Ligand Effects in the Palladium-Catalyzed Reductive Carbonylation of Nitrobenzene

Petra Wehman, Georg C. Dol, Eddy R. Moorman, Paul C. J. Kamer, Piet W. N. M. van Leeuwen, Jan Fraanje, and Kees Goubitz

Organometallics, **1994**, 13 (12), 4856-4869• DOI: 10.1021/om00024a031 • Publication Date (Web): 01 May 2002

Ligand Effects in the Palladium-Catalyzed Reductive Carbonylation of Nitrobenzene

Petra Wehman, Georg C. Dol, Eddy R. Moorman, Paul C. J. Kamer, and Piet W. N. M. van Leeuwen*

J. van het Hoff Research Institute, Department of Inorganic Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Jan Fraanje and Kees Goubitz

Laboratory of Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Received May 19, 1994[⊗]

Reductive carbonylation of nitrobenzene in methanol in the presence of a palladium catalyst yields mainly methyl *N*-phenylcarbamate. Diphenylurea is formed as the most important byproduct. A series of 4,4′-disubstituted-2,2′-bipyridyl ligands (R = F_3C, Cl, H, Me, MeO, and Me_2N) has been used to study the influence of the donating capacity of the ligand on the catalytic activity and selectivity. By way of two different types of complexes, Pd(ligand)$_2$(OTf)$_2$ and Pd(ligand)Cl(OTf), the influence of the anions in the catalytic system has also been studied. Electron-withdrawing substituents on the bipyridyl ligand turned out to completely deactivate the catalyst, while only small differences were found between the ligands with electron-donating substituents. Chloride anions showed an inhibiting effect. The presence of water reduced the selectivity toward carbamate. At prolonged reaction times the urea side product was catalytically converted into the desired carbamate. Under more severe conditions carbamates, urea side products, and anilines were found with methoxy substituents on their phenyl rings. X-ray structures were elucidated for Pd(bpy)$_2$(OTf)$_2$ and Pd(Me-bpy)$_2$(OTf)$_2$. The Pd(bpy)$_2$(OTf)$_2$ crystals were monoclinic, space group $P2_1/n$, a = 8.0186(8) Å, b = 28.459(4) Å, c = 11.315(3) Å, β = 97.59(3)°, Z = 8, and final R = 0.046 for 3194 observed reflections. The Pd(Me-bpy)$_2$(OTf)$_2$ crystals were triclinic, space group $P1$, a = 11.726(6) Å, b = 11.870(3) Å, c = 13.871(2) Å, α = 103.63(6)°, β = 107.78(2)°, γ = 113.32(3)°, Z = 2, and final R = 0.147 for 5462 observed reflections. The $CF_3SO_3^-$ moieties were not stable during refinement.

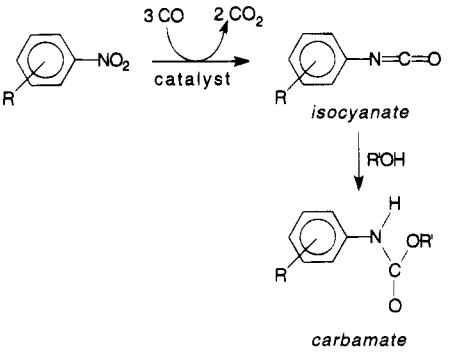
Introduction

Carbamates and isocyanates are commercially important products. Toluene 2,4-diisocyanate, for instance, is a well-known isocyanate that is used on a large scale in the production of polyurethane foams. Carbamates are also applied in the pharmaceutical industry and as agrochemicals.[1,2]

Traditionally, isocyanates are synthesized from nitro compounds, which are first catalytically hydrogenated to amines. Subsequently, the amines are reacted with phosgene, yielding the isocyanates. Carbamates can be produced from isocyanates by reaction with an alcohol. The use of extremely toxic phosgene as well as production of large quantities of HCl as a byproduct are severe disadvantages to this traditional route.[1,2]

Reductive carbonylation of the nitro compound, in which the nitro function reacts directly with CO giving the desired isocyanate, is a very attractive alternative route. For this one-step process a catalyst is required (Scheme 1). Ever since 1962 this nitro reduction has been the subject of several investigations, which is especially reported in the patent literature. Much research has been conducted on the use of sulfur, selenium, or tellurium as catalyst. The problem with these systems remains, however, the purification of the product from small but definite amounts of catalyst, especially selenium or selenium compounds.[3]

Scheme 1. Reductive Carbonylation of Aromatic Nitro Compounds in General



Another possibility is the use of a group 8–10 metal compound as catalyst. These compounds are especially used in the synthesis of carbamates. One of the most active and selective catalysts known is based on palladium. This metal was first applied as a catalyst in a heterogeneous system.[4] Supported palladium on active

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

(1) Braunstein, P. *Chem. Rev.* **1989**, *89*, 1927.

(2) Watanabe, Y.; Tsjui, Y.; Takeuchi, R.; Suzuki, N. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3343.

(3) Drent, E.; van Leeuwen, P. W. N. M. EP 86281, 1983.

0276-7333/94/2313-4856$04.50/0

carbon or alumina turned out to be active in the presence of a bidentate nitrogen-donor ligand, such as 2,2′-bipyridine. A ligand with a higher σ-donating capacity such as 1,10-phenanthroline leads to even higher activities.[5-7]

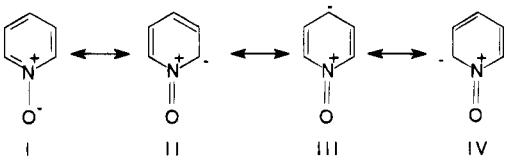
In the homogeneously catalyzed reductive carbonylation of nitrobenzene, palladium is often applied in the form of $PdCl_2$. Again, addition of a nitrogen-donor ligand is necessary. Monodentate ligands already lead to substantial activity of the catalyst[8] but bidentate ligands remain by far superior. In 1983 a catalyst system for the reductive carbonylation of nitro compounds was patented, which contains palladium and a bidentate nitrogen, phosphorus, arsenic, or antimony ligand. In particular the use of 1,10-phenanthroline or 1,3-bis(diphenylphosphino)propane (dppp) is discussed in detail.[3]

The effect of the donating capacity of the bidentate ligand on the catalytic activity of [Pd(bidentate ligand)$_2$]-[PF_6]$_2$ systems is even more pronounced than for the supported Pd/C systems. Mestroni et al. found that the conversion of nitrobenzene within 2 h rises from 14.5% to 72% on going from 2,2′-bipyridine to 1,10-phenanthroline.[9] It should be noted, however, that next to the higher degree of σ-donation the rigidity of 1,10-phenanthroline could also be highly responsible for this increase in activity.

Besides the ligand effect, the anion also seems to play an important role. With the [Pd(bidentate ligand)$_2$]-[PF_6]$_2$ complexes as catalyst precursor no cocatalyst is required. Replacing the PF_6 anions by chloride anions leads to a serious loss of activity. On the other hand, traces of chloride appear to have a positive effect on the catalytic performance.[9] If Pd(acetate)$_2$ is used in combination with a bidentate ligand the addition of a cocatalyst is needed.[10] According to studies by Drent et al., the electrophilicity of the complex must be delicately balanced in order to get efficient catalysis. With hard-base, electron-donating ligands as 2,2′-bipyridine or 1,10-phenanthroline, anions with a relatively strong electron affinity are required. Strong acids like *p*-toluenesulfonic acid can then be used as cocatalyst, yielding noncoordinating or weakly coordinating anions by replacement of the acetates.[10]

In this article a more thorough study of the influence of the donating capacity of the ligand on the catalytic activity and selectivity will be presented. Therefore various 4,4′-disubstituted-2,2′-bipyridyl ligands (R = F_3C, Cl, H, Me, MeO, and Me_2N) have been synthesized to study the effect of the degree of σ-donation at equal structural rigidity. The ligands were tested in the reductive carbonylation of nitrobenzene in combination with Pd(acetate)$_2$ and *p*-toluenesulfonic acid. Furthermore two other types of complexes, Pd(ligand)$_2$(OTf)$_2$ and Pd(ligand)Cl(OTf), have been prepared to study the influence of the anion in a more precise way with a better defined catalyst precursor. Next to the study on the influence of ligand and anion research has been done on the product distribution. A comparison has been made between relatively short reaction times (2 h) and longer reaction times (16 h). Also, eight until now unidentified products that are formed under more extreme conditions have been analyzed and characterized.

