# Crystal Structure and Dynamic Behavior of a New Class of Monocationic Organometallic $Pd^{II}$ Compounds with Two Molecules of Bidentate Ligands: $[Pd(L–L)(N–N)(CH_2NO_2)][PF_6]$ (L–L = N–N, dppp)

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Two new classes of organometallic palladium(II) compounds, namely $[Pd(N–N)(CH_2NO_2)_2]$ and $[Pd(L–L)(N–N)(CH_2NO_2)][PF_6]$ [N–N = 2,2′-bipyridine, 1,10-phenanthroline and their substituted derivatives; L–L = 1,3-bis(diphenylphosphino)propane or N–N] have been synthesized and fully characterized both in the solid state and in solution. The crystal structures of $[Pd(phen)_2(CH_2NO_2)][PF_6]$ and of $[Pd(dppp)(tmphen)(CH_2NO_2)][PF_6]$ show a square-planar coordination geometry for the palladium atom and an unexpected monodentate coordination for the N–N ligand. The behavior in solution, investigated by NMR spectroscopy, shows the presence of dynamic processes involving only the N–N molecules. This fluxional behavior is different for $[Pd(N–N)_2(CH_2NO_2)][PF_6]$ and $[Pd(dppp)(N–N)(CH_2NO_2)][PF_6]$: in the former it most likely involves the substitution of the nitrogen atom *trans* to the $CH_2NO_2$ moiety by the uncoordinated nitrogen atom of the other N–N ligand; in the latter it may involve the exchange of the two nitrogen atoms at the same coordination site (flipping).

## Introduction

Recent developments in homogeneous catalysis show an increasing interest in the use of nitrogen-donor molecules as ancillary ligands.[1] Among the wide variety of nitrogen compounds, ligands containing $sp^2$-hybridized nitrogen atoms, especially when the N-atom is part of an aromatic ring, like 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) and bis-oxazoline, have been applied to two reactions of high industrial interest: the reductive carbonylation of nitroaromatic compounds to urethanes[2–4] and the CO/olefin co- and terpolymerization reactions.[5–8]

For several years we have been studying bis(chelate) palladium(II) compounds of general formula $[Pd(N-N)_2][PF_6]_2$ (**I**) and $[Pd(dppp)(N-N)][PF_6]_2$ (**II**) {dppp = 1,3-bis(diphenylphosphino)propane; N−N = bipy, 4,4′-dimethyl-2,2′-bipyridine (dmbipy), phen, 4,7-dimethyl-1,10-phenanthroline (dmphen), 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen)}, which were found to be efficient catalyst precursors for the above-mentioned reductive carbonylation (compounds of class **I**)[9][10] and copolymerization (compounds of class **I** and **II**)[11–13] reactions. In particular, in the CO/olefin copolymerization reaction the influence of the nitrogen ligand has been investigated in detail with monocationic $Pd^{II}$ compounds which have only one molecule of chelating ligand (N−N) bound to the metal center. The effect of N−N on the stereochemistry of the resulting polyketones was studied by Brookhart,[8] while the influence of N−N in the first and successive insertion steps of CO and alkenes in the copolymerization mechanism was reported by Elsevier and Vrieze.[14] To the best of our knowledge, we are the only group to use $Pd^{II}$ compounds with two molecules of chelating ligand (N−N and/or P−P) as precatalysts for the CO/olefin copolymerization. In this catalytic system the second molecule of chelating ligand, N−N in both classes of complexes, plays an important role, which has been partially examined[12,13,15] although some aspects still remain unclear.

In this paper we report the synthesis and characterization, both in the solid state and in solution, of two new series of stable organometallic $Pd^{II}$ compounds of general formula $[Pd(N-N)(CH_2NO_2)_2]$ and $[Pd(L-L)(N-N)(CH_2NO_2)][PF_6]$ (L−L = dppp, N−N) (Figure 1).

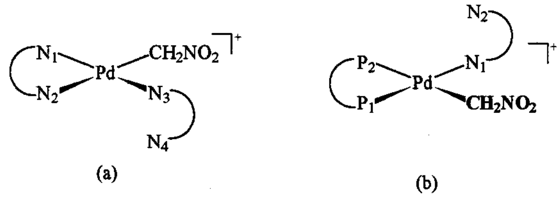

Figure 1. Schematic drawing of complexes $[Pd(N-N)_2(CH_2NO_2)][PF_6]$ and $[Pd(dppp)(N-N)(CH_2NO_2)][PF_6]$

## Results and Discussion

### Synthesis of the Complexes $[Pd(N-N)(CH_2NO_2)_2]$ (1−5) and $[Pd(L-L)(N-N)(CH_2NO_2)][PF_6]$ (6−11)

The synthesis of the new series of organometallic $Pd^{II}$ compounds, $[Pd(N-N)(CH_2NO_2)_2]$, is achieved by the treatment of a methanolic suspension of the bischelated complexes $[Pd(N-N)_2][PF_6]_2$ with nitromethane in the

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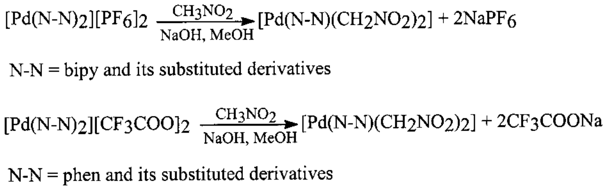
presence of a strong base, at room temperature. Depending on the nature of the nitrogen-donor chelating ligand the obtained solid has a different composition. When N−N is 2,2′-bipyridine, or its substituted derivatives, only [Pd(N−N)($CH_2NO_2$)$_2$] is obtained as a yellow solid (Scheme 1). On the other hand, when N−N is 1,10-phenanthroline, or its substituted derivatives, we obtain a mixture of compounds containing [Pd(N−N)($CH_2NO_2$)$_2$], as expected, and a new species formulated as [Pd(N−N)$_2$($CH_2NO_2$)][$PF_6$].



$$[Pd(N\text{-}N)_2][PF_6]_2 \xrightarrow[NaOH,\ MeOH]{CH_3NO_2} [Pd(N\text{-}N)(CH_2NO_2)_2] + 2NaPF_6$$

N-N = bipy and its substituted derivatives

$$[Pd(N\text{-}N)_2][CF_3COO]_2 \xrightarrow[NaOH,\ MeOH]{CH_3NO_2} [Pd(N\text{-}N)(CH_2NO_2)_2] + 2CF_3COONa$$

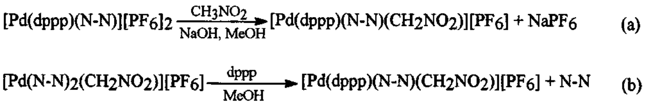
N-N = phen and its substituted derivatives

Scheme 1. Synthesis of complexes [Pd(N−N)($CH_2NO_2$)$_2$] (**1**−**5**)

