Subtle Balance between Various Phenanthroline Ligands and Anions in the Palladium-Catalyzed Reductive Carbonylation of Nitrobenzene

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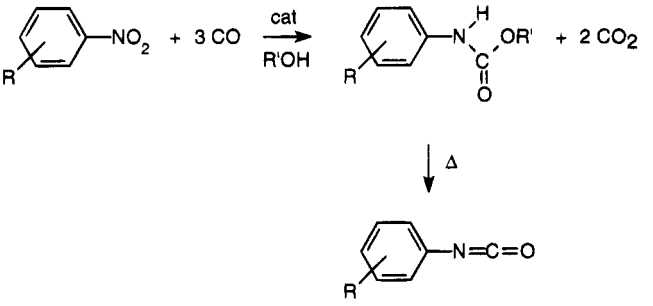
Palladium–phenanthroline catalyst systems for the reductive carbonylation of nitrobenzene in methanol yield methyl *N*-phenylcarbamate as the major product next to small amounts of *N,N'*-diphenylurea, aniline, and azoxybenzene. The influence of a series of 4,7-disubstituted 1,10-phenanthroline ligands (R = Cl, H, Me, MeO, and Me_2N) in close correlation with two different noncoordinating anions (triflate or tetrafluoroborate) on the catalytic activity and selectivity was studied. Though all the rigid phenanthroline ligands afford stable catalyst precursors, no conversion into carbamate was obtained under the influence of the electron-withdrawing chloride substituents on the ligand. With the mildly electron-donating substituents H, Me, and MeO, high activities up to 311 mol/(mol/h) could be measured. A very subtle balance between the donating capacity of the ligand and the particular noncoordinating anion used was found. A cyclic voltammetric study established that the reduction of the originally Pd^{II} species into a Pd^0 intermediate becomes more difficult with increasing donating capacity of the phenanthroline ligand. An X-ray structure was elucidated for $Pd(phen)_2(OTf)_2$. The $Pd(phen)_2(OTf)_2$ crystals were triclinic, space group $P\bar{1}$, $a = 10.387(1)$ Å, $b = 11.539(2)$ Å, $c = 13.449(3)$ Å, $\alpha = 70.53(1)°$, $\beta = 67.42(2)°$, $\gamma = 81.51(1)°$, $Z = 2$, and final $R = 0.045$ for 6448 observed reflections.

Introduction

Aromatic isocyanates and carbamates have become increasingly important ever since the work of O. Bayer in 1937 led to the formation of polyurethanes from diisocyanates and diols. Traditionally these isocyanates and carbamates are prepared via the phosgene route, in which a nitro compound is first catalytically hydrogenated to an amine. Subsequent reaction of the amine with phosgene yields the isocyanate, which can be converted into the carbamate by reaction with an alcohol. MDI, 1,1'-methylenebis(4-isocyanatobenzene), is the most widely applied diisocyanate nowadays, and it is produced by condensation of two molecules of aniline with formaldehyde prior to the reaction with phosgene.[1-3]

Because the reaction requires the use of the extremely toxic phosgene and because the reaction produces large quantities of HCl as a side product, two major disadvantages to the phosgene route, research is done on the reductive carbonylation of aromatic nitro compounds as an attractive alternative process for the production of isocyanates and carbamates. This way, an isocyanate is formed by direct reaction of the nitro function with CO, under the influence of a catalyst. If the reaction is performed in an alcohol a carbamate is formed as main product, which can be thermally degraded into the isocyanate (Scheme 1). The only waste product in this reaction is the relatively harmless CO_2. This route can also be applied for the production of MDI by condensation of two of the carbamate molecules with formaldehyde, as was found by workers at the Atlantic Richfield Co. (Arco) and Asahi Chemical, independently, for ethyl *N*-phenylcarbamate.[1,4]

Scheme 1. Reductive Carbonylation of Aromatic Nitro Compounds



The catalyst system that is required for the reaction between the nitro function and CO can be based on group 8–10 metals. Ruthenium is a frequently applied

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metal, especially in mechanistic studies.[5] The most active and selective systems known use palladium as the active metal center, often applied as $PdCl_2$. Although mechanistically less well clarified,[6] it is known that addition of a nitrogen-donor ligand to the palladium system is needed to obtain catalytic activity, and it was found that bidentate ligands are by far superior.[7] A catalyst system consisting of palladium and a bidentate nitrogen, phosphorus, arsenic, or antimony ligand for the reductive carbonylation of nitro compounds was patented in 1983, with the emphasis on the use of 1,10-phenanthroline and 1,3-bis(diphenylphosphino)propane (dppp).[8]

Mestroni et al. already reported the influence of the donating capacity of the bidentate ligand on the catalytic activity and selectivity. For [Pd(bidentate ligand)$_2$][PF_6]$_2$ the catalytic activity increases in the series 2,2′-bipyridine < 1,10-phenanthroline < 3,4,7,8-tetramethyl-1,10-phenanthroline.[9] The relatively high activity of the 1,10-phenanthroline ligands is probably caused by the rigidity of these ligands, in contrast to the more flexible 2,2′-bipyridine ligand in which free rotation around the linking bond is possible. This results in lower complexation constants for the bipyridine ligand.[10]

In a more detailed study on the influence of the donating capacity of the ligand on the catalytic activity and selectivity using 4,4′-disubstituted 2,2′-bipyridyl ligands, we found an absolute lack of conversion under the influence of electron-withdrawing substituents on the bipyridyl ligand. With the electron-donating substituents, on the other hand, only small differences were found.[11] A problem with these bipyridyl–palladium systems remained, however: the stability of the active species.

As part of our ongoing research, the effect of rigid 4,7-disubstituted 1,10-phenanthroline ligands (R = Cl, H, Me, MeO, and Me_2N) on the palladium-catalyzed reductive carbonylation of aromatic nitro compounds was studied. With these ligands more stable catalyst systems could be obtained, compared to the bipyridine analogues. Higher catalytic activities were therefore expected, even under the influence of electron-withdrawing substituents on the phenanthroline ligand. The ligands were tested in combination with Pd(acetate)$_2$ and *p*-toluenesulfonic acid in the reductive carbonylation of nitrobenzene. Next to these *in situ* studies, Pd–phenanthroline complexes with noncoordinating anions have been prepared. Two different noncoordinating anions (OTf and BF_4) have been used to study the exact influence of the anion on the catalytic activity and selectivity, in intimate interplay with the various ligands.

Results and Discussion

Synthesis of the Ligands. Introduction of electron-withdrawing or electron-donating substituents at C(4) and C(7) (R = Cl, MeO, and Me_2N) of 1,10-phenanthroline is not readily achieved because of the strong resistance of phenanthroline toward electrophilic reagents. This resistance cannot be easily overcome by oxidation at the nitrogen atom as in 2,2′-bipyridine.[11] Although 1,10-phenanthroline can be converted into 1,10-phenanthroline *N*-oxide under the influence of hydrogen peroxide in glacial acetic acid, it will not react to produce 1,10-phenanthroline *N*,*N*′-dioxide. This is probably caused by steric hindrance introduced by the first oxygen atom together with the relatively high stability of the conjugate acid of 1,10-phenanthroline *N*-oxide, which will be formed under the acidic conditions used in the oxidation. As a result only one of the heteroaromatic rings in this fused system will be activated toward substitution. Moreover, C(2) becomes the most activated position instead of the desired C(4), which is expressed in the relatively easy introduction of a cyano group at C(2) via this route by Corey et al.[12]

In contrast to other *N*-oxides like those of pyridine and 2,2′-bipyridine, the mono-oxidized 1,10-phenanthroline fails to undergo nitration. This rules out the possibility of a facile nucleophilic displacement of a thus introduced nitro group para to the *N*-oxide, a method we used with success for 2,2′-bipyridine 1,1′-dioxide. Nitration of plain 1,10-phenanthroline occurs in a high yield, but only at C(5).[11-13]

Activation of 1,10-phenanthroline by quaternization of the nitrogen atom by methyl iodide also results in substitution at C(2) only, as is shown by the synthesis of 2-chloro-1,10-phenanthroline by Halcrow et al.[14]

We therefore decided to use a Skraup-type synthesis of 1,10-phenanthroline with good leaving groups already present at the crucial carbon atoms in the starting materials, as is described by Snyder et al.[15] Starting from *o*-phenylenediamine and ethoxymethylenemalonic ester, 4,7-dihydroxy-1,10-phenanthroline can be prepared in four steps. The hydroxy groups that are initially positioned at the desired C(4) and C(7) atoms can be replaced by chloride substituents to afford 4,7-dichloro-1,10-phenanthroline (Cl_2-phen, **1a**).[15] Cl_2-phen (**1a**) is a convenient starting material for the preparation of other 4,7-disubstituted 1,10-phenanthroline ligands (R = MeO or Me_2N; compounds **1d,e**, Scheme 2). Similar to the substitution of the nitro functions in 4,4′-dinitro-2,2′-bipyridine 1,1′-dioxide, the chloride substituents in Cl_2-phen (**1a**) can be replaced by methoxy groups under the influence of sodium methoxide. Dimethylamino groups can be introduced by refluxing Cl_2-phen (**1a**) in DMF, as has been previously described for halogenopyridines and -quinolines as well as for 4,4′-dichloro-2,2′-bipyridine 1,1′-dioxide.[11,16] A small percentage of 4-(dimethylamino)-7-chloro-1,10-phenanthroline remains present in the reaction mixture, which has to be removed by means of column chromatography. To separate the monosubstituted from the disubstituted product, careful elution in the absence of a base like triethylamine has to be used for the first half of the column. One side effect of this procedure, however, is