Scheme 2. Resonance Structures of Pyridine *N*-Oxide



Results and Discussion

Synthesis of the Ligands. Direct synthesis of 4,4′-disubstituted-2,2′-bipyridyl ligands (compound **4**, Scheme 3) with R = Cl, MeO, and Me_2N from 2,2′-bipyridine by electrophilic substitution is difficult because the starting material is inert toward electrophilic reagents. However, it can be made more susceptible to substitution by oxidation at the nitrogen atom. This method of activation is based on the work of Ochiai et al. with pyridine.[11] Especially the 4-position is strongly activated, as is explained by the resonance structures II–IV (Scheme 2). The reactivity of the 2-positions is reduced by the inductive effect of the *N*-oxide function.

Haginiwa prepared 2,2′-bipyridine 1,1′-dioxide (**1**) by oxidizing 2,2′-bipyridine with H_2O_2.[12] We found, however, that the oxidation of the first nitrogen atom occurs readily while oxidation of the nitrogen atom in the second pyridyl ring is far more difficult. Oxidation with H_2O_2 did not yield the desired 2,2′-bipyridine 1,1′-dioxide (**1**). Peracetic acid, a more powerful oxidizing agent, turned out to be able to oxidize both nitrogen atoms. An additional advantage of the use of peracetic acid was the absence of water in the reaction mixture. bpy *N*-oxide (**1**) is highly soluble in this medium, which makes it hard to recover the product from an alkaline aqueous solution.

Once the bipyridyl system is oxidized it can be nitrated at the 4- and 4′-positions. If the reaction time of the nitration exceeds 24 h, a small amount of 4,4′,6-trinitro-2,2′-bipyridine 1,1′-dioxide is formed next to the desired 4,4′-dinitro-2,2′-bipyridine 1,1′-dioxide (**2**). The same happens if the temperature is raised above 100 °C during the nitration reaction.

Introduction of the nitro groups provides a starting material for the preparation of various 4,4′-disubstituted derivatives, as has already been shown for 4-nitropyridine 1-oxide.[13] The NO_2 group is easily replaced by a methoxy or chloride substituent. The chloride substituent in its turn can be exchanged for a dimethylamino group by refluxing in DMF, as is known for halogenopyridines and -quinolines.[14] However, the bipyridyl system still has to be activated by oxidation at the nitrogen atoms for this exchange to take place,

(4) Hardy, W. B.; Bennett, R. P. *Tetrahedron Lett.* **1967**, *11*, 961. American Cyanamid Co., Netherlands. Patent 6,513,844, 1966.
(5) Alessio, E.; Mestroni, G. *J. Organomet. Chem.* **1985**, *291*, 117.
(6) Alessio, E.; Mestroni, G. *J. Mol. Catal.* **1984**, *26*, 337.
(7) Cenini, S.; Ragaini, F.; Pizzotti, M.; Porta, F.; Mestroni, G.; Alessio, E. *J. Mol. Catal.* **1991**, *64*, 179.
(8) Gupte, S.; Chaudhari, R. V. *J. Mol. Catal.* **1984**, *24*, 197.
(9) Bontempi, A.; Alessio, E.; Chanos, G.; Mestroni, G. *J. Mol. Catal.* **1987**, *42*, 67.
(10) Drent, E. *Pure Appl. Chem.* **1990**, *62*, 661.
(11) Ochiai, E. *J. Org. Chem.* **1953**, *18*, 534.
(12) Haginiwa, J. *Chem. Abstr.* **1956**, *50*, 3435.
(13) Den hertog, H. J.; Combé, W. P. *Recl. Trav. Chim.* **1951**, *70*, 581.
(14) Heindel, N. D.; Kennewell, P. D. *J. Chem. Soc., Chem. Commun.* **1969**, 38.

Scheme 3. General Scheme for the Complex Synthesis

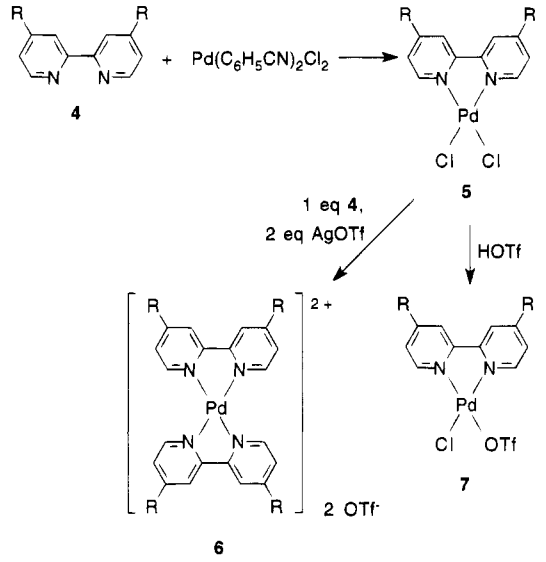


Table 1. IR Data for Pd(4,4′-R_2-2,2′-bipyridine)Cl_2 Complexes (in KBr)

R	ν(Pd−N) (cm^{-1})	ν(Pd−Cl) (shoulder) (cm^{-1})
F_3C	413	345 (352)
Cl	419	327 (343)
H	415	335 (342)
Me	421	330 (340)
MeO	435	325 (332)
Me_2N	437	315 (322)

because no reaction is observed between 4,4′-dichloro-2,2′-bipyridine (**4b**) and DMF. In all cases it is easy to reduce the oxide function with PCl_3, without affecting the substituents in the 4- and 4′-positions.

The 4,4′-bis(trifluoromethyl)-2,2′-bipyridyl ligand (**4a**) is prepared by an alternative approach. Two molecules of 2-chloro-4-(trifluoromethyl)pyridine are coupled under the influence of an in situ prepared Ni(0) complex, as described by Tiecco et al.[15] This coupling procedure requires less drastic experimental conditions and results in higher yields than the classical Ullman reaction. The only disadvantage of this method is the large excess of triphenylphosphine that has to be used in order to generate a stable $Ni(PPh_3)_4$ complex. The product and the excess PPh_3 are difficult to separate.

Synthesis of the Complexes. The preparation of the Pd(ligand)Cl_2 complexes proceeds readily for all bipyridyl ligands from Pd(benzonitrile)$_2Cl_2$ or Pd(acetonitrile)$_2Cl_2$. IR data for the complexes are collected in Table 1. The Pd−Cl stretching mode is found in the range 315−345 cm^{-1}, as is to be expected.[16] The second Pd−Cl mode, caused by the C_{2v} symmetry of the complexes, is less pronounced, as it is superimposed as a shoulder on the first signal. The value of ν(Pd−N) increases, going from the electron-withdrawing substituent F_3C (413 cm^{-1}) to the electron-donating Me_2N substituent (437 cm^{-1}). According to the IR data the donating capacities of 4,4′-dimethoxy-2,2′-bipyridine (**4e**) and 4,4′-bis(dimethylamino)-2,2′-bipyridine (**4f**) appear to be at the same level. The 4,4′-dichloro-2,2′-bipyridine system (**5b**) does not really fit into the sequence, probably due to the fact that the chloride substituent can also be seen as a mesomerically donating substituent. Care should be taken, however, in the interpretation of these data. Unlike, for example, ν(CO) frequencies in carbonyl complexes the ν(Pd−N) frequencies are only a rough indication of the coordination properties.

It was attempted to convert the Pd(ligand)Cl_2 systems into Pd(ligand)$(OTf)_2$ complexes. A reaction with triflic acid has been described by Diver and Lawrance for several bidentate nitrogen ligands, including 2,2′-bipyridine.[17] Formation of the desired complexes failed in our hands for all the bipyridyl ligands. Neither heating the reaction mixture nor bubbling through of nitrogen to ease the release of HCl could cause the second chloride ligand to be displaced by a triflate anion. Only in the case of 4,4′-dimethoxy-2,2′-bipyridine (**4e**) is Pd(MeO-bpy)$(OTf)_2$ formed to some extent. Separation of the mono- and bis(triflate) complexes, however, is not possible. 4,4′-Bis(trifluoromethyl)-2,2′-bipyridine (**4a**) turns out to be such a weakly coordinating ligand that only Pd black is formed in an attempt to replace the stabilizing chloride ligands by noncoordinating triflate anions. The formed Pd(ligand)Cl(OTf) complexes are characterized by means of NMR and IR. ^1H NMR at low temperatures shows an asymmetric complex with different resonance signals for all bipyridyl protons. The presence of a remaining chloride ligand is shown by IR. The triflate anion also shows up in the IR spectra, $\nu(-SO_2O-) \approx 1260$ and $\nu(C-F) \approx 1170$ cm^{-1} in KBr. Its presence in solution has been checked by ^{19}F NMR. Elemental analysis definitely confirms the molecular formula.