The bis(nitromethyl) compounds with N−N = phen, dmphen and tmphen can easily be synthesized in high yield starting from the more soluble [Pd(N−N)$_2$][$CF_3COO$]$_2$, rather than from the corresponding hexafluorophosphate derivatives (Scheme 1).[16] The related monosubstituted derivatives [Pd(N−N)$_2$($CH_2NO_2$)][$PF_6$] are obtained in pure form as orange solids starting from [Pd(N−N)$_2$][$PF_6$]$_2$ and separating the solid from the reaction mixture as soon as the colour turns from yellow to orange, followed by recrystallization of the solid (see Experimental Section). Starting from [Pd(N−N)$_2$][$PF_6$]$_2$ the formation of [Pd(N−N)$_2$($CH_2NO_2$)][$PF_6$] (N−N = phen, dmphen, tmphen) was followed by recording the $^1$H NMR spectrum of the solid isolated from the reaction mixture at different reaction times. In all cases the solid isolated after 15 min does not contain the starting material and is found to be a mixture of the monosubstituted derivative [Pd(N−N)$_2$($CH_2NO_2$)][$PF_6$] and the disubstituted derivative [Pd(N−N)($CH_2NO_2$)$_2$] in different ratios depending on the nature of N−N. This ratio increases on going from phen to tmphen.

Therefore, the synthesis of the complexes [Pd(N−N)($CH_2NO_2$)$_2$] is a two-step nucleophilic substitution reaction: the first step, which is very fast, is the attack of the $CH_2NO_2^-$ with formation of the addition product [Pd(N−N)$_2$($CH_2NO_2$)][$PF_6$]; the second step requires dissociation of one of the two chelating ligands and coordination of the second molecule of nucleophile. The second step is slower than the first one, and its rate depends on the nature of the chelating ligand, being fast for unsubstituted phen and slow for tmphen. In the case of bipy as ligand the addition product was never isolated, but the transient orange colour of the synthetic solution of the bis(nitromethyl) derivatives suggests its formation, followed by a very fast reaction to give the final product.

In the case of the mixed-ligand complexes, [Pd(dppp)(N−N)][$PF_6$]$_2$, the addition product [Pd(dppp)(N−N)($CH_2NO_2$)][$PF_6$] (**9**−**11**) is synthesized following two different procedures: (i) a direct reaction of [Pd(dppp)(N−N)][$PF_6$]$_2$ with nitromethane, as for the [Pd(N−N)$_2$][$PF_6$]$_2$ complexes (Scheme 2a); (ii) a ligand exchange reaction of one N−N molecule with a molecule of dppp starting from the complexes [Pd(N−N)$_2$($CH_2NO_2$)][$PF_6$] (Scheme 2b).



$$[Pd(dppp)(N\text{-}N)][PF_6]_2 \xrightarrow[NaOH,\ MeOH]{CH_3NO_2} [Pd(dppp)(N\text{-}N)(CH_2NO_2)][PF_6] + NaPF_6 \quad (a)$$

$$[Pd(N\text{-}N)_2(CH_2NO_2)][PF_6] \xrightarrow[MeOH]{dppp} [Pd(dppp)(N\text{-}N)(CH_2NO_2)][PF_6] + N\text{-}N \quad (b)$$

Scheme 2. Synthesis of complexes [Pd(dppp)(N−N)($CH_2NO_2$)][$PF_6$] (**9**−**11**)

## Characterization of Complexes [Pd(N−N)($CH_2NO_2$)$_2$] (1−5)

The solid-state infrared spectra show two strong bands, one in the range 1481−1457 cm$^{-1}$ and the other between 1348 and 1345 cm$^{-1}$, which are assigned to the asymmetric and symmetric nitrogen-oxygen stretching frequency, respectively.

The characterization in solution was done by $^1$H NMR spectroscopy in [D$_6$]DMSO (Table 1). The spectra of all the complexes show a series of signals equal to half the number of chemically equivalent groups for the nitrogen ligand protons, indicating the equivalence of the two halves of the complex. All signals are downfield-shifted with respect to those of the free ligand. The assignments were made as previously reported.[17] The signal due to the two methylenic protons of $CH_2NO_2^-$ appears as a singlet between 5.06 and 4.88 ppm, depending on the nature of N−N (Table 1).

As has already been pointed out,[17a] the signals in the $^1$H NMR spectrum of H$^{2,9}$ in the phenanthroline series, and

Table 1. $^1$H-NMR data for complexes **1**−**8** compared to those of free N−N[a]

| Compound/ Ligand | N−N protons $H^{2,9}$ | $H^{4,7}$ | $H^{5,6}$ | $H^{3,8}$ | $CH_2NO_2$ |
|---|---|---|---|---|---|
| phen | 9.11 (dd) | 8.50 (dd) | 8.00 (s) | 7.79 (dd) | |
| **1** | 9.48 (dd) | 8.93 (dd) | 8.25 (s) | 8.20 (dd) | 5.06 (s) |
| **6** | 8.96 (d) | 8.92 (d) | 8.32 (s) | 8.00 (dd) | 4.97 (s) |
| dmphen | 8.94 (d) | | 8.16 (s) | 7.61 (d) | |
| **2** | 9.37 (d) | | 8.38 (s) | 8.06 (d) | 5.03 (s) |
| **7** | 8.77 (d) | | 8.41 (s) | 7.82 (d) | 4.90 (s) |
| tmphen[b] | 8.83 (s) | | 8.16 (s) | | |
| **8** | 8.68 (s) | | 8.42 (s) | | 4.87 (s) |

| | N−N protons $H^{6,6'}$ | $H^{3,3'}$ | $H^{4,4'}$ | $H^{5,5'}$ | $CH_2NO_2$ |
|---|---|---|---|---|---|
| bipy | 8.69 (m) | 8.39 (m) | 7.95 (m) | 7.46 (m) | |
| **4** | 9.16 (d) | 8.64 (d) | 8.33 (t) | 7.89 (t) | 4.91 (s) |
| dmbipy | 8.53 (d) | 8.23 (s) | | 7.27 (dd) | |
| **5** | 8.97 (d) | 8.52 (s) | | 7.70 (d) | 4.88 (s) |

[a] In [D$_6$]DMSO at room temperature: region of aromatic and $CH_2NO_2^-$ protons. − [b] Compound **3** is not soluble in [D$_6$]DMSO at room temperature. − s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets.

of H$^{6,6'}$ in the bipyridine series, are excellent probes for the evaluation of the coordination environment of the palladium atom. Their chemical shifts and bandshape are highly sensitive to the nature of the other ligands bound to the metal and to the presence of dynamic phenomena in solution.

A comparison of the NMR spectra of bis(nitromethyl) complexes [Pd(N−N)(CH$_2$NO$_2$)$_2$] and of monochelated carboxylato derivatives [Pd(N−N)(CF$_3$COO)$_2$][17a] shows that, in the first series, the frequencies of the "probe-protons" are downfield shifted with respect to the free ligand, while in the second one they are upfield shifted (Table 2). This observation, together with a lower CIS value (CIS = coordination induced shift; Δδ) (Table 2) for the bis(nitromethyl) derivatives with respect to that of the trifluoroacetato compounds, suggests a weaker Pd-N bond in the former, in agreement with the *trans* influence of the CH$_2$NO$_2$$^-$ fragment.