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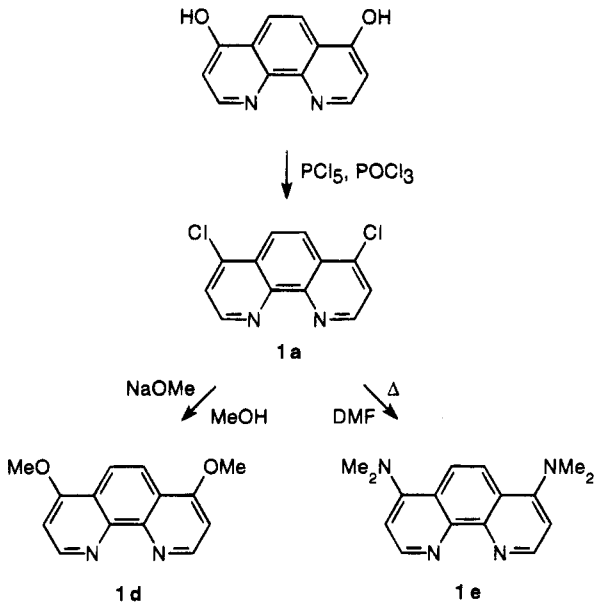
Scheme 2. Synthesis of the Substituted Phenanthroline Ligands with R = Cl, MeO, and Me_2N



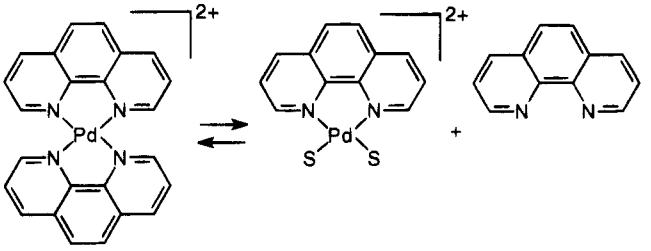
the partial protonation of the relatively alkaline $(Me_2N)_2$-phen compound (**1e**) by the slightly acidic silica gel. Therefore the product has to be dissolved in dichloromethane after purification by column chromatography and washed with an NaOH solution to obtain the fully deprotonated $(Me_2N)_2$-phen ligand (**1e**).

Synthesis of the Complexes. All phenanthroline complexes (**2a–c** and **3a–c**) had to be prepared from a tetrakis(acetonitrile) precursor $Pd(CH_3CN)_4(Y)_2$ (Y = OTf or BF_4), as the Pd(phenanthroline ligand)Cl_2 complexes were essentially insoluble for all ligands other than unsubstituted phenanthroline (**1b**). For the substituted phenanthroline ligands this insolubility ruled out the convenient route in which the formed dichloride complex is subsequently reacted with silver triflate and 1 additional equiv of the ligand.

For the tetrafluoroborate anion the tetrakis(acetonitrile) precursor could be prepared from Pd metal and nitrosyl tetrafluoroborate in acetonitrile, according to the method of Hathaway and Underhill.[17] Though very moisture-sensitive, the resulting precursor complex is stable under inert atmosphere.

For the triflate anion, however, it was not possible to perform the same reaction because nitrosyl triflate is not available. We therefore tried a similar reaction to the one Hartley et al. performed with $Pd(CH_3CN)_2Cl_2$, silver perchlorate, and dithioether ligands in acetonitrile.[18] The same procedure with Pd(benzonitrile)$_2Cl_2$, silver triflate, and phenanthroline ligands in benzonitrile failed to give the desired exchanges, while the same reaction in acetone resulted in the formation of Pd black. We were able though to prepare $Pd(CH_3CN)_4(OTf)_2$ through an exchange reaction between $Pd(CH_3CN)_2Cl_2$ and silver triflate in acetonitrile. The compound, however, remains sticky even after repeated azeotropic distillation with toluene. It is unstable as a semisolid compound under inert atmosphere. Probably partial dissociation of the acetonitrile occurs, resulting in the stickiness and eventually yielding Pd black. Only in an acetonitrile solution under inert atmosphere it is possible to store the compound at −20 °C for several days, but best results are always obtained with a freshly prepared batch of $Pd(CH_3CN)_4(OTf)_2$.

Scheme 3. Equilibrium between a Bis(phenanthroline) and a Mono(phenanthroline) Complex



The exchange reactions between the various phenanthroline ligands and the tetrakis(acetonitrile) precursors $Pd(CH_3CN)_4(Y)_2$ (Y = OTf or BF_4) proceed without difficulties. Only in the case of $Pd(phen)_2(OTf)_2$ (**2b**) does a mixture of the bis(phenanthroline) complex **2b**, a mono(phenanthroline) complex, and free phenanthroline **1b** remain in solution next to the precipitation of the desired bis(phenanthroline) complex **2b**. This might suggest an equilibrium between the bis(phenanthroline) and the mono(phenanthroline) complexes, as is depicted in Scheme 3. The dissociation of one of the phenanthroline ligands (**1b**) is probably caused by the steric hindrance between the α-hydrogens of the two ligands in the $Pd(phen)_2(OTf)_2$ complex (**2b**), which will be discussed in more detail in the next section on the X-ray structural analysis of the complex. The resulting mono(phenanthroline) complex might be slightly stabilized by weak coordination of the triflate anions, as this behavior is not found for $Pd(phen)_2(BF_4)_2$ (**3b**). Due to their perfect symmetry, BF_4 anions are better noncoordinating anions than the triflate anions, which have a slight tendency to coordinate very weakly through the oxygen atoms of the SO_3 moiety.

If hexanes were added to the crude reaction mixture of $Pd(phen)_2(OTf)_2$ (**2b**) as is done for all other complexes, the equilibrium of Scheme 3 is apparently disturbed due to the solubility of phenanthroline (**1b**) in hexanes. Various unknown complexes are formed, which results in broad signals in the ^{1}H-NMR spectrum, next to the known signals of the desired $Pd(phen)_2(OTf)_2$ (**2b**).

Broadened NMR signals are also found for $Pd(Cl_2\text{-phen})_2(OTf)_2$ (**2a**). Presumably, the same kind of equilibrium as drawn in Scheme 3 occurs for the relatively weakly coordinating Cl_2-phen ligand (**1a**) in a coordinating solvent as DMSO-d_6. Apparently coordination of the SO_3 moieties of the triflate anions is involved, as $Pd(Cl_2\text{-phen})_2(BF_4)_2$ (**3a**) only shows sharp signals. The triflate complexes of the ligands with a higher donating capacity (**1c–e**) also give sharp signals, due to the better coordinating properties of these ligands.

Molecular Structure of $Pd(phen)_2(OTf)_2$ (2b). The molecular structure of $Pd(phen)_2(OTf)_2$ (**2b**) was determined to assure that it is possible for two phenanthroline ligands (**1b**) to coordinate to one Pd center, in spite of the easy dissociation of one of the ligands that is found by ^{1}H NMR (Scheme 3). We were also inter-

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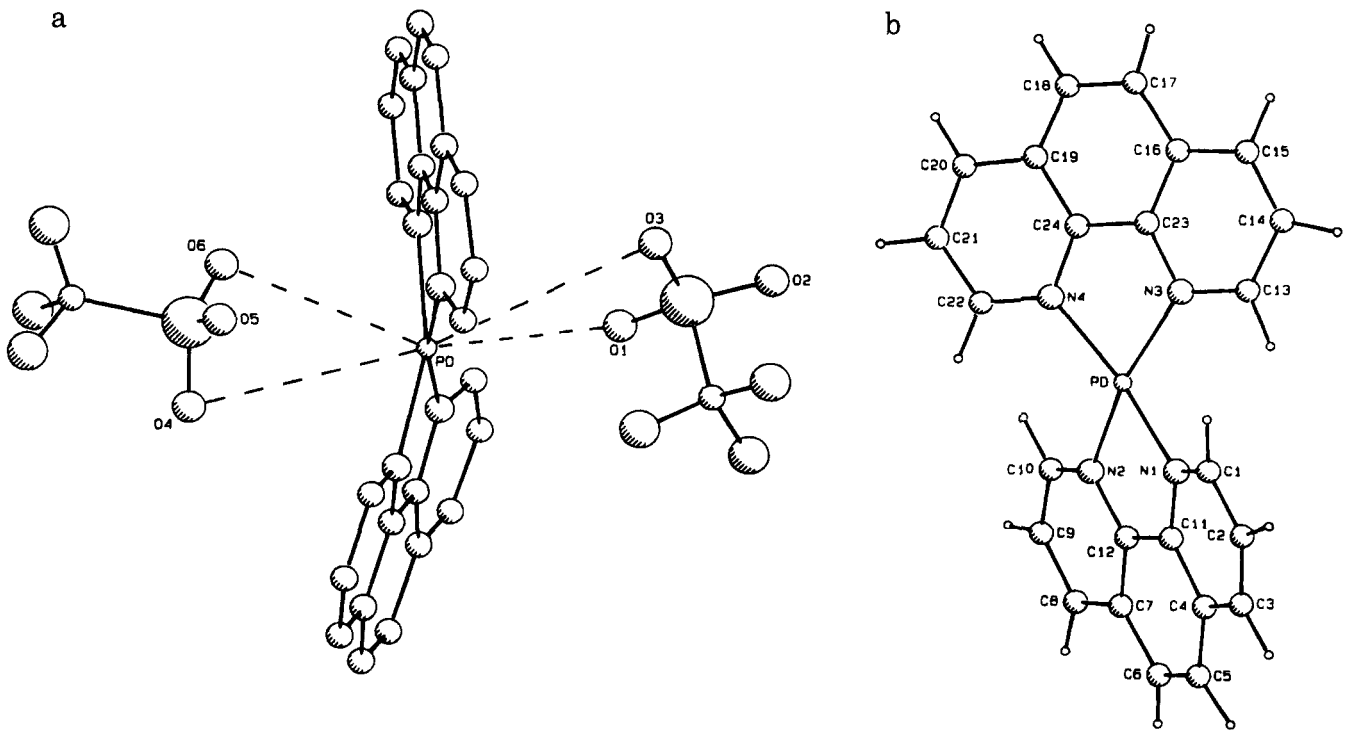

Figure 1. (a) ORTEP drawing of $Pd(phen)_2(OTf)_2$ (**2b**), showing the relative orientation of the triflate anions with respect to the $[Pd(phen)_2]^{2+}$ cation. (b) ORTEP drawing of the $Pd(phen)_2$ moiety of $Pd(phen)_2(OTf)_2$ (**2b**), depicting the applied numbering scheme.