The exchange reaction between chloride of Pd(ligand)Cl_2 and two molecules of AgOTf also fails to yield Pd(ligand)$(OTf)_2$ and results in the formation of Pd black. Addition of an extra equivalent of free ligand, however, yields stable Pd(ligand)$_2(OTf)_2$ complexes for R = Cl, H, Me, MeO, and Me_2N. The F_3C-bpy ligand (**4a**) again shows its weakly coordinating properties; Pd(F_3C-bpy)$_2(OTf)_2$ is only stable in solution in the presence of extra, free F_3C-bpy (**4a**). Otherwise Pd black is formed rapidly. With the Me_2N-bpy ligand (**4f**) a different problem occurs. Due to the low solubility of Pd(Me_2N-bpy)$_2(OTf)_2$ (**6f**) this bis(triflate) complex precipitates together with AgCl. The problem can be avoided by reaction of Me_2N-bpy (**4f**) with Pd(acetonitrile)$_4(OTf)_2$. Because of the lability of Pd(acetonitrile)$_4(OTf)_2$, even as a solid under an Ar atmosphere, this starting material has to be prepared freshly each time prior to use.

Molecular Structures of Pd(bpy)$_2(OTf)_2$ (6c) and Pd(Me-bpy)$_2(OTf)_2$ (6d). Molecular structures of Pd(bpy)$_2(OTf)_2$ (**6c**) and Pd(Me-bpy)$_2(OTf)_2$ (**6c**) were determined to establish the exact coordination of the bipyridyl ligands to the palladium center. Especially the Pd−N distances were of interest, as we hoped that a higher degree of σ-donation of the ligand would be reflected in a shortening of this distance. Unfortunately, the data obtained for Pd(Me-bpy)$_2(OTf)_2$ (**6d**) should be considered with more restraint than those of Pd(bpy)$_2(OTf)_2$ (**6c**), as the CF_3SO_3 moieties were not stable during refinement. Flipping of the anions causes

(15) Tiecco, M.; Testaferi, L.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Synthesis* **1984**, 736.
(16) Walton, R. A. *Spectrochim. Acta* **1965**, *21*, 1795.
(17) Diver, C.; Lawrance, G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 933.

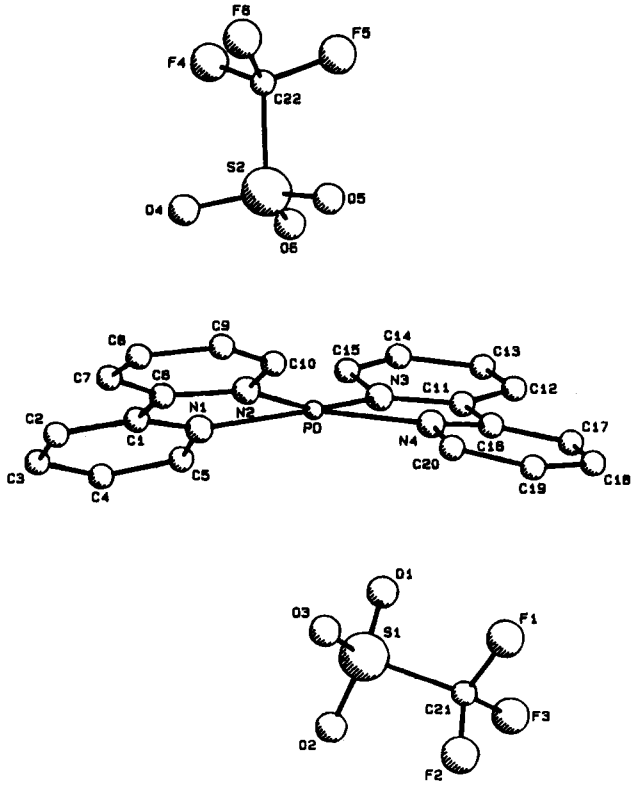


Figure 1. ORTEP drawing of $Pd(bpy)_2(OTf)_2$ (**6c**).

Table 2. Bond Distances (Å) of the Non-Hydrogen Atoms of $Pd(bpy)_2(OTf)_2$ (6c) (with Esd's in Parentheses)

Pd–N(1)	2.020(6)	C(8)–C(9)	1.36(1)
Pd–N(2)	2.041(6)	C(9)–C(10)	1.38(1)
Pd–N(3)	2.039(6)	C(10)–N(2)	1.343(9)
Pd–N(4)	2.043(6)	C(11)–C(12)	1.38(1)
S(1)–C(21)	1.81(1)	C(11)–C(16)	1.47(1)
S(1)–O(1)	1.432(8)	C(11)–N(3)	1.352(9)
S(1)–O(2)	1.431(7)	C(12)–C(13)	1.38(1)
S(1)–O(3)	1.418(7)	C(13)–C(14)	1.38(1)
S(2)–C(22)	1.81(1)	C(14)–C(15)	1.39(1)
S(2)–O(4)	1.434(6)	C(15)–N(3)	1.356(9)
S(2)–O(5)	1.448(6)	C(16)–C(17)	1.36(1)
S(2)–O(6)	1.426(6)	C(16)–N(4)	1.366(9)
C(1)–C(2)	1.37(1)	C(17)–C(18)	1.38(1)
C(1)–C(6)	1.477(9)	C(18)–C(19)	1.38(1)
C(1)–N(1)	1.355(9)	C(19)–C(20)	1.39(1)
C(2)–C(3)	1.38(1)	C(20)–N(4)	1.347(9)
C(3)–C(4)	1.38(1)	C(21)–F(1)	1.31(1)
C(4)–C(5)	1.38(1)	C(21)–F(2)	1.30(1)
C(5)–N(1)	1.353(9)	C(21)–F(3)	1.32(1)
C(6)–C(7)	1.36(1)	C(22)–F(4)	1.34(1)
C(6)–N(2)	1.377(9)	C(22)–F(5)	1.34(1)
C(7)–C(8)	1.40(1)	C(22)–F(6)	1.33(1)

some disorder in the crystal, resulting in a higher R value which implicates a higher uncertainty in the data. Because of this high R value and the very small differences found between the various Pd–N distances, nothing can be said about the influence of the donating capacity of the ligand on the Pd–N distances. We did find, however, some important structural features which could be of interest in view of the catalytic activity of the complexes.

A view of the molecular structure of $Pd(bpy)_2(OTf)_2$ (**6c**) is shown in Figure 1. The hydrogen atoms are omitted for the sake of clarity. In Table 2 the bond distances of the non-hydrogen atoms are listed, whereas the bond angles of these atoms are collected in Table 3. Figure 2 shows the $Pd(Me\text{-}bpy)_2$ moiety of $Pd(Me\text{-}bpy)_2(OTf)_2$ (**6d**). Again the hydrogen atoms are omitted for the sake of clarity. The bond distances of the non-hydrogen atoms are given in Table 4, while the bond angles of the non-hydrogen atoms are listed in Table 5.

Table 3. Bond Angles (deg) of the Non-Hydrogen Atoms of $Pd(bpy)_2(OTf)_2$ (6c) (with Esd's in Parentheses)