Table 2. CIS value (Δδ)[a] for the "probe protons" in the two series of complexes [Pd(N−N)(CF$_3$COO)$_2$] and [Pd(N−N)(CH$_2$NO$_2$)$_2$]

| N−N | [Pd(N−N)(CH$_2$NO$_2$)$_2$] Δδ (ppm) | [Pd(N−N)(CF$_3$COO)$_2$] Δδ (ppm) |
|---|---|---|
| phen | 0.37 | −0.68 |
| dmphen | 0.43 | −0.74 |
| bipy | 0.47 | −0.60 |
| dmbipy | 0.44 | −0.63 |

[a] CIS values are positive when shifted downfield with respect to free ligand and negative when shifted upfield.

## Characterization of the Complexes [Pd(L−L)(N−N)(CH$_2$NO$_2$)][PF$_6$] (6−11)

The solid-state infrared spectra show the familiar bands of the asymmetric and symmetric nitrogen-oxygen stretching frequency, together with those of the hexafluorophosphate anion.

The molecular structures of the complex cations in **6** and **11** are shown in Figures 2 and 3, respectively, and relevant geometrical parameters are reported in Table 3.

In the [Pd(phen)$_2$(CH$_2$NO$_2$)]$^+$ cation, **6**, the Pd atom exhibits a distorted square planar coordination geometry with one phen molecule acting as a monodentate ligand[18] and the other as a bidentate one (Figure 2), with the metal displaced out of the plane of the four donors by 0.037(2) Å towards N(2).

The chelating phen ligand and the unidentate one are planar within ±0.033(4) and ±0.077(4) Å, respectively, and their mean planes are nearly perpendicular to each other {dihedral angle of 88.91(5)°}. Because of the *trans* influence exerted by the CH$_2$NO$_2$ moiety, the Pd-N(5) distance {2.076(3) Å} is longer by 0.035 Å than the Pd-N(4) one {2.042(3) Å}. The latter distance has a value slightly longer than those of about 2.00 Å reported for [Pd(phen)X$_2$] species,[17a] where X is a weak *trans* influencing ligand and very close to those of about 2.04 Å in the bischelating [Pd(phen)$_2$]$^{2+}$ cations,[17a] which suggests greater steric crowding in the cation of **6** than in [Pd(phen)X$_2$] complexes. The monodentate phen ligand is bonded to Pd through N(1) {2.065(3) Å}, the other nitrogen being at a distance of 2.674(3) Å.

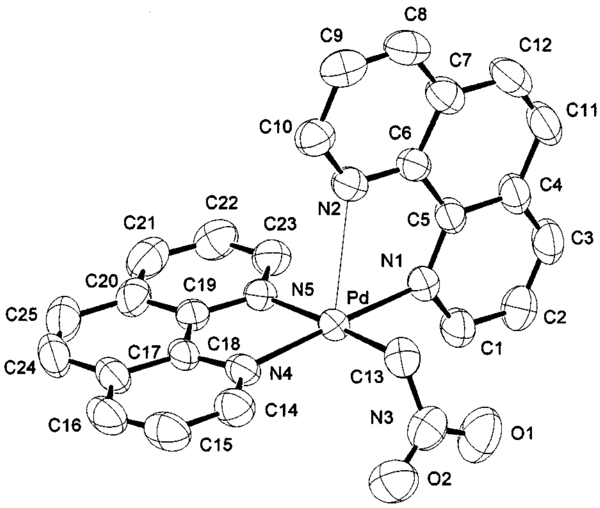


Figure 2. An ORTEP drawing (40% probability thermal ellipsoids) with atom numbering scheme of the cation of **6**

Table 3. Selected bond lengths [Å] and angles [°]

| | | | |
|---|---|---|---|
| **6**: | | | |
| Pd−N(1) | 2.065(3) | Pd−C(13) | 2.052(5) |
| Pd−N(4) | 2.042(3) | Pd−N(2) | 2.674(3) |
| Pd−N(5) | 2.076(3) | N(3)−C(13) | 1.414(6) |
| N(1)−Pd−N(4) | 174.36(12) | N(4)−Pd−N(2) | 112.91(10) |
| N(1)−Pd−N(2) | 70.74(11) | N(5)−Pd−N(2) | 88.74(11) |
| N(1)−Pd−C(13) | 88.4(2) | N(4)−Pd−N(5) | 80.81(12) |
| N(1)−Pd−N(5) | 95.16(12) | N(3)−C(13)−Pd | 108.8(3) |
| C(13)−Pd−N(2) | 92.7(2) | C(1)−N(1)−Pd | 117.2(3) |
| C(13)−Pd−N(4) | 95.7(2) | C(5)−N(1)−Pd | 123.6(2) |
| C(13)−Pd−N(5) | 176.47(14) | C(6)−N(2)−Pd | 104.9(2) |
| | | C(10)−N(2)−Pd | 135.5(3) |
| **11**: | | | |
| Pd−N(1) | 2.104(5) | Pd−C(13) | 2.157(8) |
| Pd−P(1) | 2.245(2) | Pd−N(2) | 2.562(6) |
| Pd−P(2) | 2.333(2) | N(3)−C(13) | 1.417(12) |
| N(1)−Pd−P(1) | 179.2(2) | P(1)−Pd−N(2) | 109.21(14) |
| N(1)−Pd−N(2) | 71.5(2) | P(1)−Pd−P(2) | 90.69(7) |
| N(1)−Pd−C(13) | 88.2(3) | P(2)−Pd−N(2) | 88.0(2) |
| N(1)−Pd−P(2) | 89.0(2) | N(3)−C(13)−Pd | 112.9(6) |
| C(13)−Pd−N(2) | 102.9(3) | C(1)−N(1)−Pd | 119.3(5) |
| C(13)−Pd−P(1) | 91.9(2) | C(5)−N(1)−Pd | 122.2(4) |
| C(13)−Pd−P(2) | 167.3(2) | C(6)−N(2)−Pd | 107.6(5) |
| | | C(10)−N(2)−Pd | 133.9(5) |

The CH$_2$NO$_2$ group, characterized by the Pd−C(13) distance and the N(3)−C(13)−Pd bond angle of 2.052(5) Å and 108.8(3)°, respectively, is oriented in such a way that NO$_2$ points to the less "crowded" side of the coordination plane (Figure 2), i.e. towards the coordinated side of the unidentate phen.

In the [Pd(dppp)(tmphen)(CH$_2$NO$_2$)]$^+$ cation, **11**, the metal shows a distorted square planar geometry with the tmphen ligand binding in a monodentate fashion through N(1), the other positions being occupied by the diphosphine and the $CH_2NO_2$ group (Figure 3). The metal ion is displaced by 0.129(3) Å out of the plane of the four donors, towards the N(2) atom of tmphen, resulting in a slightly disphenoidal distorsion[19] of the Pd, C(13), N(1), P(1) and P(2) atoms.