Table 1. Bond Distances (Å) of the Non-Hydrogen Atoms of $Pd(phen)_2(OTf)_2$ (2b)[a]

Pd–N(1)	2.044 (3)	C(11)–C(12)	1.421 (4)
Pd–N(2)	2.053 (3)	C(11)–N(1)	1.372 (4)
Pd–N(3)	2.058 (3)	C(12)–N(2)	1.367 (4)
Pd–N(4)	2.042 (3)	C(13)–C(14)	1.410 (7)
S(1)–C(25)	1.809 (7)	C(13)–N(3)	1.327 (5)
S(1)–O(1)	1.425 (5)	C(14)–C(15)	1.357 (7)
S(1)–O(2)	1.435 (4)	C(15)–C(16)	1.411 (8)
S(1)–O(3)	1.437 (4)	C(16)–C(17)	1.434 (8)
S(2)–C(26)	1.79 (1)	C(16)–C(23)	1.408 (6)
S(2)–O(4)	1.417 (6)	C(17)–C(18)	1.353 (9)
S(2)–O(5)	1.380 (6)	C(18)–C(19)	1.429 (7)
S(2)–O(6)	1.369 (6)	C(19)–C(20)	1.406 (7)
C(1)–C(2)	1.404 (5)	C(19)–C(24)	1.411 (6)
C(1)–N(1)	1.332 (4)	C(20)–C(21)	1.354 (8)
C(2)–C(3)	1.377 (6)	C(21)–C(22)	1.397 (7)
C(3)–C(4)	1.400 (5)	C(22)–N(4)	1.339 (5)
C(4)–C(5)	1.439 (6)	C(23)–C(24)	1.418 (6)
C(4)–C(11)	1.400 (5)	C(23)–N(3)	1.371 (5)
C(5)–C(6)	1.364 (5)	C(24)–N(4)	1.370 (5)
C(6)–C(7)	1.431 (5)	C(25)–F(1)	1.302 (9)
C(7)–C(8)	1.416 (5)	C(25)–F(2)	1.316 (8)
C(7)–C(12)	1.408 (5)	C(25)–F(3)	1.32 (1)
C(8)–C(9)	1.363 (6)	C(26)–F(4)	1.20 (1)
C(9)–C(10)	1.043 (6)	C(26)–F(5)	1.26 (1)
C(10)–N(2)	1.328 (4)	C(26)–F(6)	1.37 (2)

[a] Esd's in parentheses.

Table 2. Bond Angles (deg) of the Non-Hydrogen Atoms of $Pd(phen)_2(OTf)_2$ (2b)[a]

N(1)–Pd–N(2)	80.7 (1)	C(15)–C(16)–C(17)	124.8 (4)
N(1)–Pd–N(3)	100.5 (1)	C(15)–C(16)–C(23)	117.0 (4)
N(1)–Pd–N(4)	168.7 (2)	C(17)–C(16)–C(23)	118.1 (5)
N(2)–Pd–N(3)	163.9 (2)	C(16)–C(17)–C(18)	121.4 (5)
N(2)–Pd–N(4)	101.1 (1)	C(17)–C(18)–C(19)	121.6 (5)
N(3)–Pd–N(4)	80.9 (1)	C(18)–C(19)–C(20)	124.6 (5)
C(25)–S(1)–O(1)	104.6 (3)	C(18)–C(19)–C(24)	117.8 (5)
C(25)–S(1)–O(2)	103.7 (3)	C(20)–C(19)–C(24)	117.5 (4)
C(25)–S(1)–O(3)	103.9 (3)	C(19)–C(20)–C(21)	119.5 (5)
O(1)–S(1)–O(2)	112.8 (2)	C(20)–C(21)–C(22)	120.3 (5)
O(1)–S(1)–O(3)	113.5 (3)	C(21)–C(22)–N(4)	122.2 (4)
O(2)–S(1)–O(3)	116.7 (3)	C(16)–C(23)–C(24)	120.3 (4)
C(26)–S(2)–O(4)	103.8 (5)	C(16)–C(23)–N(3)	122.8 (4)
C(26)–S(2)–O(5)	103.6 (5)	C(24)–C(23)–N(3)	117.0 (3)
C(26)–S(2)–O(6)	104.8 (5)	C(19)–C(24)–C(23)	120.7 (4)
O(4)–S(2)–O(5)	110.7 (4)	C(19)–C(24)–N(4)	122.3 (4)
O(4)–S(2)–O(6)	114.1 (4)	C(23)–C(24)–N(4)	117.0 (3)
O(5)–S(2)–O(6)	118.0 (5)	S(1)–C(25)–F(1)	112.3 (7)
C(2)–C(1)–N(1)	122.2 (3)	S(1)–C(25)–F(2)	111.8 (4)
C(1)–C(2)–C(3)	119.5 (3)	S(1)–C(25)–F(3)	110.9 (5)
C(2)–C(3)–C(4)	119.2 (3)	F(1)–C(25)–F(2)	107.7 (6)
C(3)–C(4)–C(5)	123.7 (3)	F(1)–C(25)–F(3)	107.5 (6)
C(3)–C(4)–C(11)	118.1 (3)	F(2)–C(25)–F(3)	106.4 (8)
C(5)–C(4)–C(11)	118.2 (3)	S(2)–C(26)–F(4)	119.3 (9)
C(4)–C(5)–C(6)	120.8 (4)	S(2)–C(26)–F(5)	114 (1)
C(5)–C(6)–C(7)	121.1 (4)	S(2)–C(26)–F(6)	107.3 (8)
C(6)–C(7)–C(8)	123.8 (3)	F(4)–C(26)–F(5)	116 (1)
C(6)–C(7)–C(12)	119.1 (3)	F(4)–C(26)–F(6)	96 (1)
C(8)–C(7)–C(12)	117.0 (3)	F(5)–C(26)–F(6)	99 (1)
C(7)–C(8)–C(9)	118.8 (4)	Pd–N(1)–C(1)	128.5 (3)
C(8)–C(9)–C(10)	120.7 (3)	Pd–N(1)–C(11)	113.0 (2)
C(9)–C(10)–N(2)	122.3 (4)	C(1)–N(1)–C(11)	118.3 (3)
C(4)–C(11)–C(12)	121.3 (3)	Pd–N(2)–C(10)	129.4 (3)
C(4)–C(11)–N(1)	122.3 (3)	Pd–N(2)–C(12)	112.3 (2)
C(12)–C(11)–N(1)	116.3 (3)	C(10)–N(2)–C(12)	117.6 (3)
C(7)–C(12)–C(11)	119.3 (3)	Pd–N(3)–C(13)	129.2 (3)
C(7)–C(12)–N(2)	123.5 (3)	Pd–N(3)–C(23)	112.2 (2)
C(11)–C(12)–N(2)	117.2 (3)	C(13)–N(3)–C(23)	118.2 (3)
C(14)–C(13)–N(3)	122.2 (4)	Pd–N(4)–C(22)	128.9 (3)
C(13)–C(14)–C(15)	119.9 (5)	Pd–N(4)–C(24)	112.8 (3)
C(14)–C(15)–C(16)	119.8 (4)	C(22)–N(4)–C(24)	117.9 (4)

[a] Esd's in parentheses.

ested in the distances between the Pd center and the triflate anions, to see whether slight stabilization of the Pd cation by its anions would be plausible.

Two views of the molecular structure of $Pd(phen)_2(OTf)_2$ (**2b**) are shown in Figure 1a,b. In Figure 1a the hydrogen atoms are omitted for the sake of clarity, but the relative orientation of the triflate anions is shown. In Figure 1b the numbering scheme of the $Pd(phen)_2$ moiety is depicted. The bond distances of the non-hydrogen atoms are listed in Table 1, whereas the bond angles of these atoms are given in Table 2.

Both phenanthroline units turned out to be similarly coordinated to the Pd center, with a mean Pd–N value

of 2.049 Å. This value is in good agreement with the mean Pd–N distance in the $Pd(phen)_2(ClO_4)_2$ complex determined by Rund (2.051 Å)[19] and somewhat longer than the distance we found in the analogous $Pd(bpy)_2(OTf)_2$ complex (2.036 Å).[11] In contrast to these complexes, there appears to be a weak interaction between the Pd center and the anions in our $Pd(phen)_2(OTf)_2$ complex (**2b**). Both triflate anions are oriented with their oxygen atoms toward the Pd center, and the shortest Pd–O distance is only 2.922 Å. Weak interactions between the Pd center and a nitrate anion in $Pd(bpy)_2(NO_3)_2{\cdot}2H_2O$ were reported with a Pd–O distance of 3.089 Å.[20] Therefore we concluded that this is also the case in the $Pd(phen)_2(OTf)_2$ complex (**2b**).

Mestroni et al. did not find any interaction between the highly symmetrical PF_6 anions and the Pd center in a $Pd(phen)_2(PF_6)_2$ complex.[21] This might suggest that the highly delocalized PF_6 and BF_4 anions are actually better noncoordinating anions than the triflate and nitrate anions, as was also implicated by our NMR studies. The $Pd(phen)_2(PF_6)_2$ complex by Mestroni also shows a different conformation of the $Pd(phen)_2$ cation itself. In this compound the steric repulsion between the α-hydrogen atoms (H_2 and H_9) of the separate phenanthroline ligands is alleviated by a so-called "bow–step" conformation in which both ligands are slightly bowed, resulting in nonplanar structures of the ligands, while one of the ligands is lifted above the coordination plane and the other one is situated beneath this plane. The out of plane bending within one ligand is expressed in the angle that is found between the two equivalent parts of the ligand. In the $Pd(phen)_2(PF_6)_2$ complex a value of 13.4° is found for this angle,[21] which is much larger than the angles found in our $Pd(phen)_2(OTf)_2$ complex (**2b**) (5.3° and 3.7° for both phenanthroline ligands, respectively).