N(1)–Pd–N(2)	80.2(2)	C(11)–C(12)–C(13)	120.4(7)
N(1)–Pd–N(3)	101.1(2)	C(12)–C(13)–C(14)	118.2(7)
N(1)–Pd–N(4)	164.9(2)	C(13)–C(14)–C(15)	120.1(7)
N(2)–Pd–N(3)	164.8(2)	C(14)–C(15)–N(3)	120.6(7)
N(2)–Pd–N(4)	102.7(2)	C(11)–C(16)–C(17)	123.7(6)
N(3)–Pd–N(4)	80.1(2)	C(11)–C(16)–N(4)	114.6(6)
C(21)–S(1)–O(1)	103.9(5)	C(17)–C(16)–N(4)	121.7(6)
C(21)–S(1)–O(2)	101.2(4)	C(16)–C(17)–C(18)	120.3(8)
C(21)–S(1)–O(3)	104.2(4)	C(17)–C(18)–C(19)	118.9(8)
O(1)–S(1)–O(2)	114.8(4)	C(18)–C(19)–C(20)	118.9(7)
O(1)–S(1)–O(3)	114.3(5)	C(19)–C(20)–N(4)	121.8(7)
O(2)–S(1)–O(3)	116.0(4)	S(1)–C(21)–F(1)	112.2(8)
C(22)–S(2)–O(4)	103.9(4)	S(1)–C(21)–F(2)	112.9(8)
C(22)–S(2)–O(5)	102.6(4)	S(1)–C(21)–F(3)	111.6(7)
C(22)–S(2)–O(6)	102.5(4)	F(1)–C(21)–F(2)	105.6(8)
O(4)–S(2)–O(5)	114.8(4)	F(1)–C(21)–F(3)	107.7(9)
O(4)–S(2)–O(6)	115.6(4)	F(2)–C(21)–F(3)	106.6(9)
O(5)–S(2)–O(6)	114.9(4)	S(2)–C(22)–F(4)	112.2(6)
C(2)–C(1)–C(6)	123.1(6)	S(2)–C(22)–F(5)	110.9(6)
C(2)–C(1)–N(1)	122.3(6)	S(2)–C(22)–F(6)	111.9(6)
C(6)–C(1)–N(1)	114.6(6)	F(4)–C(22)–F(5)	107.3(7)
C(1)–C(2)–C(3)	120.0(7)	F(4)–C(22)–F(6)	107.4(7)
C(2)–C(3)–C(4)	118.1(7)	F(5)–C(22)–F(6)	106.9(7)
C(3)–C(4)–C(5)	119.8(7)	Pd–N(1)–C(1)	116.1(4)
C(4)–C(5)–N(1)	122.0(7)	Pd–N(1)–C(5)	125.7(5)
C(1)–C(6)–C(7)	124.4(6)	C(1)–N(1)–C(5)	117.7(6)
C(1)–C(6)–N(2)	114.6(6)	Pd–N(2)–C(6)	114.5(4)
C(7)–C(6)–N(2)	120.9(6)	Pd–N(2)–C(10)	127.3(5)
C(6)–C(7)–C(8)	120.6(7)	C(6)–N(2)–C(10)	117.7(6)
C(7)–C(8)–C(9)	117.9(7)	Pd–N(3)–C(11)	114.9(4)
C(8)–C(9)–C(10)	119.7(7)	Pd–N(3)–C(15)	124.7(5)
C(9)–C(10)–N(2)	122.9(7)	C(11)–N(3)–C(15)	119.6(6)
C(12)–C(11)–C(16)	123.7(6)	Pd–N(4)–C(16)	114.4(4)
C(12)–C(11)–N(3)	120.9(6)	Pd–N(4)–C(20)	126.0(5)
C(16)–C(11)–N(3)	115.4(6)	C(16)–N(4)–C(20)	118.1(6)

Both structures show a $Pd(ligand)_2^{2+}$ cation with two bidentate coordinated ligands. The triflates are present as noncoordinating anions, which is obvious from the Pd–O distance of at least 3.3 Å.

It is known that palladium(II) distinctly favors a square planar configuration over any other geometry.[18] In the present compounds this results in a large steric strain, due to the close approach of the α-hydrogen atoms (H_6 and $H_{6'}$) of two opposite ligands. The internuclear separation between those hydrogen atoms would be only around 1 Å in the ideal square planar configuration, assuming a metal to nitrogen distance of 2.0 Å. In our complexes a Pd–N distance of approximately 2.0 Å is found, implying that the internuclear separation between the α-hydrogen atoms of two opposite ligands would be far smaller than twice the "normal" Van der Waals radius for hydrogen (=2 × 1.2 Å) in the ideal geometry. To relieve this steric strain, distortions of the PdN_4 skeleton are expected. Calculations have been made for the repulsion energy in relation to the dihedral angle between the planes of the two chelating ligands, the torsion angle.[18] Dependent on the model used ("soft", "intermediate", or "hard") various, quite large torsion angles have been calculated. Even in the soft model a twist of already 30° is required to lower the repulsion energy below 1 kcal/mol (for Pd–N = 2.0 Å). With the hard model this angle increases to about 50°.

We found torsion angles of 24.3 and 22.7° for $Pd(bpy)_2(OTf)_2$ (**6c**) and $Pd(Me\text{-}bpy)_2(OTf)_2$ (**6d**), respectively.

(18) McKenzie, E. D. *Coord. Chem. Rev.* **1971**, *6*, 187.

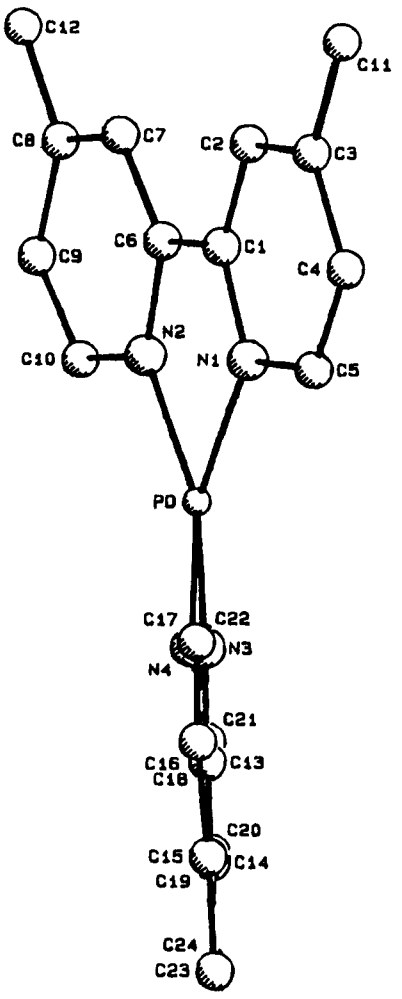


Figure 2. ORTEP drawing of the Pd(Me-bpy)$_2$ moiety of Pd(Me-bpy)$_2$(OTf)$_2$ (**6d**).

Table 4. Bond Distances (Å) of the Non-Hydrogen Atoms of Pd(Me-bpy)$_2$(OTf)$_2$ (6d) (with Esd's in Parentheses)

Pd–N(1)	2.05(1)	C(8)–C(12)	1.49(3)
Pd–N(2)	2.06(1)	C(9)–C(10)	1.36(3)
Pd–N(3)	2.03(1)	C(10)–N(2)	1.33(2)
Pd–N(4)	2.03(1)	C(13)–C(14)	1.34(3)
S(1)–C(25)	1.74(2)	C(13)–C(18)	1.47(2)
S(1)–O(1)	1.34(2)	C(13)–N(3)	1.40(2)
S(1)–O(2)	1.30(2)	C(14)–C(15)	1.40(2)
S(1)–O(3)	1.40(5)	C(15)–C(16)	1.40(2)
S(2)–C(26)	1.77(3)	C(15)–C(23)	1.48(4)
S(2)–O(4)	1.37(2)	C(16)–C(17)	1.35(3)
S(2)–O(5)	1.35(2)	C(17)–N(3)	1.36(2)
S(2)–O(6)	1.37(3)	C(18)–C(19)	1.37(2)
C(1)–C(2)	1.37(2)	C(18)–N(4)	1.35(2)
C(1)–C(6)	1.44(2)	C(19)–C(20)	1.39(2)
C(1)–N(1)	1.34(2)	C(20)–C(21)	1.35(3)
C(2)–C(3)	1.37(2)	C(20)–C(24)	1.51(2)
C(3)–C(4)	1.37(3)	C(21)–C(22)	1.37(2)
C(3)–C(11)	1.52(2)	C(21)–C(22)	1.36(2)
C(4)–C(5)	1.38(2)	C(22)–N(4)	1.28(3)
C(5)–N(1)	1.34(2)	C(25)–F(2)	1.29(2)
C(6)–C(7)	1.38(2)	C(25)–F(3)	1.38(5)
C(6)–N(2)	1.39(2)	C(26)–F(4)	1.28(4)
C(7)–C(8)	1.40(2)	C(26)–F(5)	1.27(5)
C(8)–C(9)	1.40(2)	C(26)–F(6)	1.30(3)

They are in the same range as the torsion angle (24.3°) found for an aquobis(2,2′-bipyridine)palladium(II) nitrate complex by Chieh.[19] If these angles are used in the calculations of the repulsion energy even in the soft model, an energy of approximately 8 kcal/mol remains,

(19) Chieh, P. C. *J. Chem. Soc., Dalton Trans.* **1972**, 1643.