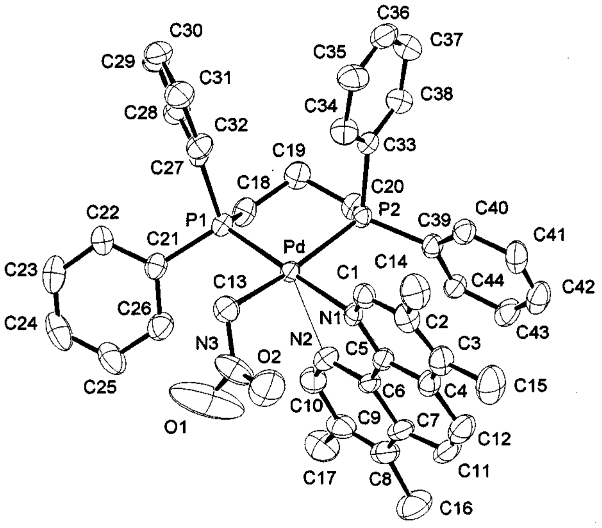


Figure 3. An ORTEP drawing (40% probability thermal ellipsoids) with atom numbering scheme of the cation of **11**

The tmphen ligand is planar within ±0.063(7) Å and makes an angle of 78.9(1)° with the mean coordination plane. It binds with a Pd−N(1) bond length of 2.104(5) Å, longer than that found in **6**, in agreement with the greater *trans* influence of P with respect to that of N. It is worthwhile to note in Figure 3 the stacking of the tmphen ligand with one of the phenyl rings at P(2). The corresponding mean planes make a dihedral angle of 11.5(1)°, with the shortest non-bonding distance N(1)···C(39) of 3.10 Å.

The Pd−P distances are significantly different {2.245(2) and 2.333(2) Å}, the longer one, Pd−P(2), reflecting the *trans* influence of the $CH_2NO_2$ ligand. The Pd−P(1) distance is similar to those of 2.244(1) and 2.249(2) Å detected in $[Pd(dppp)Cl_2]$[20] and does not significantly differ from the values of 2.262(3) Å found for both the phosphorus atoms in the $[Pd(dppp)(bipy)]^{2+}$ cation.[12] Likewise, steric strains are evidenced in the diphosphine ligand by the large deviations from ideality of the bond angles in the propylenic bridge {from 111.7(5) to 117.4(5)°}.

The $Pd-CH_2NO_2$ fragment is characterized by a Pd−C(13) distance and a N(3)−C(13)−Pd angle of 2.157(8) Å and 112.9(6)°, respectively. Comparison with the analogous fragment of the cation of **6** shows that in **11** the metal-donor distance is increased by ≈ 0.1 Å and the angle by ≈ 4°. This observation, together with the orientation of the $CH_2NO_2$ group (towards the uncoordinated side of tmphen), suggests that the latter undergoes more strained interactions with respect to those in the cation of **6**. However, it cannot be excluded that, at least partially, the elongation of the Pd−C(13) bond can be ascribed to the *trans* influence of the P atom as compared to that exerted in **6** by N(5).

The shorter Pd−N(2) distance in the cation of **11** {2.562(6) Å} relative to that found in **6** (2.674(3) Å) is probably due to to the greater coordinating capability of tmphen with respect to that of phen.

These structural results prompted us to indicate for $Pd^{II}$ a strong tendency to be square planar. Very recently the closely related complex $[Pd(phen)_2(COOMe)][PF_6]$ has been reported together with its crystal structure.[21] Although the authors described the complex to be pentacoordinate, the Pd−N distance {2.637(4) Å}, rather longer than normal,[17] and the ratio of the axial/equatorial bond lengths of 1.29 are distinctive of a square planar coordination geometry rather than of a square pyramidal one, as recently reported by Vrieze et al.[18] However, the displacement of the Pd atom towards the uncoordinated nitrogen of the phen (or tmphen) base is indicative of a weak Pd−N interaction both in the present complexes and in the one mentioned above.

The chemical behavior in solution for the $[Pd(N-N)_2(CH_2NO_2)][PF_6]$ compounds (**6-8**) was studied by $^1H$ NMR spectroscopy in $[D_6]DMSO$ (Table 1). The spectra of $[Pd(N-N)_2(CH_2NO_2)][PF_6]$ show, for the nitrogen ligands, four signals integrating for a quarter of the number of chemically equivalent groups, indicating the equivalence of the two ligands bound to palladium and of the two halves of each ligand. In these complexes the signal attributed to the "probe-protons" is shifted upfield with respect to the same signal in the free ligand. The singlet due to the methylenic protons of $CH_2NO_2$ moiety falls in the range between 4.97 and 4.87 ppm. Its chemical shift is upfield-shifted on going from phen to dmphen and to tmphen. This trend might be related to the electron-donor properties of the ligands. Moreover in the complex $[Pd(tmphen)_2(CH_2NO_2)][PF_6]$ it is possible to unambiguously distinguish the singlet due to the $H^{2,9}$ protons from that of $H^{5,6}$ on the basis of their positive NOE effect with the protons of $CH_2NO_2$.

For the $[Pd(dppp)(N-N)(CH_2NO_2)][PF_6]$ derivatives (**9-11**) in the $^1H$ NMR spectra (Table 4), recorded in $CD_2Cl_2$ at room temperature, three different groups of signals are present: that of the aromatic protons, where the resonances due to the N−N ligand are separated from those of the dppp allowing a clear assignment; that of the $CH_2NO_2^-$, and that of the protons of the propylenic bridge of dppp. The protons of the N−N ligand generate four signals of equal intensity indicating, again, the equivalence of the two halves of this ligand (Table 4a). All signals are shifted with respect to those of the free ligand and, in particular, that due to $H^{2,9}$ is downfield shifted. No signal due to free ligand is present.

The protons of coordinated 1,3-bis(diphenylphosphino)-propane give the same pattern for all complexes: three broad multiplets at high field for the propylenic bridge and four multiplets at low field for the phenyl rings (Table 4b). The number of signals, and their integration, indicates the non-equivalence of the two halves of the diphosphine ligand, as can also be seen from the X-ray structure.