In the $Pd(phen)_2(OTf)_2$ complex (**2b**), however, the steric crowding is relieved by a completely different, twist conformation. In this conformation a tetrahedral distortion of the square-planar PdN_4 skeleton occurs, resulting in one coordinating nitrogen atom above the coordination plane and one beneath it for each phenanthroline ligand (**1b**). This way a torsion angle between the two ligands is obtained, which amounts to 28.2° for $Pd(phen)_2(OTf)_2$ (**2b**). The same conformation has already been found for $Pd(phen)_2(ClO_4)_2$,[19] $Pd(bpy)_2(OTf)_2$,[11] and $Pd(bpy)_2(NO_3)_2{\cdot}2H_2O$[20] with torsion angles of 22.5, 24.3, and 33.2°, respectively.

The relatively large torsion angle in $Pd(phen)_2(OTf)_2$ (**2b**) compared to the torsion angle in the closely related $Pd(phen)_2(ClO_4)_2$ system might be caused by the fact that the phenanthroline ligands are less bent in the triflate complex. Although the exact angles between the chemically equivalent parts of the phenanthroline ligands in the $Pd(phen)_2(ClO_4)_2$ complex are not given in ref 19, it can be deduced from the listed deviations of the ligand atoms from the plane through the cation that these angles in this complex are larger than the ones we have measured. As a result, less twisting of the ligands is needed to get to the same relief of steric hindrance.

From a comparison of the torsion angles and the Pd–N distances in $Pd(phen)_2(ClO_4)_2$ and $Pd(bpy)_2(NO_3)_2{\cdot}2H_2O$, it was concluded that a larger torsion angle leads to a decrease of the Pd–N distance.[19] This view should be corrected, however, if the $Pd(phen)_2(OTf)_2$ complex (**2b**) is taken into account. Though this complex shows a larger torsion angle than the $Pd(phen)_2(ClO_4)_2$ complex, there is no significant difference in Pd–N distances. This trend can also be found if $Pd(bpy)_2(NO_3)_2{\cdot}2H_2O$ is compared with $Pd(bpy)_2(OTf)_2$.[11,19] Apparently, it is the difference in flexibility and donating capacity between the bipyridine and the phenanthroline ligands that causes the differences in Pd–N distances, instead of the different torsion angles.

Altogether, the molecular structure of $Pd(phen)_2(OTf)_2$ (**2b**) has made it clear that there are actually two phenanthroline ligands (**1b**) coordinated to the Pd metal, but dissociation of one of these ligands is easily achieved due to the steric overcrowding in the complex. This property could be of importance for the catalytic activity of the complex, as it most probably has to lose one ligand before it can act as a catalyst.

Table 3. Reduction Potentials of Some Pd(bidentate ligand)$_2$(Y)$_2$ Complexes and of the Corresponding Free Ligands[a]

compd	$E_{p,c}$ (V)[b]
BIAN	−1.82
bpy	−2.60
phen	−2.55
$Pd(BIAN)_2(BF_4)_2$	−0.96
$Pd(bpy)_2(OTf)_2$	−1.31
$Pd(Cl_2\text{-phen})_2(OTf)_2$ (**2a**)	−1.17
$Pd(phen)_2(OTf)_2$ (**2b**)	−1.22
$Pd(Me_2\text{-phen})_2(OTf)_2$ (**2c**)	−1.27
$Pd((MeO)_2\text{-phen})_2(OTf)_2$ (**2d**)	−1.30
$Pd(phen)_2(BF4)_2$ (**3b**)	−1.22
$Pd(Me_2\text{-phen})_2(BF_4)_2$ (**3c**)	−1.25

[a] See Cyclic voltammetry in the Experimental Section for the precise conditions. [b] $E_{p,c}$ (V) vs $E_{1/2}$ of Fc/Fc^+.[23]

Cyclic Voltammetry. Cyclic voltammograms of the $Pd(R_2\text{-phen})(Y)_2$ complexes (R = Cl, H, Me, or MeO and Y = OTf or BF_4) were recorded in DMSO in order to study the influence of the 4,7-disubstituted 1,10-phenanthroline ligands on the Pd^{II}/Pd^0 redox couple, which could play a crucial role in the catalytic reductive carbonylation of aromatic nitro compounds.

In addition, two other Pd(bidentate ligand)$_2$(Y)$_2$ complexes were measured in the cyclic voltammetric study as reference compounds. In these reference complexes the bidentate ligands were either the α-diimine ligand bis(*p*-anisylimino)acenaphthene (BIAN)[22] or 2,2′-bipyridine. The electrode potentials, presented in Table 3, were measured against the standard Fc/Fc^+ couple.[23]

The reductions of all complexes under study were found at significantly more positive potentials with respect to those of the corresponding free ligands (Table 3). The difference between the reduction potentials of the free ligands was found to be much larger than the difference between the $E_{p,c}$ values of the complexes of the corresponding ligands. For all complexes the reduction was chemically totally irreversible, as was evidenced by complete absence of the anodic counterpeaks. At the same time no new anodic peaks, which might belong to reoxidation of some secondary reduction

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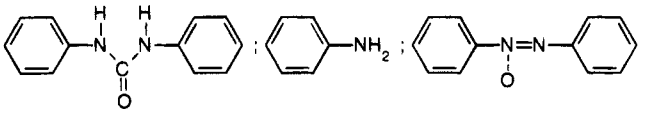
products, were observed on the reversed scans. If an excess of free ligand is added, resulting in the same ligand:Pd ratio as is used in the catalysis, the system becomes chemically slightly more reversible. This implies that the chemical irreversibility of the reduction is caused by dissociation of the phenanthroline ligands from the reduced Pd^0 species, which can be suppressed by the presence of an excess of ligand. All measurements on the complexes were strongly disturbed by sorption at the working electrode, which had to be polished with a 1 μm diamond paste before each repeated scan. This sorption might indicate the formation of Pd metal. The overall behavior of the Pd complexes resembles the reduction of some [Cu(bidentate ligand)$_2$]$^+$ complexes (bidentate ligand = phen or bpy), which also occured at relatively positive potentials and was only poorly reversible, ultimately leading to metallic copper.[24]

From the results it can be concluded that the irreversible reduction of the Pd(bidentate ligand)$_2^{2+}$ species is predominantly localized on the Pd^{II} center rather than on the lowest π^* orbital of the bidentate ligands. In the case of a ligand-localized reduction the difference between the reduction potentials of Pd(BIAN)$_2$(BF$_4$)$_2$ and those of the phenanthroline complexes would have been expected to be roughly as large as for the free ligands, as was also observed for Re(CO)$_3$Cl(bidentate ligand) and PtPh$_2$(bidentate ligand) complexes containing 2,2′-bipyridine or 4,4′-bipyrimidine.[25,26]

Although the reduction is mainly localized on the metal center, an influence of the ligand is apparent, as can best be seen from the series of Pd(R$_2$-phen)$_2$(Y)$_2$ complexes. The results reveal that the reduction of the Pd(R$_2$-phen)$_2$(Y)$_2$ complexes becomes more negatively shifted in the order Cl$_2$-phen < H$_2$-phen < Me$_2$-phen < (MeO)$_2$-phen, i.e., with an increasing donating capacity of the R$_2$-phen ligand. Cl$_2$-phen (**1a**) is apparently the weakest σ-donor ligand in the series, and the Pd(Cl$_2$-phen)$_2^{2+}$ species is consequently most easily reduced. For the catalysis this might imply that the conversion of nitrobenzene is readily initiated under the influence of a Cl$_2$-phen ligand (**1a**). In contrast to the chemical irreversibility of the reduction observed in the cyclic voltammetric study, it is expected that, during the reductive carbonylation, the reduced Pd species are stabilized to some extent by the aromatic nitro substrate and CO, though this effect could not be found by cyclic voltammetric measurements on a CO-saturated solution and in the presence of a 5-fold excess of nitrobenzene. However, the high concentration of nitrobenzene and the high pressure of CO that are used in the catalysis cannot be mimicked in the cyclic voltammetric study. Under these more stabilizing conditions the reduced Pd^0/Cl$_2$-phen species is expected to be the relatively most stable species in the series of Pd(R$_2$-phen)$_2^{2+}$ complexes, as Cl$_2$-phen (**1a**) is apparently the weakest σ-donor ligand. This relatively high stability of the reduced Pd complex might well account for the low overall activity for the Cl$_2$-phen systems, as was also found for the Cl$_2$-bpy ligand.[11] Eventually, decomposition of the reduced Pd/Cl$_2$-phen catalyst system into Pd black will occur.

Chart 1. Side Products in the Reductive Carbonylation of Nitrobenzene by a Pd/R$_2$-phen Catalyst System



N,N′-diphenyl urea aniline azoxybenzene

Catalysis. With the 4,7-disubstituted 1,10-phenanthroline ligands (**1a–e**) two different types of catalytic systems have been used to study the influence of the ligand as well as the anions on the catalytic activity and selectivity in the reductive carbonylation of aromatic nitro compounds: (type I) the catalyst is generated in situ from Pd(acetate)$_2$, 6 equiv of one of the ligands, and 3 equiv of *p*-toluenesulfonic acid as cocatalyst; (type 2) a presynthesized complex Pd(ligand)$_2$(Y)$_2$ (Y = OTf or BF$_4$) is used in combination with 4 equiv of free ligand.