Table 5. Bond Angles (deg) of the Non-Hydrogen Atoms of Pd(Me-bpy)$_2$(OTf)$_2$ (6d) (with Esd's in Parentheses)

N(1)–Pd–N(2)	79.2(5)	C(3)–C(4)–C(5)	119(2)
N(1)–Pd–N(3)	101.8(5)	C(4)–C(5)–N(1)	122(2)
N(1)–Pd–N(4)	165.9(5)	C(1)–C(6)–C(17)	126(1)
N(2)–Pd–N(3)	166.2(5)	C(1)–C(6)–N(2)	115(1)
N(2)–Pd–N(4)	103.4(5)	C(7)–C(6)–N(2)	119(1)
N(3)–Pd–N(4)	79.0(5)	C(6)–C(7)–C(8)	121(1)
C(25)–S(1)–O(1)	109.8(9)	C(7)–C(8)–C(9)	118(2)
C(25)–S(1)–O(2)	114(1)	C(7)–C(8)–C(12)	121(2)
C(25)–S(1)–O(3)	81(2)	C(9)–C(8)–C(12)	122(2)
O(1)–S(1)–O(2)	136(1)	C(8)–C(9)–C(10)	119(2)
O(1)–S(1)–O(3)	94(2)	C(9)–C(10)–N(2)	124(1)
O(2)–S(1)–O(3)	91(2)	C(14)–C(13)–C(18)	127(1)
C(26)–S(2)–O(4)	107(1)	C(14)–C(13)–N(3)	120(1)
C(26)–S(2)–O(5)	102(1)	C(18)–C(13)–N(3)	112(1)
C(26)–S(2)–O(6)	101(2)	C(13)–C(14)–C(15)	122(1)
O(4)–S(2)–O(5)	116(4)	C(14)–C(15)–C(16)	116(2)
O(4)–S(2)–O(6)	114(1)	C(14)–C(15)–C(23)	121(1)
O(5)–S(2)–O(6)	115(2)	C(16)–C(15)–C(23)	123(1)
C(2)–C(1)–C(6)	123(1)	C(15)–C(16)–C(17)	121(1)
C(2)–C(1)–N(1)	121(1)	C(16)–C(17)–N(3)	123(1)
C(6)–C(1)–N(1)	116(1)	C(13)–C(18)–C(19)	121(2)
C(1)–C(2)–C(3)	121(2)	C(13)–C(18)–N(4)	116(1)
C(2)–C(3)–C(4)	118(1)	C(19)–C(18)–N(4)	123(1)
C(2)–C(3)–C(11)	122(2)	C(18)–C(19)–C(20)	120(2)
C(4)–C(3)–C(11)	120(2)	C(19)–C(20)–C(21)	117(1)
C(21)–C(20)–C(24)	123(2)	C(19)–C(20)–C(24)	120(2)
C(20)–C(21)–C(22)	121(2)	F(5)–C(26)–F(6)	102(2)
C(21)–C(22)–N(4)	123(2)	Pd–N(1)–C(1)	116(1)
S(1)–C(25)–F(1)	120(1)	Pd–N(1)–C(5)	126(1)
S(1)–C(25)–F(2)	121(2)	C(1)–N(1)–C(5)	118(1)
S(1)–C(25)–F(3)	97(2)	Pd–N(2)–C(6)	114.2(9)
F(1)–C(25)–F(2)	120(2)	Pd–N(2)–C(10)	127(1)
F(1)–C(25)–F(3)	86(3)	C(6)–N(2)–C(10)	119(1)
F(2)–C(25)–F(3)	87(2)	Pd–N(3)–C(13)	116.4(9)
S(2)–C(26)–F(4)	115(2)	Pd–N(3)–C(17)	126(1)
S(2)–C(26)–F(5)	117(3)	C(13)–N(3)–C(17)	117(1)
S(2)–C(26)–F(6)	109(2)	Pd–N(4)–C(18)	116.3(8)
F(4)–C(26)–F(5)	109(3)	Pd–N(4)–C(22)	127(1)
F(4)–C(26)–F(6)	103(3)	C(18)–N(4)–C(22)	115(1)

which is balanced apparently by the distortion of the ideal square planar configuration.

There is, however, a second mechanism which helps to relieve the overcrowding. The bipyridyl ligand can twist around its C_2–$C_{2'}$ axis, as is found in several bipyridyl complexes.[18] The twist in the coordinated ligand is probably at least partly the result of another atom overcrowding in the complex, as the distance between H_3 and $H_{3'}$ is within their normal Van der Waals radii. Due to the twist the two pyridyl rings which form together the bipyridyl ligand are no longer in one plane. In Pd(bpy)$_2$(OTf)$_2$ (**6c**) this angle in the first bpy ligand (**4c**) has a value of 3.9(0.3)°, which is a little more pronounced than in the Chieh complex Pd(bpy)$_2$(NO$_3$)$_2$·H$_2$O where the angle is only 1.8°.[19] The second bpy ligand (**4c**) in the Pd(bpy)$_2$(OTf)$_2$ complex (**6c**) is a bit more twisted with an angle of 7.4(0.3)° to give more relief to the repulsion of the α-interligand hydrogens. This is approximately the same value as was found for the second ligand in Pd(bpy)$_2$(NO$_3$)$_2$·H$_2$O (7.6°).[19] In the Pd(Me-bpy)$_2$(OTf)$_2$ complex (**6d**) the observed twisting angles are smaller: 0.8(0.4)° for the first Me-bpy ligand (**4d**) and 2.2(0.5)° for the second. This might implicate a somewhat larger steric restraint in the Pd(Me-bpy)$_2$(OTf)$_2$ complex (**6d**) than in the Pd(bpy)$_2$(OTf)$_2$ complex (**6c**). However, the high R value for this structure determination may not allow too detailed an explanation of these data.

Together all these distortions lead to reasonable hydrogen–hydrogen separation between opposite ligands, although slightly less than the Van der Waals radii. It

should be noted that many overcrowded aromatic hydrocarbons are known from organic chemistry, in which hydrogen–hydrogen distances can be as low as 1.8 Å.[18]

The steric effect is not only manifested structurally but also chemically by the lability of one of the ligands. Pd(1,10-phenanthroline)$_2$(ClO_4)$_2$ is a remarkable example of this lability.[20] Although phenanthroline is a very strongly coordinating ligand that should result in thermodynamically stable complexes, treatment of the compound with an aqueous, chloride-containing solution gives immediate precipitation of Pd(phenanthroline)Cl_2. This property could be important in the reductive carbonylation of aromatic nitro compounds, as the Pd(ligand)$_2$(OTf)$_2$ complexes (**6b–f**) most probably have to lose one ligand to act as catalyst.

Catalysis. The various substituted bipyridyl ligands (R = F_3C, Cl, H, Me, MeO, and Me_2N) have all been tested in the reductive carbonylation of aromatic nitro compounds. Nitrobenzene has been used as a model substrate, and all tests have been performed in methanol. Therefore, in all cases methyl *N*-phenylcarbamate is found as the main reaction product. The most important byproduct is diphenylurea. In a few tests a little aniline is found as well as some previously undescribed products.

The catalytic runs are performed in two different ways: (I) by in situ generation of the catalyst from Pd(acetate)$_2$, 16 equiv of one of the ligands, and 10 equiv of *p*-toluenesulfonic acid as cocatalyst; (II) by using a presynthesized complex, either of the type Pd(ligand)$_2$(OTf)$_2$ or Pd(ligand)Cl(OTf), together with 5 equiv of free ligand.

Both methods yield Pd black to some extent at the end of each run. To make sure that we are working with a homogeneous catalyst system, several known tests have been performed.[21,22] Starting from a truly heterogeneous system, using Pd/C instead of Pd(acetate)$_2$ under the standard conditions for the acetate systems, a conversion into carbamate of 67% was reached with Me-bpy (**4d**) as ligand. The experiment was repeated with addition of metallic mercury to the reaction mixture, which is known to poison heterogeneous catalyst systems. The catalyst system used here, however, still showed activity, although the conversion into carbamate was lowered to 21%. This could indicate that, although started from a heterogeneous system, the active species is a homogeneous compound, in situ generated from Pd/C, the Me-bpy ligand (**4d**), and the cocatalyst *p*-tsa, but the generation of the homogeneous catalyst is slowed down by mercury on the solid palladium. This view is consistent with the results of Mestroni et al.[5–7] They found typical charge transfer bands in the visible spectra of their reaction mixtures at the end of the catalytic runs, although they started with a heterogeneous catalyst system (Pd/C, phenanthroline, and 2,4,6-trimethylbenzoic acid). As the charge transfer bands shift with a change of the ligand, these bands are ascribed to some active, homogeneous palladium complex, which is probably in equilibrium with the supported metal.

(20) Rund, J. V. *Inorg. Chem.* **1968**, *7*, 24.
(21) Whiteside, G. M.; Hackett, M.; Brainard, R. L.; Lavallege, J-P. P. M.; Sowinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. N.; Staudt, E. M. *Organometallics* **1955**, *4*, 1819.
(22) Hamlin, J. E.; Hirai, K.; Millan, A.; Maitlis, P. M. *J. Mol. Catal.* **1980**, *7*, 543.