Table 4. $^1$H- and $^{31}$P{$^1$H}-NMR data of complexes **9**−**11** in $CD_2Cl_2$

a)

| Compound/Ligand | N−N protons<br>H$^{2,9}$ | H$^{4,7}$ | H$^{5,6}$ | H$^{3,8}$ | $CH_2NO_2$ [$^3J$(P−H)][a] |
|---|---|---|---|---|---|
| phen | 9.13 (dd) | 8.27 (dd) | 7.82 (s) | 7.63 (dd) | |
| **9** | 9.36 (d) | 8.31 (d) | 7.70 (s) | 7.87 (dd) | 4.16 (dd) [3.91, 8.79] |
| dmphen | 8.94 (d) | | 8.04 (s) | 7.45 (d) | |
| **10** | 9.17 (d) | | 7.87 (s) | 7.68 (d) | 4.17 (dd) [3.91, 8.79] |
| tmphen | 8.86 (s) | | 8.06 (s) | | |
| **11** | 8.99 (s) | | 7.87 (s) | | 4.18 (dd) [3.91, 8.78] |

b)

| Compound/Ligand | dppp protons | | | | | | |
|---|---|---|---|---|---|---|---|
| | *o* | *m* + *p* | | | $CH_2$ (α) | | $CH_2$ (β) |
| dppp | 7.36 (m) | 7.30 (m) | | | 2.19 (t) | | 1.56 (m) |
| | *o*[b] | *p* + *m*[b] | *p*[c] | *o* + *m*[c] | $CH_2$ (α)[b] | $CH_2$ (α)[c] | $CH_2$ (β) |
| **9** | 7.89 (m) | 7.63 (m) | 6.97 (m) | 6.72 (m) | 2.81 (br.) | 2.56 (br.) | 2.03 (br.) |
| **10** | 7.79 (m) | 7.62 (m) | 6.97 (m) | 6.70 (m) | 2.78 (br.) | 2.53 (br.) | 2.01 (br.) |
| **11** | 7.82 (m) | 7.64 (m) | 6.99 (m) | 6.71 (m) | 2.78 (br.) | 2.53 (br.) | 2.03 (br.) |

c)[d]

| Compound | $^{31}P_1$ | $^{31}P_2$ | $^2J$(P−P)[a] |
|---|---|---|---|
| **9** | 15.22(d) | 3.84(d) | 21.5 |
| **10** | 15.25(d) | 3.73(d) | 21.5 |
| **11** | 15.03(d) | 3.80(d) | 21.4 |

[a] In Hz. − [b] Protons of groups bonded to $P_1$ (Figure 1b). − [c] Protons of groups bonded to $P_2$ (Figure 1b). − [d] $^{31}$P NMR of free dppp: $\delta = -17.6$.

On the basis of the chemical shift (Table 4b), the four multiplets of the protons of the aromatic rings of dppp can be divided into two sets of two multiplets each: one set is formed by the two multiplets which are upfield shifted with respect to the signals of free dppp (hereafter referred to as the *upfield set*), and the other one by the two multiplets which are shifted downfield (the *downfield set*). The cross peaks in the COSY spectrum correlate the two multiplets inside each set and no cross peak between the *upfield set* and the *downfield* one is present. Therefore, each set is generated by protons belonging to the same phenyl group. The total integration of each set is for ten protons, accounting for two phenyl rings. The comparison of the $^1$H NMR spectra of these compounds and those of the [Pd(dppp)(N−N)][$PF_6$]$_2$ series[12] allows us to assign the *downfield set* to the protons of the two phenyl rings bound to the phosphorus atom *trans* to the Pd−N bond ($P_1$ in Figure 1b). This assignment is also in agreement with the upfield shift of the resonances of the other two phenyl rings. Indeed, due to the stacking interactions observed in the X-ray structure, their protons are affected by the shielding anisotropy of the tmphen ligand. A similar situation has previously been reported by Natile et al. for the compound *trans*-[Pt(2,9-dmphen)Br($PPh_3$)$_2$][Br].[22]

In the $^1$H NMR spectra, the signal due to the methylenic protons of the $CH_2NO_2$ moiety appears as a doublet of doublets centered at 4.17 ppm (Table 4a). Its chemical shift is practically unaffected by the nature of N−N. Its fine structure is due to a $^1$H−$^{31}$P coupling with the two different phosphorus atoms of dppp with coupling constants $^3J(P-H)_{cis}$ = 3.9 Hz and $^3J(P-H)_{trans}$ = 8.8 Hz.

The $^{31}$P{$^1$H} NMR spectra present, at room temperature, two sharp doublets, in agreement with the different coordination environment of the phosphorus atoms (Table 4c). The doublet at lowest frequency is attributed to the phosphorus *trans* to the organic fragment ($P_2$ in Figure 1b).[23] Both of them are at higher frequencies than the signal of free dppp.

## Fluxional Behavior of Complexes 6−11

The most important feature in the spectra of the compounds [Pd(N−N)$_2$($CH_2NO_2$)][$PF_6$] and [Pd(dppp)(N−N)($CH_2NO_2$)][$PF_6$] is the equivalence of the bidentate nitrogen ligand. The presence of a dynamic process has been demonstrated by recording the spectra at low temperature in $CD_2Cl_2$.

For the complexes [Pd(N−N)$_2$($CH_2NO_2$)][$PF_6$] at room temperature all signals are sharp. The decrease of temperature causes a progressive broadening of the aromatic frequencies which is particularly evident in the case of H$^{2,9}$ signals. For these protons the signal disappears at T = 193 K. At the lowest temperature we reached, T = 163 K, at least eight signals can be detected (Figure 4). Unfortunately they are still too broad to allow a clear assignment. On the contrary, the signal due to the $CH_2NO_2$ protons is unaffected by the variation of temperature.

These experiments indicate that at room temperature the dynamic process, which makes the two N−N ligands equivalent, is fast on the $^1$H NMR time scale. When one equivalent of the N−N ligand is added to a solution of the com-

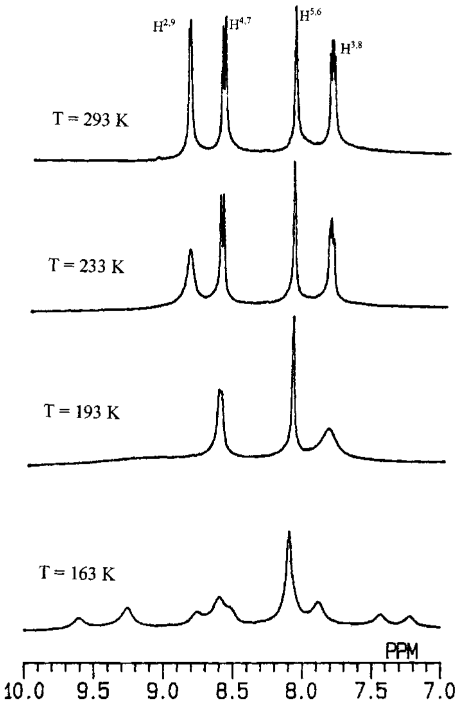
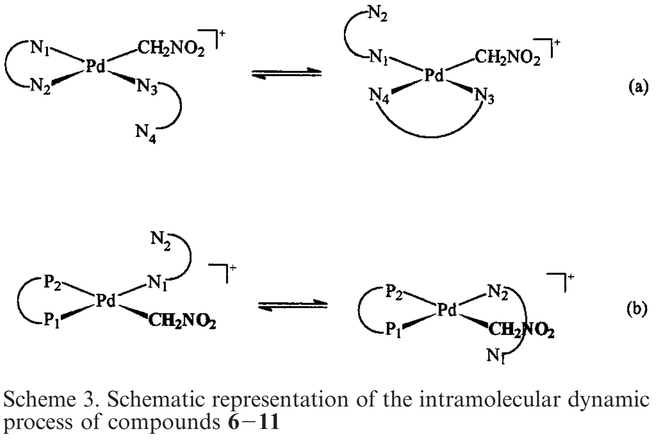


Figure 4. $^1$H-NMR spectra of $[Pd(phen)_2(CH_2NO_2)][PF_6]$ in $CD_2Cl_2$: variation with temperature; region of signals of aromatic protons

plex $[Pd(N-N)_2(CH_2NO_2)][PF_6]$, the spectrum measured at room temperature, also shows slightly broadened signals due to free ligand. Therefore, the dynamic process also involves an exchange with the free ligand, which is slower than the intramolecular one. On the basis of these results, one of the possible fluxional processes is the exchange between the unbound nitrogen of the monocoordinated phen ($N_4$) and one of the two bound nitrogens of the chelated phen, probably the one *trans* to the $CH_2NO_2$ fragment ($N_2$) (Scheme 3a).