All reactions have been performed in methanol with nitrobenzene as a model substrate, resulting in methyl *N*-phenylcarbamate as the main product in all cases. The side products consisted mainly of *N,N′*-diphenylurea, next to some aniline and a small but significant amount of azoxybenzene (Chart 1). In comparable experiments with 4,4′-disubstituted 2,2′-bipyridyl ligands the urea derivative was mostly found to be the only important side product along with traces of aniline. No azoxybenzene was detected with these systems, and the selectivity could be very well expressed in the carbamate:urea ratio.[11] For the phenanthroline systems, however, the selectivity is given by a product distribution to show the amounts of urea derivative, aniline, and azoxybenzene relative to the amount of desired carbamate. Roughly speaking, we found that the selectivity toward the carbamate is reduced from 90%–95% with the bipyridyl systems[11] to 80%–85% under the influence of the phenanthroline ligands (**1a–e**).

Azoxybenzene has been reported before as an important product in the reductive carbonylation of nitrobenzene, especially with supported Pd on carbon or Al$_2$O$_3$ systems in the presence of a phenanthroline ligand. Addition of 2,4,6-trimethylbenzoic acid has proven to reduce the amount of azoxybenzene in favor of the carbamate or isocyanate.[27,28] Bontempi et al. also found azoxybenzene as main product with their [Pd(3,4,7,8-tetramethyl-1,10-phenanthroline)$_2$][BPh$_4$]$_2$ catalyst complex. They claim a chelated Pd^0 carbonyl intermediate species to be responsible for the formation of azoxybenzene, as the same result could be obtained using a Pd^0 complex as catalyst precursor.[9]

In contrast to the bipyridine systems,[11] only the experiments with Cl$_2$-phen (**1a**) yield a significant amount of Pd black at the end of the catalytic runs. Apparently the better coordinating properties of the phenanthroline ligands induce a higher degree of stabilization of catalytic intermediates, which is also expressed in a higher overall activity of the phenanthroline systems. If the phenanthroline ligands (**1a–e**) are applied under the same conditions as were used

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Table 4. Results of the Reductive Carbonylation of Nitrobenzene in Methanol with Pd(acetate)$_2$/Ligand (1a–e)/*p*-tsa[a]

ligand	tof (mol/(mol/h))	product distribution (%)[b] CA	UR	AN	AZOX
Cl_2-phen (**1a**)	26	0.0	0.0	85.7	14.3
H_2-phen (**1b**)	207	85.4	11.3	0.6	2.8
Me_2-phen (**1c**)	255	84.7	10.7	1.1	3.4
$(MeO)_2$-phen (**1d**)	249	82.6	10.8	0.0	6.3
$(Me_2N)_2$-phen (**1e**)	105	80.2	5.9	0.0	13.9

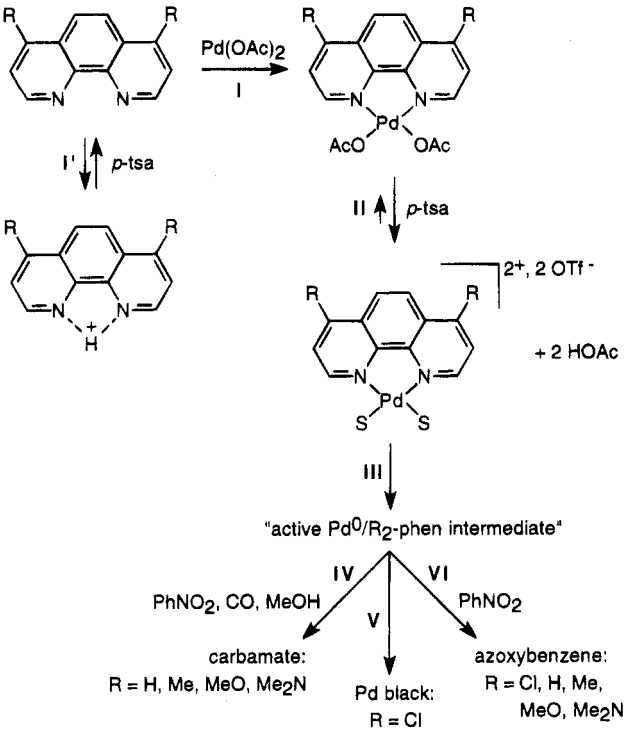
[a] See Experimental Section for the precise conditions. [b] CA = methyl *N*-phenylcarbamate; UR = *N,N'*-diphenylurea; AN = aniline; AZOX = azoxybenzene.

for the bipyridine ligands, complete conversion of the substrate is reached within the 2 h of standard reaction time. To enable a comparison among the various phenanthroline ligands (**1a–e**) the concentration of Pd and the ligand:Pd ratio had to be reduced with respect to the bipyridine experiments.[11] Due to the higher stability of the phenanthroline catalyst systems, the reproducibility of the catalytic results was strongly improved, allowing us to confine to measurements in duplicate.

Pd(acetate)$_2$, a Phenanthroline Ligand, and *p*-Toluenesulfonic Acid. In the catalytic runs of type I, with the in situ generated catalyst, the reaction conditions have deliberately been tuned to yield a conversion into carbamate of approximately 50% with H_2-phen (**1b**) as the reference. As this required a ligand: Pd ratio of only 6 at a total Pd concentration of 0.002 M, the *p*-tsa:Pd ratio also had to be kept low (3) to maintain an excess of ligand with respect to the acid. The results of the in situ generated catalyst systems are listed in Table 4.

Even under the adjusted experimental conditions the phenanthroline systems are about twice as active as their corresponding bipyridine systems.[11] Throughout this work we use the average turnover frequencies (tof) to compare the activities of the catalysts. This is a reasonable method for these catalysts since the reactions are approximately 0 order in substrate concentration. The rate of conversion is constant unless the catalyst decomposes. The turnover frequencies obtained with H_2-bpy and Me_2-bpy (118 and 140 mol/(mol/h), respectively) are increased by a factor 1.8 if the ligands are replaced by their phenanthroline analogues H_2-phen (**1b**) and Me_2-phen (**1c**), while $(MeO)_2$-phen (**1d**) is even 2.3 times as active as $(MeO)_2$-bpy with a tof of 109 mol/(mol/h). This higher activity for the phenanthroline systems is most probably caused by the rigidity of these ligands. The differences between the phenanthroline and the bipyridine systems are less than the factor 5 observed by Mestroni et al. for the difference between Pd(1,10-phenanthroline)$_2$(PF$_6$)$_2$ and Pd(2,2'-bipyridine)$_2$(PF$_6$)$_2$.[9] It should be pointed out, however, that Mestroni's experiments were carried out under completely different reaction conditions, resulting in far lower overall activities (tof = 90 and 18 mol/(mol/h), respectively). Furthermore, these experiments started with presynthesized catalyst complexes, thus omitting the acidic cocatalyst. As phenanthroline is a stronger base than bipyridine (pK_b - values of 9.2 [12] and 9.7,[29] respectively) the activity of the phenanthroline systems is probably more influenced by the competition between Pd^{2+} and H^+ for the ligand.

Scheme 4. Catalysis with the in Situ Generated Systems from Pd(acetate)$_2$, R$_2$-phen, and *p*-tsa



The variations among the R_2-phen systems with R = H, Me, or MeO are smaller than in the case of the R_2-bpy systems. The highest activity is found for Me_2-phen (**1c**) (tof = 255 mol/(mol/h)), which might indicate that this ligand has the optimum donating capacity for the palladium-catalyzed reductive carbonylation of nitrobenzene. However, the influence of the amount of acid present in the reaction mixture in correlation with the basicity of the particular ligand has not been taken into account in this study. Yet this basicity will be decisive for the competition between reaction step I and the undesired side reaction step I' in Scheme 4. Previous results with the substituted bipyridine systems have shown that at least 2 equiv of *p*-tsa to Pd are required in order to replace the coordinating acetate anions with noncoordinating tosylate anions.[11] Because the phenanthroline ligands are applied in a 6-fold excess to palladium and an overall excess of ligand to acid is needed, only little variation of the amount of acid in the reaction mixture is possible. Still, the *p*-tsa:Pd ratio of 3 that is used could be most appropriate for Me_2-phen (**1c**).

For $(Me_2N)_2$-phen (**1e**) a sharp decrease in the catalytic activity was observed. Though this could be caused by the high donating capacity of this ligand it is more likely to be a result of partial protonation of the amino function by the acidic cocatalyst. In view of the ready protonation of part of the ligand by slightly acidic silica gel, as was observed in the ^{1}H-NMR spectrum after column chromatography with the ligand, a strong acid as *p*-tsa should certainly be able to protonate the amino function. That way this highly electron-donating substituent is transformed into a strongly electron-withdrawing group.

From the results with Cl_2-phen (**1a**) it is obvious that such electron-withdrawing substituents have a severe negative effect on the catalytic activity. Under the

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Table 5. Results of the Reductive Carbonylation of Nitrobenzene in Methanol with $Pd(R_2\text{-phen})_2(OTf)_2$ (2a–e)/Ligand (1a–e)[a]

ligand	tof (mol/(mol/h))	product distribution (%)[b] CA	UR	AN	AZOX
Cl_2-phen (**1a**)	11	0.0	0.0	100	0.0
H_2-phen (**1b**)	234	83.5	7.2	2.5	6.9
Me_2-phen (**1c**)	311	83.9	9.9	2.6	3.6
$(MeO)_2$-phen (**1d**)	179	82.5	8.1	0.0	9.3
$(Me_2N)_2$-phen (**1e**)	95	67.8	5.7	8.0	18.3

[a] See Experimental Section for the precise conditions. [b] CA = methyl *N*-phenylcarbamate; UR = *N,N'*-diphenylurea; AN = aniline; AZOX = azoxybenzene.