Table 6. Results of the Reductive Carbonylation of Nitrobenzene in Methanol with Pd(acetate)$_2$/Ligand (4a–e)/*p*-tsa under Standard Conditions[a]

ligand	conversion into carbamate (%) (σ; n)[b]	carbamate:urea ratio (σ; n)[b]
none	0	
F_3C-bpy (**4a**)	0	
Cl-bpy (**4b**)	0	
bpy (**4c**)	56 (σ = 4.8; n = 3)	6.7 (σ = 0.6; n = 3)
Me-bpy (**4d**)	71 (σ = 2.2; n = 3)	9.9 (σ = 4.2; n = 3)
MeO-bpy (**4e**)	53 (σ = 4.1; n = 3)	7.9 (σ = 0.3; n = 3)

[a] See Experimental Section on Catalysis for the standard conditions. [b] σ = standard deviation; n = number of experiments.

Addition of metallic mercury to the originally homogeneous system consisting of Pd(acetate)$_2$/16 equiv of MeO-bpy (**4e**)/5 equiv of *p*-tsa also resulted in a decrease of the conversion into carbamate, from 79% without Hg to 14% with Hg. This decrease can be explained by the fact that Hg facilitates the decomposition of the homogeneous catalyst system into Pd black. Blocking its way back into the solution shifts the equilibrium between Pd black and palladium in solution. This idea is supported by a test in which the Hg of the just described experiment was filtered over Celite filter agent at the end of the run and the filtrate was used again. Without addition of fresh catalyst renewed conversion of nitrobenzene into carbamate (another 9%) was obtained, meaning that still a part of the active species had remained in solution. Confirmation of an equilibrium between an active species in solution and inactive Pd black stems from a test in which filtrate and residue from a reaction with Pd(acetate)$_2$, 16 equiv of Me-bpy (**4d**), and 4 equiv of *p*-tsa were both used again after 1.5 h of original reaction. While the filtrate gave considerable extra conversion (from 43 to 83%), no conversion at all was found for the residue. The low grade of dispersion of the Pd black formed as residue probably prevented the formation of new, active palladium complexes in spite of the addition of new ligand and *p*-tsa.

On the basis of these combined results it seems likely that the systems used in this study do work as homogeneous catalysts, although they partly decompose into Pd black. This decomposition might occur via Pd(0) (monometallic or as clusters), which is capable of reentering the catalytic cycle.

Pd(acetate)$_2$, a Bipyridyl Ligand, and *p*-Toluenesulfonic Acid. In the catalytic runs of type I, with the in situ generated catalyst, the bipyridyl ligands with R = F_3C, Cl, H, Me, and MeO have been tested for the influence of the donating capacity of the ligand on the catalytic activity and selectivity. Me_2N-bpy (**4f**) has not been used in this system because of the presence of *p*-tsa, which will probably protonate the amine group. The experimental conditions have deliberately been chosen to yield a conversion into carbamate of around 50% for the bpy ligand **4c** as the reference. All experiments have been conducted in triplicate, because partial decomposition of the catalyst system into Pd black causes a decrease of the reproducibility of the catalytic runs. The results of the in situ generated catalyst systems from Pd(acetate)$_2$, ligand, and *p*-tsa are shown in Table 6.

Electron-withdrawing substituents (F_3C and Cl) on the bipyridyl skeleton are obviously disastrous for the catalytic activity. No conversion at all is found with

F_3C-bpy (**4a**) and Cl-bpy (**4b**). Neither carbamate nor any other products are found; only nitrobenzene is recovered. In the case of the Cl-bpy ligand (**4b**) as well as for F_3C-bpy (**4a**), a large amount of Pd black is observed at the end of each catalytic run. Careful examinations of the ^{1}H-NMR spectra of the reaction mixtures at the end of the catalytic runs reveal that both ligands remain intact. Their ^{1}H-NMR signals are shifted 0.05−0.1 ppm, which could indicate that the ligands are partly protonated. There is always an excess of ligand compared to acid, so this protonation could never be complete, resulting in averaged ^{1}H-NMR signals. The small ^{1}H-NMR shifts can also be easily explained by a kind of solvent effect, caused by the relatively large amount of nitrobenzene present in the NMR solutions. Due to the electron-withdrawing effect of the substituents these ligands become weakly coordinating, as was already observed in the attempts to prepare Pd(F_3C-bpy)Cl(OTf) and Pd(F_3C-bpy)$_2$(OTf)$_2$. The lack of activity could probably be explained by rapid decomposition of the catalyst caused by the weakly coordinating properties of the ligands. Although the Cl-bpy complexes turn out to be more stable than the F_3C-bpy complexes in the synthesis, they are apparently not sufficiently stable under the reaction conditions of the catalytic experiments.

bpy (**4c**), Me-bpy (**4d**), and MeO-bpy (**4e**) all give a reasonable conversion. At first sight an optimum is found at Me-bpy (**4d**) with 71% conversion into carbamate. The standard deviation for this ligand is smaller than the ones for bpy (**4c**) and MeO-bpy (**4e**). This could indicate that the systems with Me-bpy (**4d**) are the most stable systems applied in this sequence. The selectivity also shows its optimum value at the Me-bpy ligand (**4d**). With this ligand most carbamate is formed with respect to the urea byproduct. No other byproducts are observed. The high value for the standard deviation on the selectivity with the Me-bpy (**4d**) system, however, slightly enfeebles this result.

The first sight conclusion that Me-bpy (**4d**) gives the most active and selective catalyst, should be modified by taking into account the effect of the acidity of the reaction mixture on the activity and selectivity. The acidic cocatalyst *p*-tsa is needed to replace the acetate anions by noncoordinating tosylate anions in order to establish the desired overall electrophilicity of the complex. The second role of the acid might be to act as a source for protons needed at some stage of the catalytic cycle. Osborn et al. have isolated a metallacyclic Pd complex which may be an intermediate in the catalytic cycle.[23] On addition of H^+ an increase in the rate of conversion of this complex into the final carbamate is observed. It is suggested that the required ring opening of the metallacycle to free the carbamate is catalyzed by a proton. Thus, the presence of protons is essential for the product formation.

However, a side effect of the acidic cocatalyst is protonation of the bipyridyl ligands. This results in a complicated competition between Pd^{2+} and H^+ for the ligand. As a higher electron-donating capacity increases the basicity of the ligand, it was expected that MeO-bpy (**4d**) would be most prone toward protonation at a certain amount of *p*-tsa in the reaction mixture. On varying the amount of *p*-tsa such a trend was indeed found. The optimal activity with MeO-bpy (**4e**) was found at a *p*-tsa:Pd ratio of 5. The conversion into carbamate had increased from 53% under standard conditions up to 73% ($\sigma = 7.8$; $n = 3$). The selectivity also improved. The carbamate:urea ratio went up from 7.9 to 10.3 ($\sigma = 3.4$; $n = 3$). With bpy (**4c**) as ligand the effect of the acidity of the reaction mixture is less pronounced. In the range 2−16 for *p*-tsa:Pd the conversion remains more or less constant within the observed scatter ($\sigma \approx 5$). With Me-bpy (**4d**) the optimal activity was found at a *p*-tsa:Pd ratio of 10, exactly the ratio that was used under standard conditions.

For all three active ligands, bpy (**4c**), Me-bpy (**4d**), and MeO-bpy (**4e**), a sharp decrease of the activity is observed if *p*-tsa:Pd is lowered below 2. Obviously, two molecules of *p*-tsa are needed to replace the two acetate anions, so a minimal amount of acid is required for a reasonable conversion.

As for the selectivity it can be remarked in general that the carbamate:urea ratio decreases with an enhancement of the *p*-tsa:Pd ratio. This might be due to the fact that more *p*-tsa in the reaction mixture induces a larger amount of water, as *p*-tsa is used as monohydrate. Water favors the production of diphenylurea, because it enables the formation of the required aniline. This was tested by addition of water (1 mL) to the reaction mixture with Pd(acetate)$_2$, bpy (**4c**), and *p*-tsa under standard conditions. With this relatively high amount of water complete decomposition of the catalyst into Pd black was observed and only a trace of carbamate could be detected. The conversion of nitrobenzene into aniline, however, had increased to 25%. Yet, water turned out not to be the only source of hydrogen for the formation of aniline. Addition of trimethyl orthoformate to take away the water[24] in a standard reaction mixture with Pd(acetate)$_2$, bpy (**4c**), and *p*-tsa increased the carbamate:urea ratio from 6.7 to 13 but did not completely suppress the urea production. This suggests that methanol might also act as a hydrogen source for the reduction of nitrobenzene into aniline, which is in agreement with the experiments by Liu and Cheng.[25] On using a $Rh(CO)_4^-$ catalyst in the reductive carbonylation of nitrobenzene in 2-butanol, they found, next to the desired carbamate, formation of aniline and 2-butanone in a 1:1 molar ratio. Analogously, using methanol as reducing agent would yield formaldehyde, which is probably converted into dimethoxymethane or CO and H_2.

