6)

following Lehmann and Larsen.¹⁶ Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.314 and 0.791).¹⁷ Only the observed reflections

(16) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* 1974, 30, 580.

were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all the non-hydrogen atoms. Sixteen hydrogen atoms were clearly localized in the final ΔF map and refined isotropically; 12 were placed at their geometrically calculated positions ($C-H = 1.08$ Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 446 variables; after the last cycles, no parameters shifted by more than 1.60 esd. The biggest remaining peak (close to the Pd atom) in the final difference map was equivalent to about $1.22 e/\text{Å}^3$. In the final cycles of refinement a weighting scheme, $w = [\sigma^2(F_o) + gF_o^2]^{-1}$, was used; at convergence the g value was 0.0072. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 18. All calculations were carried out on the Cray X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna, Italy) and on the Gould Powernode 6040 computer of the "Centro di Studio per la Strutturistica Diffattometrica" del CNR, Parma, Italy, by using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.¹⁹ The final atomic coordinates for the non-hydrogen atoms are given in Table III. The atomic coordinates of the hydrogen atoms and the thermal parameters are given in Tables SI and SII (supplementary material).

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Registry No. 1, 136545-68-1; 2, 136545-70-5; [PPh₃(CH₂Ph)₂][Pd(C₆H₃Me-2,NO₂-6)Cl(μ -Cl)]₂, 114110-06-4; [PPh₃(CH₂Ph)₂][Pd(C₆H₂(NO₂)₃-2,4,6)Cl(μ -Cl)]₂, 123951-64-4.

Supplementary Material Available: Tables of hydrogen atom coordinates (Table SI), thermal parameters for the non-hydrogen atoms (Table SII), and bond distances and angles, torsion angles, and least-squares planes (Table SIII) (19 pages); a listing of observed and calculated structure factors (Table SIV) (25 pages). Ordering information is given on any current masthead page.

(17) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* 1983, 39, 158. Ugozzoli, F. *Comput. Chem.* 1987, 11, 109.

(18) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(19) Sheldrick, G. M. SHELX-76 Program for crystal structure determination. University of Cambridge, England, 1976. Sheldrick, G. M. SHELXS-86 Program for the solution of crystal structures, University of Göttingen, 1986.