Table 6. Resuls of the Reductive Carbonylation of Nitrobenzene in Methanol with $Pd(R_2\text{-phen})_2(BF_4)_2$ (3a–e)/Ligand (1a–e)[a]

ligand	tof (mol/(mol/h))	product distribution (%)[b] CA	UR	AN	AZOX
Cl_2-phen (**1a**)	37	0.0	0.0	91.1	8.8
H_2-phen (**1b**)	247	86.7	8.3	1.2	3.8
Me_2-phen (**1c**)	271	85.7	9.2	1.2	3.9
$(MeO)_2$-phen (**1d**)	255	80.4	10.6	1.7	7.3
$(Me_2N)_2$-phen (**1e**)	207	79.1	8.3	0.0	12.5

[a] See Experimental Section for the precise conditions. [b] CA = methyl *N*-phenylcarbamate; UR = *N,N'*-diphenylurea; AN = aniline; AZOX = azoxybenzene.

influence of the chloride substituents only small amounts of aniline and azoxybenzene could be measured at the end of the catalytic runs. No conversion into carbamate at all was detected, but a large amount of Pd black was found. The overall turnover frequency therefore amounted to only 26 mol of nitrobenzene converted per mol of Pd catalyst per hour. As little aniline and azoxybenzene are formed it appears that a start has been made with the conversion of nitrobenzene, but the catalyst decomposes in some intermediate stage before the carbamate can be formed. In spite of the good coordinating properties of the rigid phenanthroline skeleton, the Cl_2-phen ligand (**1a**) still seems not donating enough to fully stabilize the catalytic intermediates. An intermediate Pd^0/Cl_2-phen system, which is readily formed as is shown by the cyclic voltammetric study, might be able, however, to cause the formation of azoxybenzene as was described by Bontempi et al.[9] before it decomposes into Pd metal (reaction steps I–III, V, and VI in Scheme 4).

In contrast to Cl_2-phen (**1a**), the $(Me_2N)_2$-phen (**1e**) system does not result in a large amount of Pd black at the end of the catalytic runs. Apparently, the equilibrium between the normal $(Me_2N)_2$-phen ligand (**1e**) and its protonated form is sufficient to prevent large-scale decomposition of the catalytic intermediates but does cause the decrease in catalytic activity.

The effect of the donating capacity of the active ligands on the selectivity of the catalyst toward carbamate turned out to be almost negligible. Only a very slight increase could be found in the sequence $(Me_2N)_2$-phen (**1e**) (selectivity toward carbamate, 80.2%) < $(MeO)_2$-phen (**1d**) (82.9%) < Me_2-phen (**1c**) (84.7%) < H_2-phen (**1b**) (85.4%).

Presynthesized Complexes $Pd(ligand)_2(Y)_2$, with Y = OTf or BF_4. Catalytic runs of type II with the presynthesized complexes have the advantage that no more *p*-tsa has to be added, as the complexes already contain noncoordinating anions. Results of the triflate complexes are collected in Table 5, while Table 6 gives the results obtained with the analogous tetrafluoroborate complexes.

Though the presynthesized complexes are generally more active than the corresponding in situ systems, the differences are smaller than those observed before for the bipyridine systems.[11] Therefore the experimental conditions need not be changed for the phenanthroline complexes with respect to the catalytic runs with the in situ systems, thus allowing a better comparison between the activities and selectivities of the two types of systems. The relatively small difference between the presynthesized complexes and the in situ systems for the phenanthroline ligands compared to the bipyridine case is probably caused by the better coordinating properties of the phenanthroline ligands. This results in an easier formation of the active complex from Pd(acetate)$_2$, the ligand, and *p*-tsa (reaction steps I–III in Scheme 4).

Under the milder conditions the presynthesized phenanthroline complexes are still far more active than the bipyridine analogues. The smallest increase is found for the $(Me_2N)_2$-phen ligand (**1e**) which is only 1.5 times more active than its bipyridine analogue. However, with Me_2-phen (**1c**) an increase by a factor of 4.6 is obtained, nearly resembling the enhancement found by Mestroni et al. for $Pd(ligand)_2(PF_6)_2$ (ligand = H_2-phen and H_2-bpy) under more favorable reaction conditions.[9]

From the turnover frequencies listed in the Tables 5 and 6 it becomes clear that the differences in activity between the various phenanthroline ligands are larger for the presynthesized complexes than for the in situ systems, which might be caused by the better defined starting systems. Within the triflate series the internal differences are even larger than within the series of BF_4 complexes. This might have to do with the very weak coordination of the triflate anions compared to the absolutely noncoordinating BF_4 anions. As one of the ligands presumably has to dissociate to create two vacant coordination sites for the catalysis, stabilization of the coordinatively unsaturated intermediate by a weak interaction with the triflate anions might have a positive effect in the case of the mildly donating phenanthroline ligands. For the ligands with a high donating capacity, on the other hand, vacant coordination sites are less readily available, and weak interaction with the anions would only reduce this availability even more (equilibrium of Scheme 3 in which S can be either an OTf anion or a solvent molecule in the case of the BF_4 complexes).

This complete picture of the donating capacity of the ligand and the degree of coordination of the anion results in the subtle balance that can be found between the ligand used and the particular noncoordinating anion that is needed to obtain the optimum activity. For instance, for Me_2-phen (**1c**) best results are clearly obtained with the weakly coordinating triflate anions, while for $(MeO)_2$-phen (**1d**) the tetrafluoroborate anions are the best choice.

For Cl_2-phen (**1a**) again hardly any activity is observed, neither with the OTf anions nor with the BF_4 anions. No conversion into carbamate is found. Only traces of aniline and azoxybenzene can be detected, next to a large amount of Pd black. Although the Cl_2-phen

ligand (**1a**) is coordinated to Pd at the beginning of the catalytic run, it is obviously not capable of stabilizing the intermediate Pd species, as was also found for the in situ generated systems.

All other phenanthroline ligands yield very stable catalyst systems, as was already observed with the in situ experiments of type I. For the presynthesized complexes the optimum activity is found at Me_2-phen (**1c**) for both types of anion. As this was also the case with the in situ systems, it might suggest that Me_2-phen actually has the optimum donating capacity for this process, independent of the anion or the presence of an acidic cocatalyst.

Of the active ligands $(Me_2N)_2$-phen (**1e**) always gives the lowest turnover frequency. As the acidic cocatalyst could be left out in the catalytic runs of type II, the amino function has to be present as a strongly electron-donating group in the presynthesized complexes. This means that under the influence of this substituent the electron density at the Pd center might be too high at some stage in the catalytic cycle. The inhibiting step, however, could also be the first dissociation of one of the ligands, which is hampered by the strong coordination of this $(Me_2N)_2$-phen ligand (**1e**).

The selectivity toward the carbamate appears to be rather unaffected by the system used. For the active ligands (**1b–e**) roughly the same selectivity is reached with the in situ generated systems and with both types of presynthesized complexes. For the $Pd((Me_2N)_2\text{-phen})_2(Y)_2$ complexes (**2e** and **3e**) a relatively low selectivity toward the carbamate is obtained, especially in the case of the triflate complex (**2e**). Because of the slow reactions with these catalysts a relatively high concentration of nitrene and nitroso intermediates might be present, resulting in an easy formation of azoxybenzene and reduction of the selectivity toward the carbamate.

Conclusions

Phenanthroline ligands with moderately donating substituents (H, Me, or MeO) yield stable and active palladium catalyst systems for the reductive carbonylation of nitrobenzene. A subtle balance has been found between the ligand used and the particular noncoordinating anion for the optimum activity. The best catalyst among these systems consists of $Pd(Me_2\text{-phen})_2(OTf)_2$ (**2c**).

Electron-withdrawing substituents like chloride on the phenanthroline ligand completely deactivate the catalyst, in spite of the good coordinating properties of the rigid phenanthroline skeleton.

Experimental Section

Materials and Analyses. $PdCl_2$ and $Pd(acetate)_2$ were purchased from Degussa and used as received. All other chemicals were purchased from Aldrich or Janssen.

The solvents were purified prior to use. Acetone was distilled from anhydrous K_2CO_3; methanol, dichloromethane, DMF, DMSO, and acetonitrile from CaH_2 (5 g/L); chloroform from $CaCl_2$; hexanes from sodium/benzoylbiphenyl; and toluene from sodium/benzophenone.

4,7-Dichloro-1,10-phenanthroline was synthesized as described in literature.[15,30] The 4,7-disubstituted 1,10-phenanthroline ligands with R = methoxy and dimethylamino were prepared according to a modified literature procedure.[11,16]

$Pd(acetonitrile)_2Cl_2$ was prepared analogously to $Pd(benzonitrile)_2Cl_2$ in refluxing acetonitrile according to a literature procedure.[31] $Pd(acetonitrile)_4(BF_4)_2$ was prepared as described in literature.[17]

Column chromatography was performed using silica gel (Kieselgel 60, 70–230 mesh ASTM, purchased from Merck) as the stationary phase.

Infrared (IR) spectra were recorded on a Nicolet 510m FT-IR spectrophotometer. ^{1}H-NMR spectra were obtained on a Bruker AMX 300 instrument. Chemical shifts are given in ppm. TMS was used as reference with $CDCl_3$ as internal standard. Mass spectral data were recorded on a JEOL JMS SX/SX 102A four-sector mass spectrometer equipped with a JEOL MSMP7000 data system, using a nitrobenzyl alcohol matrix solution. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were carried out by the Department of Micro Analysis, University of Groningen. Cyclic voltammetry measurements were performed with a PA4 (EKOM, Czech Republic) potentiostat in a vacuum-tight cyclic voltammetric cell, equipped with a Pt-disk electrode of 0.38 mm^2 apparent surface area, a Pt-gauze auxiliary electrode, and an Ag-wire as a pseudoreference electrode.