Except for low carbamate:urea ratios at high *p*-tsa:Pd values, the selectivity is further reduced by formation of previously unpublished side products, which will be discussed in more detail in the next paragraph. Use of 1,2-dimethoxybenzene as an internal standard has enabled us to establish the total amount of these unknown side products at 15%.

In view of the results on variation of the *p*-tsa:Pd-ratio, Me-bpy (**4d**) and MeO-bpy (**4e**) appear to give the same activity and selectivity, each under their own optimal conditions. The reproducibility for MeO-bpy (**4e**), however, is somewhat lower than that for Me-bpy (**4d**), which could be due to the relatively low amount

(23) Leconte, P.; Metz, F.; Mortreux, A.; Osborn, J. A.; Paul, F.; Petit, F.; Pillot, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1616.

(24) Van Leeuwen, P. W. N. M.; Groeneveld, W. L. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 145.

(25) Liu, C. H.; Cheng, C. H. *J. Organomet. Chem.* **1991**, *420*, 119.

Table 7. Results of the Reductive Carbonylation of Nitrobenzene in Methanol with Pd(acetate)$_2$/Ligand (4a–e)/ *p*-tsa over a Reaction Period of 16 h[a]

ligand	conversion into carbamate (%)	carbamate:urea ratio
F_3C-bpy (**4a**)	0	
Cl-bpy (**4b**)	0	
bpy (**4c**)	99	500
Me-bpy (**4d**)	99+	∞
MeO-bpy (**4e**)	93	100

[a] See Experimental Section on Catalysis for further conditions.

of *p*-tsa used in the optimum for MeO-bpy (**4e**). Under all conditions the bpy ligand (**4c**) is the least active and selective.

On prolongation of the reaction time to 16 h still no conversion is found with F_3C-bpy (**4a**) or Cl-bpy (**4b**). This emphasizes that the catalyst has completely decomposed before it can show any activity. Again the ligands are found to remain intact. With bpy (**4c**) and Me-bpy (**4d**) no nitrobenzene is detected anymore at the end of the 16 h runs. The carbamate:urea ratio for bpy (**4c**) is high (500). In the case of Me-bpy (**4d**) no urea is found at all. The system containing MeO-bpy (**4e**) still shows a small amount of nitrobenzene after 16 h. A conversion into carbamate of 93% is measured with a carbamate:urea ratio of 100. The data for the 16 h runs are summarized in Table 7. The fact that MeO-bpy (**4e**) does not reach complete conversion of the substrate could be due to the high *p*-tsa:Pd-ratio (10) that is used, since reactions over a period of 2 h had already shown that this makes the reaction mixture too acidic for MeO-bpy (**4e**) to work optimally. The strongly increased carbamate:urea ratios compared to the values found after 2 h can be explained by degradation of the urea byproduct into carbamate and aniline. Separate experiments have proven that diphenyl urea is thermally degraded into methyl *N*-phenylcarbamate and aniline. This methanolysis occurs more rapidly, however, in the presence of a palladium catalyst. Starting from a mixture of nitrobenzene and diphenylurea in a molar ratio of 10:1 in the presence of Pd(acetate)$_2$, bpy (**4c**), and *p*-tsa under standard conditions yields an overall conversion of 38% of diphenylurea into carbamate after 2 h. This results in a corrected carbamate:urea ratio of 14, which is twice as high as the normal value. This means that even in the presence of the nitro substrate the urea side product can be converted into the carbamate. The carbamate itself turned out to be thermally stable as well as under the influence of the palladium catalyst.

On prolongation of the reaction time some of the previously unknown side products were also found again, although the *p*-tsa:Pd ratio was kept at a value of 10. Their structures will also be discussed in the next paragraph.

Characterization of the Unknown Side Products. The previously unpublished side products, which were formed at a high *p*-tsa:Pd ratio or on prolongation of the reaction time, could be partly identified by means of LC–MS measurements. Methoxy substituents were found on the phenyl rings of aniline, carbamate, and urea derivatives. To determine the substitution pattern of the side products, the various possibilities were prepared in a noncatalytic way according to a modified literature procedure[26] by reacting the methoxyphenyl isocyanate with aniline or a methoxyaniline in a suitable solvent. As no direct route could be found for the synthesis of the methyl *N*-(methoxyphenyl)carbamates the urea preparation was conveniently adapted by reacting the methoxyphenyl isocyanate with methanol. Co-injection of the thus prepared compounds with samples of the reaction mixtures on the HPLC showed that the methoxy substituents were placed at positions C(2) and C(4), but never at C(3). For the urea side product it was even possible to detect the nonsymmetric *N*-(2-methoxyphenyl)-*N'*-(4-methoxyphenyl)urea. The relative product distribution for these methoxy-substituted side products is given in Table 8. A normal nucleophilic aromatic substitution reaction seems rather unlikely as the mechanism, since in this reaction a H atom is replaced instead of the NO_2 function, which is of course the better leaving group. Stern et al., however, have reported a direct displacement of hydrogen from nitrobenzene using amines or amides as nucleophiles.[27,28] Yet in contrast to our acidic reaction mixtures, their reactions require alkaline conditions. Also the oxidation of the σ-complex, primarily formed by the nucleophilic attack, into an O analogue of the R–N=C–R′ intermediate obtained with the amines or amides is hard to envisage. A second argument against nucleophilic aromatic substitution is the absence of methoxynitrobenzene although nitrobenzene can be recovered in substantial amounts. The nitro substrate would be expected to be the most prone toward the substitution reaction under influence of the strongly electron-withdrawing nitro group. Palladium-catalyzed C–H activation of the aromatic ring could be a possibility, as the substitution did not occur in the absence of Pd. Finally, only one yet unidentified side product remains, which amounts to approximately 1–2% of the total product distribution.

Table 8. Product Distribution of the Methoxy-Substituted Side Products at a High *p*-tsa:Pd Ratio[a]

compd	rel amt
N,*N'*-bis(4-methoxyphenyl)urea	1
N-(2-methoxyphenyl)-*N'*-(4-methoxyphenyl)urea	1
N,*N'*-bis(2-methoxyphenyl)urea	3
N-(2-methoxyphenyl)-*N'*-phenylurea	3
2-methoxyaniline	4
methyl *N*-(2-methoxyphenyl)carbamate	4
N-(4-methoxyphenyl)-*N'*-phenylurea	8
methyl *N*-(4-methoxyphenyl)carbamate	29

[a] Catalyst system: Pd(acetate)$_2$, bpy (**4c**), *p*-tsa; *p*-tsa:Pd = 16.

On prolongation of the reaction time to 16 h at a *p*-tsa:Pd ratio of 10 some of the methoxy-substituted side products were found again. Methyl *N*-(2-methoxyphenyl)carbamate and methyl *N*-(4-methoxyphenyl)-carbamate could be detected in approximately the same ratio as after the short reaction at a high *p*-tsa:Pd ratio. However, no substituted urea derivatives were observed, indicating that these side products are probably also degraded by methanolysis.

Pd(ligand)$_2$(OTf)$_2$ or Pd(ligand)Cl(OTf) and a Bipyridyl Ligand. Catalytic experiments of type II with Pd(ligand)$_2$(OTf)$_2$ have been conducted for Cl-bpy (**4b**), bpy (**4c**), Me-bpy (**4d**), MeO-bpy (**4e**), and Me_2N-bpy (**4f**). In this type of catalytic run no variations are

(26) Etter, M. C.; Urbanczyk-Lipkowska, Z.; Zia-Ebrahimi, M.; Panunto, T. W. *J. Am. Chem. Soc.* **1990**, *112*, 8415.
(27) Stern, M. K.; Hileman, F. D.; Bashkin, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 9237.
(28) Stern, M. K.; Cheng, B. K. *J. Org. Chem.* **1993**, *58*, 6883.

Table 9. Results of the Reductive Carbonylation of Nitrobenzene in Methanol with Pd(ligand)$_2$(OTf)$_2$(6b−f)/Ligand (4a−f) under Standard Conditions[a]

ligand	conversion into carbamate (%) (σ; n)[b]	carbamate:urea ratio (σ; n)[b]
Cl-bpy (**4b**)	0	
bpy (**4c**)	41 (σ = 8.8; n = 3)	12.1 (σ = 1.8; n = 3)
Me-bpy (**4d**)	33 (σ = 4.6; n = 3)	12.1 (σ = 4.0; n = 3)
MeO-bpy (**4e**)	30 (σ = 0.7; n = 3)	12.2 (σ = 0.5; n = 3)
Me$_2$N-bpy (**4f**)	31 (σ = 1.5; n = 3)	7.6 (σ = 0.8; n = 3)

[a] See Experimental Section on Catalysis for the standard conditions. [b] σ = standard deviation; n = number of experiments.

induced by the differences in the basicity of the ligands, as there is no need to add *p*-tsa. Because the presynthesized complexes give a higher conversion than the in situ generated catalysts from Pd(acetate)$_2$, ligand, and *p*-tsa, the ligand:Pd ratio has been lowered from 16 to 5. The results over a reaction period of 2 h are collected in Table 9.