Scheme 3. Schematic representation of the intramolecular dynamic process of compounds **6−11**

For the complexes $[Pd(dppp)(N-N)(CH_2NO_2)][PF_6]$ the signals due to the protons of N−N are sharper than those of the dppp phenyl rings, at room temperature. However, by lowering the temperature all of them broaden. In this case, the $H^{2,9}$ signal disappears at T = 173 K. As already observed for the compounds $[Pd(N-N)_2(CH_2NO_2)][PF_6]$, the decoalescence starts at T = 163 K and again no signal assignment could be performed (Figure 5).

In the compounds $[Pd(dppp)(N-N)(CH_2NO_2)][PF_6]$ the signal of the $CH_2NO_2$ protons also broadens when lowering the temperature and at T = 163 K it is split into two signals (Figure 5).

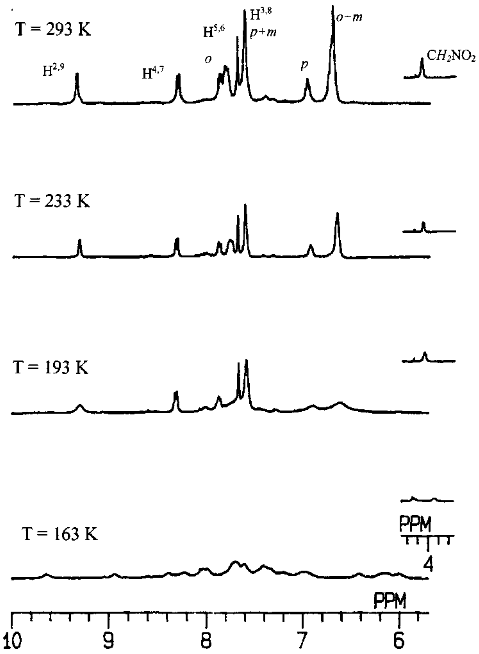


Figure 5. $^1$H-NMR spectra of $[Pd(dppp)(phen)(CH_2NO_2)][PF_6]$ in $CD_2Cl_2$: variation with temperature; region of signals of aromatic protons and of $CH_2NO_2$ moiety

It should be noted that in the $^{31}P\{^1H\}$ NMR spectrum no variation with temperature is observed, suggesting that the two phosphorus atoms are fixed on palladium.

As already observed for the $[Pd(N-N)_2(CH_2NO_2)][PF_6]$ compounds, after addition of one equivalent of N−N to a solution of $[Pd(dppp)(N-N)(CH_2NO_2)][PF_6]$ the spectrum at room temperature also exhibits the signals of free N−N ligand, indicating that the exchange between coordinated and free ligand is slow on the $^1$H NMR time scale. Therefore, as regards the fluxional behavior of the compounds $[Pd(dppp)(N-N)(CH_2NO_2)][PF_6]$, at least three intramolecular dynamic processes can be involved: (i) the movement of the dppp propylenic bridge, whose rate, at room temperature, is intermediate on the $^1$H NMR time scale; (ii) the rotation of the phenyl rings of dppp around the $P-C_{ipso}$ bond; (iii) the flipping of the N−N ligand, which exchanges the two nitrogen atoms ($N_1$ and $N_2$) at the same coordination site (Scheme 3b). This flipping might be responsible for the equivalence of the two phenyl rings bound to the phosphorus atom *cis* to N−N ($P_2$ in Figure 1b), one of which exhibits a stacking interaction in the solid state (see above). At room temperature the movements (ii) and (iii) are fast on the $^1$H NMR time scale.

At the lowest temperature we reached, the $CH_2NO_2$ protons generate two different signals (Figure 5), because they are diastereotopic as the palladium atom becomes a stereogenic center. Indeed, the pseudo-symmetry plane present for the complex at room temperature disappears at T = 163 K.

A comparison of the spectra of [Pd(phen)$_2$(CH$_2$NO$_2$)][PF$_6$] and of [Pd(dppp)(phen)(CH$_2$NO$_2$)][PF$_6$] at T = 163 K shows that the signal at lowest field (9.61 ppm and 9.64 ppm, respectively) has practically the same chemical shift, therefore it may be tentatively attributed to the proton in the *ortho* position with respect to the phen uncoordinated nitrogen atom (N$_4$ in Figure 1a and N$_2$ in Figure 1b).

## Conclusion

The Pd complexes described above represent one of the first examples of monodentate phen-type ligands with no alkyl substituents at the 2 and 9 positions.

The X-ray structural characterization of these complexes strongly indicates the tendency of palladium(II) to assume a square planar coordination. This is in support of our previous studies on bischelated species where this geometry is ensured by bowing the N−N ligand,[24] and of more recent examples where one of the two molecules of N−N is forced to act as a monodentate ligand.[18][21]

A detailed NMR investigation shows the presence of different dynamic processes in solution: (i) an exchange between coordinated and free N−N ligand; (ii) an intramolecular competition of the unbound nitrogen towards a coordination site at the expense of one N atom of the chelated phen in the [Pd(N−N)$_2$(CH$_2$NO$_2$)][PF$_6$] complexes; (iii) a flipping of the N−N ligand, in the [Pd(dppp)(N−N)(CH$_2$NO$_2$)][PF$_6$] derivatives, that exchanges the two nitrogen atoms at the same coordination site. The rate of these dynamic processes increases on going from the first to the last one, altough a complete decoalescence could not be reached.

## Experimental Section

**General Remarks:** The nitrogen-donor chelating ligands and dppp (Aldrich) together with the analytical grade solvents (Baker) were used without further purification for synthetic and spectroscopic purposes. IR spectra were recorded on a Perkin Elmer 983G spectrometer in KBr pellets. $^1$H NMR spectra were recorded at 400 MHz on a JEOL EX 400 spectrometer operating in Fourier-transform mode, with tetramethylsilane (TMS) as internal standard. Two-dimensional homonuclear correlated spectra (COSY) were obtained with the automatic program of the instrument. $^{31}$P NMR spectra were recorded at 161.86 MHz with H$_3$PO$_4$ as external reference, where positive shifts are at high frequency.