The reductive carbonylation of nitrobenzene was performed in a stainless steel (SS 316) 50 mL autoclave equipped with a glass liner, a gas inlet, a thermocouple, and a magnetic stirrer. CO 3.0 was purchased from Praxair and used as purchased. The results were analyzed by HPLC on a Gilson HPLC apparatus, using a Dynamax C18 column (eluent gradient: 45% water in methanol to 100% methanol in 20 minutes).

Syntheses. 4,7-Dimethoxy-1,10-phenanthroline ((MeO)$_2$-phen) (1d). To a freshly prepared solution of sodium methoxide (11 mmol) in 40 mL of methanol was added 250 mg of 4,7-dichloro-1,10-phenanthroline (Cl_2-phen) (**1a**) (2.38 mmol). The reaction mixture was refluxed for 24 h, after which time it was concentrated under vacuum to approximately 15 mL. A 20 mL amount of ice water was added, resulting in the formation of a yellow precipitate. The suspension was stored overnight at +4 °C to assure complete precipitation of the product. The precipitate was filtered off, washed with 3 × 15 mL of water, and dried under vacuum. Yield: 502 mg of brown powder (2.09 mmol, 88%). IR (KBr): 1225 (s, C–O), 1028 (vs, C–O) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.89 (d, 2H, $H_2 + H_9$), 8.16 (s, 2H, $H_5 + H_6$), 7.25 (d, 2H, $H_3 + H_8$), 4.12 (s, 6H, OCH_3) ppm. Mp: 207–208 °C.

4,7-Bis(dimethylamino)-1,10-phenanthroline (1e). A suspension of 0.5 g of Cl_2-phen (**1a**) (2.0 mmol) in 15 mL of DMF was refluxed under N_2 for 22 h. After the solvent was evaporated, the orange powder was treated with a mixture of 20 mL of 1 M NaOH and 25 mL of THF. The water layer was washed with 3 × 25 mL of THF. The combined THF fractions were dried over Na_2SO_4, and the solvent was evaporated. The crude product was purified by column chromatography, using 16% methanol in dichloromethane followed by 1% triethylamine and 16% methanol in dichloromethane as eluent. The product was dissolved in 16 mL of dichloromethane and washed with 2 × 10 mL of 1 M NaOH. The water layers were re-extracted with 2 × 15 mL of dichloromethane. The combined organic fractions were dried over Na_2SO_4, and the solvent was evaporated. Yield: 278 mg of beige powder (1.04 mmol, 52%). IR (KBr): 998 (m, C–N) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.88 (d, 2H, $H_2 + H_9$), 7.95 (s, 2H, $H_5 + H_6$), 6.98 (d, 2H, $H_3 + H_8$), 3.05 (s, 12H, $N(CH_3)_2$) ppm. Mp: 143–145 °C.

Pd(Cl$_2$-phen)$_2$(OTf)$_2$ (2a). $Pd(Cl_2\text{-phen})_2(OTf)_2$ (**2a**) was prepared from freshly synthesized $Pd(CH_3CN)_4(OTf)_2$. A 98 mg amount of $Pd(CH_3CN)_2Cl_2$ (0.38 mmol) was dissolved under Ar in 15 mL of acetonitrile, and 194 mg of silver triflate (0.76

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mmol) was dissolved in 5 mL of acetonitrile under Ar in the dark. The silver triflate solution was added to the solution of $Pd(CH_3CN)_2Cl_2$. The reaction mixture was stirred under Ar in the dark for 1 h. The yellow solution was decanted from the AgCl precipitate, and the solvent was evaporated. The resulting 216 mg of $Pd(CH_3CN)_4(OTf)_2$ (0.38 mmol) was dissolved in acetone and used immediately in additional syntheses.

A solution of 91 mg of $Pd(CH_3CN)_4(OTf)_2$ (0.16 mmol) in 5 mL of acetone was added dropwise to a solution of 80 mg of Cl_2-phen (**1a**) (0.32 mmol) in 15 mL of acetone and 10 mL of dichloromethane under Ar. The reaction mixture was stirred at room temperature for 16 h, after which time 20 mL of hexanes was added. The solvents were decanted, and the precipitate was washed with 2 × 5 mL of toluene. The product was dried under vacuum. Yield: 99 mg of orange-yellow powder (0.11 mmol, 69%). IR (KBr):1260 (vs, $-SO_2O-$), 1028 (s, C−F) cm^{-1}. ^1H NMR (MeOH-d_4): δ 9.28 (d, 2H, $H_2 + H_9$), 8.75 (s, 2H, $H_5 + H_6$), 8.47 (d, 2H, $H_3 + H_8$) ppm. Anal. Calcd for $C_{26}H_{12}Cl_4F_6N_4O_6S_2Pd$: C, 34.59; H, 1.34. Found: C, 33.97; H, 1.49.

Pd(phen)$_2$(OTf)$_2$ (2b). To a freshly prepared solution of 183 mg of $Pd(CH_3CN)_4(OTf)_2$ (0.32 mmol) in 10 mL of acetone under Ar was added dropwise a solution of 116 mg of phen (**1b**) (0.64 mmol) in 6 mL of acetone. The reaction mixture was stirred at room temperature for 1 h, after which time the supernatant was decanted from the precipitate. The precipitate was washed with 2 × 3 mL of hexanes and dried under vacuum. To the supernatant was added 20 mL of hexanes, resulting in a new precipitate. The solvents were decanted, and the precipitate was washed with 3 × 2 mL of toluene and dried under vacuum. Crystals were obtained from an unsaturated solution of the complex in 4 mL of methanol, to which 4 mL of hexanes was slowly added. After 3 days yellow crystals had grown in the solution. Overall yield: 168 mg of yellow powder (0.22 mmol, 69%). IR (KBr): 1260 (vs, $-SO_2O-$), 1026 (s, C−F) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.39 (d, 2H, $H_2 + H_9$), 9.18 (d, 2H, $H_4 + H_7$), 8.46 (s, 2H, $H_5 + H_6$), 8.31 (dd, 2H, $H_3 + H_8$) ppm. MS (FAB): 615 (M^+ − OTf), 466 (M^+ − 2OTf), 286 (M^+ − 2OTf − phen). Anal. Calcd for $C_{26}H_{16}F_6N_4O_6S_2Pd$: C, 40.82; H, 2.11; N, 7.32. Found: C, 40.06; H, 2.21; N, 7.00.

Pd(Me$_2$-phen)$_2$(OTf)$_2$ (2c). The synthesis of Pd(Me$_2$-phen)$_2$(OTf)$_2$ (**2c**) is analogous to the synthesis of Pd(Cl$_2$-phen)$_2$(OTf)$_2$ (**2a**) with the following modifications. A freshly prepared solution of 34 mg of $Pd(CH_3CN)_4(OTf)_2$ (0.06 mmol) in 2 mL of acetone was added dropwise to a solution of 25 mg of Me_2-phen (**1c**) (0.12 mmol) in 6 mL of acetone under Ar. No precipitate was formed until 20 mL of hexanes had been added. Yield: 34.5 mg of brown powder (0.04 mmol, 70%). IR (KBr): 1258 (vs, $-SO_2O-$), 1028 (s, C−F) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.15 (d, 2H, $H_2 + H_9$), 8.46 (s, 2H, $H_5 + H_6$), 8.02 (d, 2H, $H_3 + H_8$), 3.05 (s, 6H, CH_3) ppm. Anal. Calcd for $C_{30}H_{24}F_6N_4O_6S_2Pd$·toluene: C, 48.66; H, 3.53. Found: C, 48.24; H, 3.30.

Pd((MeO)$_2$-phen)$_2$(OTf)$_2$ (2d). Pd((MeO)$_2$-phen)$_2$(OTf)$_2$ (**2d**) was prepared analogously to Pd(Cl$_2$-phen)$_2$(OTf)$_2$ (**2a**). However, 96 mg of (MeO)$_2$-phen (**1d**) (0.40 mmol) dissolved in 15 mL of acetone and 5 mL of dichloromethane was reacted with 114 mg of freshly prepared $Pd(CH_3CN)_4(OTf)_2$ (0.20 mmol) in 8 mL of acetone under Ar. Yield: 97 mg of brown powder (0.11 mmol, 55%). IR (KBr): 1266 (vs, $-SO_2O-$), 1221 (m, C−O−C), 1032 (s, C−F), 1028 (s, C−O−C) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.07 (d, 2H, $H_2 + H_9$), 8.31 (s, 2H, $H_5 + H_6$), 7.65 (d, 2H, $H_3 + H_8$), 4.35 (s, 6H, OCH_3) ppm. Anal. Calcd for $C_{30}H_{24}F_6N_4O_{10}S_2Pd$: C, 40.71; H, 2.74. Found: C, 40.03; H, 2.72.

Pd((Me$_2$N)$_2$-phen)$_2$(OTf)$_2$ (2e). Pd((Me$_2$N)$_2$-phen)$_2$(OTf)$_2$ (**2e**) was synthesized according to the synthesis of Pd(Cl$_2$-phen)$_2$(OTf)$_2$ (**2a**), except that 85 mg of (Me$_2$N)$_2$-phen (**1e**) (0.32 mmol) was used. The precipitate was washed with 2 × 5 mL of chloroform as well as with 2 × 5 mL of toluene. Yield: 94 mg of brown powder (0.10 mmol, 65 %). IR (KBr): 1266 (vs, $-SO_2O-$), 1064 (w, C−N), 1026 (s, C−F) cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.40 (d, 2H, $H_2 + H_9$), 8.04 (s, 2H, $H_5 + H_6$), 7.04 (d, 2H, $H_3 + H_8$), 3.45 (s, 12H, $N(CH_3)_2$) ppm. Anal. Calcd for $C_{34}H_{36}F_6N_8O_6S_2Pd$·$2H_2O$: C, 42.75; H, 4.01; N, 11.73. Found: C, 42.85; H, 4.12; N, 11.51.

Pd(Cl$_2$-phen)$_2$(BF$_4$)$_2$ (3a). A solution of 24.7 mg of Cl$_2$-phen (**1a**) (0.1 mmol) in 2 mL of acetone and 4 mL of dichloromethane under Ar was added dropwise to a solution of 22 mg of $Pd(CH_3CN)_4(BF_4)_2$ (0.05 mmol) in 2 mL of acetone under Ar. The reaction mixture was stirred at room temperature for 24 h, after which time 15 mL of hexanes was added. The solvents were decanted, and the precipitate was washed with 3 × 5 mL of hexanes. The product was dried under vacuum. Yield: 28 mg of yellow powder (0.035 mmol, 70%). IR (KBr): 1061 (vs, br, BF_4) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.30 (br, 2H, $H_2 + H_9$), 8.67 (br, 2H, $H_5 + H_6$), 8.55 (br, 2H, $H_3 + H_8$) ppm. Anal. Calcd for $C_{24}H_{12}B_2Cl_4F_8N_4Pd$·$H_2O$: C, 36.20; H, 1.77. Found: C, 36.52; H, 2.08.

Pd(phen)$_2$(BF$_4$)$_2$ (3b). Pd(phen)$_2$(BF$_4$)$_2$ (**3b**) was synthesized analogously to Pd(Cl$_2$-phen)$_2$(BF$_4$)$_2$ (**3a**) with the following modifications: 144 mg of phen (**1b**) (0.8 mmol) in 10 mL of acetone was reacted with 178 mg of $Pd(CH_3CN)_2(BF_4)_2$ (0.4 mmol) in 15 mL of acetone under Ar. After the mixture had been stirred for 1 h, 30 mL of hexanes was added. The precipitate was washed with 2 × 5 mL of toluene. Yield: 205 mg of yellow powder (0.32 mmol, 81%). IR (KBr): 1061 (vs, br, BF_4) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.40 (d, 2H, $H_2 + H_9$), 9.20 (d, 2H, $H_4 + H_7$), 8.50 (s, 2H, $H_5 + H_6$), 8.33 (dd, 2H, $H_3 + H_8$) ppm. MS (FAB): 553 (M^+ − BF_4), 466 (M^+ − 2 BF_4), 286 (M^+ − 2 BF_4 − phen). Anal. Calcd for $C_{24}H_{16}B_2F_8N_4Pd$: C, 45.01; H, 2.52; N, 8.75. Found: C, 44.24; H, 2.72; N, 8.63.

Pd(Me$_2$-phen)$_2$(BF$_4$)$_2$ (3c). Pd(Me$_2$-phen)$_2$(BF$_4$)$_2$ (**3c**) was prepared as Pd(Cl$_2$-phen)$_2$(BF$_4$)$_2$ (**3a**), except that 20.8 mg of Me$_2$-phen (**1c**) (0.1 mmol) was dissolved in 3 mL of acetone and added to a solution of 22 mg of $Pd(CH_3CN)_4(BF_4)_2$ (0.05 mmol) in 2 mL of acetone under Ar. Yield: 34.5 mg of brown powder (0.04 mmol, 78%). IR (KBr): 1061 (vs, br, BF_4) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.20 (d, 2H, $H_2 + H_9$), 8.48 (s, 2H, $H_5 + H_6$), 8.10 (d, 2H, $H_3 + H_8$), 3.06 (s, 6H, CH_3) ppm. Anal. Calcd for $C_{28}H_{24}B_2F_8N_4Pd$·$2H_2O$: C, 45.91; H, 3.86. Found: C, 45.29; H, 3.83.

Pd((MeO)$_2$-phen)$_2$(BF$_4$)$_2$ (3d). Pd((MeO)$_2$-phen)$_2$(BF$_4$)$_2$ (**3d**) was prepared according to the synthesis of its triflate analogue **2d** with the following modifications: 66.6 mg of $Pd(CH_3CN)_4(BF_4)_2$ (0.15 mmol) in 5 mL of acetone under Ar was reacted with 72 mg of (MeO)$_2$-phen (**1d**) (0.30 mmol) dissolved in 15 mL of acetone and 10 mL of dichloromethane. Yield: 84 mg of brown powder (0.11 mmol, 70%). IR (KBr): 1225 (m, C−O−C), 1081 (vs, br, BF_4) cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.08 (d, 2H, $H_2 + H_9$), 8.35 (s, 2H, $H_5 + H_6$), 7.66 (d, 2H, $H_3 + H_8$), 4.38 (s, 6H, OCH_3) ppm.

Pd((Me$_2$N)$_2$-phen)$_2$(BF$_4$)$_2$ (3e). Pd((Me$_2$N)$_2$-phen)$_2$(BF$_4$)$_2$ (**3e**) was synthesized according to the synthesis of its triflate analogue **2e**. A solution of 133 mg of $Pd(CH_3CN)_4(BF_4)_2$ (0.30 mmol) in 7 mL of acetone was added dropwise to a solution of 160 mg of (Me$_2$N)$_2$-phen (**1e**) (0.60 mmol) in 15 mL of acetone under Ar. Yield: 211 mg of brown powder (0.26 mmol, 85%). IR (KBr): 1061 (vs, br, BF_4) cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.43 (d, 2H, $H_2 + H_9$), 8.08 (s, 2H, $H_5 + H_6$), 7.08 (d, 2H, $H_3 + H_8$), 3.45 (s, 12H, $N(CH_3)_2$) ppm.

X-ray Analysis. X-ray Structure Determination of Pd(phen)$_2$(OTf)$_2$ (2b). X-ray data for the pale yellow crystal were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Crystallographic data are summarized in Table 7. Reflections were measured within the range $-13 \le h \le 14$, $-14 \le k \le 16$, and $0 \le l \le 18$. The maximum value of $(\sin\theta)/\lambda$ was 0.70 $Å^{-1}$. Two reference reflections (200 and 122) were measured every hour and showed no decrease during the 90 h of collection time. Unit cell parameters were refined with a least-squares fitting procedure, using 23 reflections with $40 < 2\theta <$

Table 7. Crystallographic Data for $Pd(phen)_2(OTf)_2$ (2b)

mol formula	$C_{26}H_{16}F_6N_4O_6S_2Pd$
mol wt	765.0
cryst syst	triclinic
space group	$P\bar{1}$
temp	room temperature
radiation (λ, Å)	Mo Kα (0.710 69)
a, Å	10.387(1)
b, Å	11.539(2)
c, Å	13.449(3)
α, deg	70.53(1)
β, deg	67.42(2)
γ, deg	81.51(1)
V, Å^3	2465.6(5)
Z	2
D_{calcd}, g cm^{-3}	1.56
$F(000)$	760
cryst dimens, mm^3	0.20 × 0.50 × 0.50
μ(Mo Kα), cm^{-1}	8.81
no. of unique tot. data	8101
no. of unique obsd data	6448 ($I > 2.5\sigma(I)$)
R	0.045
R_w	0.064

41°. Corrections for Lorentz and polarization effects were applied. The Pd and S atoms were found by direct methods. The remainder of the non-hydrogen atoms was found in a subsequent ΔF synthesis. The hydrogen atoms are calculated. Full-matrix least-squares refinement on F, anistropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained constant at approximately 1.09 Å, converged to $R = 0.045$, $R_w = 0.064$, and $(\Delta/\sigma)_{max} = 0.87$. A weighting scheme $w = (6.3 + F_{obs} + 0.0080F_{obs}^2)^{-1}$ was used. An empirical absorption correction (DIFABS)[32] was applied, with coefficients in the range 0.82–1.34. The secondary isotropic extinction coefficient[33,34] was refined to Ext = 0.02(2). A final difference Fourier map revealed a residual electron density between −0.7 and 1.1 e Å^{-3}. Scattering factors were taken from refs 35 and 36. The anomalous scattering of Pd and S was taken into account. All calculations were performed with XTAL,[37] unless stated otherwise.

Cyclic Voltammetry. Cyclic voltammetry experiments were carried out in DMSO solutions at room temperature under N_2 with Bu_4NPF_6 as supporting electrolyte. The solutions were all 10^{-3} M in complex or free ligand and 10^{-1} M in Bu_4NPF_6. The Fc/Fc^+ redox couple served as an internal standard for the determination of reduction potentials.[23] The cyclic voltammograms were recorded at a scan rate of 100 mV/s.

Catalysis. Pd(acetate)$_2$/Ligand/*p*-Toluenesulfonic Acid. In a typical experiment using the in situ prepared catalyst system the autoclave was charged with 8 mL of methanol and 1.5 mL of nitrobenzene (14.6 mmol). A 4.5 mg amount of $Pd(OAc)_2$ (0.02 mmol) and 0.12 mmol of the ligand (6 equiv to Pd) were dissolved in this mixture. Subsequently, 2 mL of a 0.0295 M stock solution of *p*-tsa in methanol (0.06 mmol, 3 equiv to Pd) was added. The autoclave was pressurized with 60 bar of CO and heated to 135 °C within 35 min. The initial working pressure at 135 °C was approximately 80 bar. After 2 h, the autoclave was rapidly cooled down and the pressure was released.

Pd(ligand)$_2$(Y)$_2$/Ligand (Y = OTf or BF_4). Experiments with the presynthesized complexes were carried out as described for the in situ combination in 10 mL of methanol, with 0.02 mmol of complex and 0.08 mmol of free ligand (resulting in an overall ligand:Pd ratio of 6). No *p*-tsa was added.

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Supporting Information Available: Listings of fractional atomic coordinates for the non-hydrogen and the hydrogen atoms and the anistropic thermal parameters for $Pd(phen)_2(OTf)_2$ (**2b**) (5 pages). Ordering information is given on any current masthead page.

OM950187G

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