**Syntheses:** The compounds [(N−N)H][PF$_6$], as well as the complexes [Pd(N−N)$_2$][PF$_6$]$_2$ and [Pd(dppp)(N−N)][PF$_6$]$_2$ were synthesized according to the procedures reported in the literature.[11][12] Elemental analyses (C, H, N), performed by Dr. E. Cebulec (Dipartimento di Scienze Chimiche, Trieste, Italy), were in perfect agreement with the proposed stoichiometry (Tables 5 and 6).

**Compounds [(N−N)H][CF$_3$COO]:** The dinitrogen ligand N−N (5.0 mmol) was dissolved in acetone (15 mL) at room temperature, and trifluoroacetic acid 99% was added (0.47 mL, N−N/CF$_3$COOH = 1:1.2). Concentration of the solution to approximately a third of the original volume and addition of diethyl ether (15 mL) induced precipitation of the product as a white solid. The solid was removed by filtration and dried under vacuum. Average yield: 70%.

**Complexes [Pd(N−N)$_2$][CF$_3$COO]$_2$:** Pd(MeCOO)$_2$ (0.9 mmol) was dissolved in acetone (10 mL) at room temperature. After 30 min, [(N−N)H][CF$_3$COO] (2.0 mmol; Pd/[(N−N)H][CF$_3$COO] = 1:2.2) was added as a solid to the filtered red solution. The product readily precipitated as a yellow solid. After 30 min, it was isolated by filtration, washed with cold acetone and dried under vacuum. Average yield: 75%.

Table 5. Elemental analyses for [(N−N)H][CF$_3$COO] and [Pd(N−N)$_2$][CF$_3$COO]$_2$[a]

| Compound | C | H | N |
|---|---|---|---|
| [(phen)H][CF$_3$COO] | 57.1 (57.2) | 3.05 (3.08) | 9.55 (9.52) |
| [Pd(phen)$_2$][CF$_3$COO]$_2$ | 47.8 (48.5) | 2.40 (2.33) | 7.90 (8.09) |
| [(dmphen)H][CF$_3$COO] | 59.4 (59.6) | 4.02 (4.07) | 8.60 (8.69) |
| [Pd(dmphen)$_2$][CF$_3$COO]$_2$ | 50.5 (51.3) | 3.55 (3.60) | 9.55 (9.62) |
| [(tmphen)H][CF$_3$COO] | 60.8 (61.7) | 4.98 (4.89) | 7.96 (8.00) |
| [Pd(tmphen)$_2$][CF$_3$COO]$_2$ | 49.9 (50.6) | 4.54 (4.68) | 8.88 (8.93) |

[a] Calculated values are reported in parentheses.

**[Pd(N−N)(CH$_2$NO$_2$)$_2$] (1−5):** The complex [Pd(N−N)$_2$][X]$_2$ (X = PF$_6^-$ for N−N = bipy and dmbipy; X = CF$_3$COO$^-$ for N−N = phen, dmphen and tmphen) (0.2 mmol) was suspended in nitromethane (10 mL). A solution of NaOH 0.2 M in methanol was added (3.5 mL; Pd/OH$^-$ = 1:4), obtaining a solution from which the product precipitated as a yellow solid. After 30 min, the solid was removed by filtration, washed with methanol and vacuum dried. Average yield: 70%.

**[Pd(N−N)$_2$(CH$_2$NO$_2$)][PF$_6$] (6−7):** The complex [Pd(N−N)$_2$][PF$_6$]$_2$ (N−N = phen, dmphen; 0.5 mmol) was added with vigorous stirring to a solution of NaOH in methanol in the presence of nitromethane (4.2 mmol of NaOH in 20 mL CH$_3$OH and 1.2 mL of CH$_3$NO$_2$; Pd/OH$^-$ = 1:8; Pd/CH$_3$NO$_2$ = 1:30). The colour of the solid rapidly turned from yellow to orange. The solid was rapidly isolated by filtration, washed with cold methanol and vacuum dried. Average yield: 70%.

**Recrystallization:** The solid was dissolved in a minimal amount of CH$_2$Cl$_2$. From the filtered solution the product precipitated upon addition of diethyl ether.

**[Pd(tmphen)$_2$(CH$_2$NO$_2$)][PF$_6$] (8):** The complex [Pd(tmphen)$_2$][PF$_6$]$_2$ (0.2 mmol) was suspended in methanol (20 mL). To the suspension a solution of NaOH 0.2 M in methanol (5.0 mL; Pd/OH$^-$ = 1:4) and nitromethane (0.6 mL) were added; the colour turned from yellow to orange. After stirring for 1 h at room temperature the solid was removed by filtration, washed with methanol and vacuum dried. Yield: 80%.

**[Pd(dppp)(N−N)(CH$_2$NO$_2$)][PF$_6$] (9−11):** The complexes [Pd(dppp)(N−N)(CH$_2$NO$_2$)][PF$_6$]$_2$ can be synthesized following two different procedures: the first slightly differs depending on the nature of N−N (method A), while the second is the same with all the series (method B).

**Method A. − [Pd(dppp)(phen)(CH$_2$NO$_2$)][PF$_6$] (9):** A solution of NaOH (0.4 mmol; NaOH/Pd = 1.05:1) in methanol (3 mL) in the presence of nitromethane (0.2 mL) was added to a suspension of [Pd(dppp)(phen)][PF$_6$]$_2$ (0.4 mmol) in methanol (4 mL). The colour of the suspension immediately turned bright yellow and part of the

Table 6. Elemental analyses for the complexes **1−11**[a]

| Complex | C | H | N |
|---|---|---|---|
| **1** [Pd(phen)($CH_2NO_2$)$_2$] | 40.9 (41.3) | 2.90 (2.97) | 13.6 (13.8) |
| **2** [Pd(dmphen)($CH_2NO_2$)$_2$] | 43.9 (44.2) | 3.64 (3.71) | 12.7 (12.9) |
| **3** [Pd(tmphen)($CH_2NO_2$)$_2$] | 46.4 (46.7) | 4.24 (4.35) | 12.0 (12.1) |
| **4** [Pd(bipy)($CH_2NO_2$)$_2$] | 37.8 (37.7) | 3.13 (3.16) | 14.2 (14.6) |
| **5** [Pd(dmbipy)($CH_2NO_2$)$_2$] | 40.8 (40.9) | 3.89 (3.93) | 13.7 (13.6) |
| **6** [Pd(phen)$_2$($CH_2NO_2$)][$PF_6$] | 43.5 (44.7) | 2.56 (2.70) | 10.2 (10.4) |
| **7** [Pd(dmphen)$_2$($CH_2NO_2$)][$PF_6$] | 47.0 (47.8) | 3.50 (3.60) | 9.50 (9.62) |
| **8** [Pd(tmphen)$_2$($CH_2NO_2$)][$PF_6$] | 49.9 (50.6) | 4.53 (4.68) | 8.86 (8.93) |
| **9** [Pd(dppp)(phen)($CH_2NO_2$)][$PF_6$] | 52.7 (53.1) | 3.90 (4.01) | 4.59 (4.65) |
| **10** [Pd(dppp)(dmphen)($CH_2NO_2$)][$PF_6$] | 53.9 (54.1) | 4.33 (4.33) | 4.38 (4.51) |
| **11** [Pd(dppp)(tmphen)($CH_2NO_2$)][$PF_6$]·$CH_2Cl_2$ | 51.8 (51.7) | 4.48 (4.44) | 4.05 (4.02) |

[a] Calculated values are reported in parentheses.

solid was dissolved. After 1 h diethyl ether (50 mL) was added and the mixture was filtered, the solid was washed with cold methanol and vacuum dried. Yield: 85%.

**[Pd(dppp)(dmphen)($CH_2NO_2$)][$PF_6$] (10):** A solution of NaOH (0.1 mmol; NaOH/Pd = 1.2:1) in methanol (1 mL) in the presence of nitromethane (50 μL) was added to a suspension of [Pd(dppp)(dmphen)][$PF_6$]$_2$ (0.1 mmol) in methanol (3 mL). The colour of the suspension immediately turned bright yellow and part of the solid was dissolved. Concentration to approximately half of the original volume induced more precipitation of the product as a yellow solid. The solid was removed by filtration, washed with cold methanol and dried under vacuum. Yield: 90%.

**[Pd(dppp)(tmphen)($CH_2NO_2$)][$PF_6$] (11):** A solution of NaOH (0.4 mmol; NaOH/Pd = 4:1) in methanol (2.5 mL) in the presence of nitromethane (0.25 mL) was added to a suspension of [Pd(dppp)(tmphen)][$PF_6$]$_2$ (0.1 mmol) in methanol (1 mL). The colour of the suspension immediately turned bright yellow. After 1 min the mixture was filtered, the solid was washed with cold methanol and vacuum dried. Yield: 90%.

**Recrystallization:** Complex **10** (0.03 g) was recrystallized by dissolving it in methanol (10 mL), yielding a yellow solution from which the product precipitated upon addition of diethyl ether. Complex **11** was recrystallised from a minimal amount of dichloromethane. The solid precipitated upon addition of diethyl ether.

**Method B:** To a supension of [Pd(N−N)$_2$($CH_2NO_2$)][$PF_6$]$_2$ (0.2 mmol) in methanol (2.5 mL) was added dppp (dppp/Pd = 1:1) together with a minimal amount of dichloromethane (0.15 mL). The mixture was stirred at room temperature for 2 h yielding a bright yellow suspension. The solid was removed by filtration, washed with cold methanol and vacuum dried. Yield: **9** 30%; **10** 70%; **11** 77%.

**X-ray Analysis. − X-ray Structure Determination of 6 and 11:** Single crystals of [Pd(phen)$_2$($CH_2NO_2$)][$PF_6$] (**6**) and of [Pd(dppp)-

Table 7. Crystal data and details of structure refinements for compounds **6** and **11**

| | **6** | **11** |
|---|---|---|
| Empirical formula | $C_{28}H_{24}F_6N_5O_3PPd$ | $C_{47}H_{50}F_6N_3O_3P_3Pd$ |
| Molecular mass | 729.89 | 1018.21 |
| Crystal system | triclinic | monoclinic |
| Space group | $P\bar{1}$ (No.2) | $P2_1$ (No.4) |
| $a$ [Å] | 10.757(1) | 11.760(2) |
| $b$ [Å] | 12.042(2) | 16.667(2) |
| $c$ [Å] | 12.487(2) | 12.119(2) |
| α [°] | 62.46(1) | |
| β [°] | 82.61(1) | 106.76(1) |
| γ [°] | 86.48(1) | |
| $V$ [Å$^3$] | 1422.3(4) | 2274.5(6) |
| $Z$ | 2 | 2 |
| $D_{\mathrm{calcd.}}$ [g cm$^{-3}$] | 1.704 | 1.487 |
| μ (Mo-$K_\alpha$) [mm$^{-1}$] | 0.789 | 0.583 |
| $F$(000) | 732 | 1044 |
| Colour | orange | yellow |
| θ range | 2.50−26.98 | 2.13−27.96 |
| Octants collected | $-13 \le h \le 13$ | $-15 \le h \le 14$ |
| | $-13 \le k \le 15$ | $0 \le k \le 21$ |
| | $0 \le l \le 15$ | $0 \le l \le 15$ |
| No. of reflections collected | 6477 | 5898 |
| No. of independent reflections | 6185 [$R$(int) = 0.0205] | 5648 [$R$(int) = 0.0277] |
| Refinement method | Full-matrix least squares on $F^2$ | |
| No. of reflections with $I > 2\sigma(I)$ | 4772 | 4298 |
| No. of parameters | 434 | 572 |
| Goodness-of-fit | 1.050 | 0.986 |
| $R1$ ($F_o$) | 0.0427 | 0.0467 |
| $wR2$ ($F_o^2$) | 0.1180 | 0.1091 |
| Residuals [e Å$^{-3}$] | 0.589, −0.445 | 0.794, −0.469 |

(tmphen)($CH_2NO_2$)][$PF_6$] (**11**) suitable for X-ray analysis were obtained with the double-layer method by dissolving the complex in a minimal amount of acetone. Double the volume of diethyl ether was stratified on the filtered yellow solution. The crystals were obtained overnight.

Details of crystal parameters, data collection and refinements of compounds **6** and **11** are summarized in Table 7. Diffraction data were carried out at room temperature using the $\omega-2\theta$ scan technique on a CAD4 Enraf-Nonius single-crystal diffractometer equipped with graphite monochromator and $Mo-K_\alpha$ radiation ($\lambda = 0.7107$ Å). Three standard reflections, measured at regular intervals throughout the data collections, showed no noticeable variation in intensity for either crystal. An absorption correction based on $\psi$-scan method was applied to both the data sets.

The structures were solved by conventional Patterson[25] and Fourier analyses and refined on $F^2$ by the full-matrix anisotropic least-squares method using the SHELXL-93 package.[26] In both the crystals, a difference Fourier synthesis revealed the presence of a molecule of acetone. In compound **6** this molecule was disordered over two positions with refined site occupancies that complement to 1.0. The final cycles with the fixed contribution of hydrogen atoms, except those of the solvent molecule, converged to final $R1$ and $wR2$ factors reported in Table 3. Refined weighting schemes were $1/[\sigma^2\ (Fo^2) + (0.0805P)^2 + 0.07P]$ and $1/[\sigma^2\ (Fo^2) + (0.0746P)^2]$ for compound **6** and **11**, respectively, where $P = \{\text{Max}\ (Fo^2, 0) + 2Fc^2\}/3$. The Flack $x$ parameter[27] of 0.01(4) is indicative of the correct absolute configuration for compound **11**. Crystallographic data (excluding structure factors) for the structures reported in this paper have deposited with the Cambridge Crystallographic Data Center as supplementary publication n. CCDC-113500/113501. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336-033; E-mail:deposit@ccdc.cam.ac.uk).

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