Again with an electron-withdrawing substituent the catalyst turns out to be completely inactive. No conversion at all is observed with Cl-bpy (**4b**); only nitrobenzene, the ligand, and a large amount of Pd black are recovered. Catalysts with bpy (**4c**) as well as with the ligands substituted with an electron-donating group all show activity. In this case, however, the catalyst system based on bpy (**4c**) yields the highest conversion. The reproducibility for the substituted bipyridyl ligands is far higher than for bpy (**4c**), especially in the case of MeO bpy (**4e**) and Me$_2$N-bpy (**4f**). This might indicate that, although less active, the catalyst systems based on these ligands are more stable than the one from Pd(bpy)$_2$(OTf)$_2$ (**6c**)/bpy (**4c**).

Looking into the selectivity, a different trend is observed. Now the catalysts with bpy (**4c**), Me-bpy (**4d**), and MeO-bpy (**4e**) yield the same selectivity. Only the Me$_2$N-bpy (**4f**) catalyst system shows a somewhat lower selectivity. Compared to the in situ generated catalysts from Pd(acetate)$_2$, a bipyridyl ligand, and *p*-tsa, the presynthesized complexes appear to be a bit more selective. This result, as well as the higher activity for the presynthesized complexes, might be caused by the absence of acetic acid in the reaction mixture. Acetic acid is formed in the exchange of the coordinating acetate anions for the noncoordinating tosylates. It might of course also protonate part of the bipyridyl ligands, thus lowering the activity of the catalyst system. Its presence might influence the selectivity by facilitating the formation of aniline, which probably leads to the production of the urea byproduct.

Over a reaction period of 16 h the catalyst with Cl-bpy (**4b**) still shows no conversion, which was also observed for the in situ generated catalysts of type I. Again decomposition of the catalyst is most likely the reason for this absolute inactivity. With the other ligands the conversion is almost complete after 16 h; only traces of nitrobenzene are recovered. The conversion into carbamate varies between 92 and 98% and the carbamate:urea ratio is high (118 for bpy (**4c**)) to even very high (1000 for MeO-bpy (**4e**) or Me$_2$N-bpy (**4f**)). The exact figures are shown in Table 10. Next to the urea byproduct also traces of aniline and the methoxy-substituted carbamates are found. The explanation for the high carbamate:urea ratios lies again in the methanolysis of the urea. Compared to the in situ generated

Table 10. Results of the Reductive Carbonylation of Nitrobenzene in Methanol with Pd(ligand)$_2$(OTf)$_2$ (6b−f)/Ligand (4b−f) over a Reaction Period of 16 h[a]

ligand	conversion into carbamate (%)	carbamate:urea ratio
Cl-bpy (**4b**)	0	
bpy (**4c**)	98	118
Me-bpy (**4d**)	92	250
MeO-bpy (**4e**)	96	1000
Me$_2$N-bpy (**4f**)	99$^+$	1000

[a] See Experimental Section on Catalysis for further conditions.

Table 11. Results of the Reductive Carbonylation of Nitrobenzene in Methanol with Pd(ligand)Cl(OTf) (7b−d)/Ligand (4b−d) under Standard Conditions as Well as over a Reaction Period of 16 h[a]

ligand	reacn time (h)	conversion into carbamate (%) (σ; n)[b]	carbamate:urea ratio (σ; n)[b]
Cl-bpy (**4b**)	2	0	
	16	0	
bpy (**4c**)	2	30 (σ = 4.5; n = 3)	7.0 (σ = 1.9; n = 3)
	16	93	111
Me-bpy (**4d**)	2	28 (σ = 1.9; n = 3)	7.4 (σ = 2.0; n = 2)
	16	92	∞

[a] See Experimental Section on Catalysis for exact conditions. [b] σ = standard deviation; n = number of experiments.

systems, however, the reaction mixtures are much cleaner.

Catalytic experiments of type II have also been performed with the second type of presynthesized complexes Pd(ligand)Cl(OTf) (**7b−d**). As we have only been able to prepare these complexes with Cl-bpy (**4b**), bpy (**4c**), and Me-bpy (**4d**), there is less material for comparison. The experiments have been conducted with 5 equiv of ligand to Pd, to use the same conditions as with the Pd(ligand)$_2$(OTf)$_2$ complexes. Table 11 shows the catalytic activities and selectivities under standard conditions as well as over a prolonged reaction period.

Once again it is confirmed that the electron-withdrawing chloride substituent has a severe negative effect on the activity of the catalyst. Between the bpy (**4c**) and Me-bpy (**4d**) systems little difference is found. Compared to the runs with Pd(ligand)$_2$(OTf)$_2$/ligand the activity is somewhat lower for both ligands. This is in agreement with the studies of Drent,[10] claiming that there should only be noncoordinating anions present.

Prolongation of the reaction period to 16 h yields almost the same picture as for the Pd(ligand)$_2$(OTf)$_2$ systems. bpy (**4c**) and Me-bpy (**4d**) give 93% and 92% conversion into carbamate, respectively. Only traces of nitrobenzene are recovered. The carbamate:urea ratio is already high for bpy (**4c**) (111) but in the case of Me-bpy (**4d**) no urea is detected at all. Both systems, however, do yield a small amount of aniline and methyl *N*-(2-methoxyphenyl)carbamate as well as methyl *N*-(4-methoxyphenyl)carbamate.

Conclusions

On the basis of the combined results the best catalyst system for the reductive carbonylation of nitrobenzene appears to be a presynthesized complex with bpy (**4c**) as ligand and only noncoordinating anions: Pd(bpy)$_2$(OTf)$_2$ (**6c**). Within the series of substituted bipyridyl ligands a ligand with a higher donating capacity than bpy (**4c**) evidently does not increase the overall conversion.

Use of the catalyst systems under more extreme conditions yields a substantial amount of carbamates, urea derivatives, and anilines with methoxy substituents at their phenyl rings.

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, and DMF, and acetonitrile from CaH_2 (5 g/L), chloroform from $CaCl_2$, hexanes from sodium/benzoylbiphenyl, and diethyl ether from sodium/benzophenone.

The 4,4′-disubstituted-2,2′-bipyridine ligands with R = chloro and methoxy were prepared according to a modified literature procedure.[12,29,30]

The coupling of 2-chloro-4-(trifluoromethyl)pyridine to form 4,4′-bis(trifluoromethyl)-2,2′-bipyridine was based on the method of Tiecco et al.[15]

Pd(benzonitrile)$_2Cl_2$ was synthesized as described in the literature.[31] Pd(acetonitrile)$_2Cl_2$ was prepared analogously to Pd(benzonitrile)$_2Cl_2$ in refluxing acetonitrile.

The methoxy-substituted carbamate and urea compounds were prepared according to a modified literature procedure, involving the reaction of the aryl isocyanate with methanol or the appropriate aniline.[26]

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 Perkin-Elmer 283 and Nicolet 510 m FT-IR spectrophotometers. ^{1}H-NMR spectra were obtained on a Bruker AMX 300 instrument, while ^{19}F-NMR data were measured on a Bruker AC 100. Chemical shifts are given in ppm. TMS (^{1}H NMR) and $CFCl_3$ (^{19}F NMR) were used as references with $CDCl_3$ or DMSO-d_6 as the internal standard. Elemental analyses were carried out by the Department of Micro Analysis, University of Groningen. Melting points were measured on a Gallenkamp melting point apparatus.

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 used as purchased. The results were analyzed by HPLC on a Gilson HPLC apparatus, using a Dynamax C_{18} column (eluent 30% water in methanol). The unknown side products were analyzed by means of LC−MS with a Dynamax C_{18} column and a Finnigan MAT 900 mass spectrometer equipped with a Finnigan MAT particle-beam interface in the electron impact mode as well as with a Finnigan MAT TSQ-70 triple quadrupole mass spectrometer equipped with a Finnigan MAT thermospray interface in the discharge-on mode.

Synthesis. 2,2′-Bipyridine 1,1′-Dioxide (bpy *N*-Oxide) (1). To a solution of 2,2′-bipyridine (5 g, 32 mmol) in 5 mL of acetic acid was added dropwise 30 mL of peracetic acid (32 wt % in dilute acetic acid, 126 mmol). The addition of the peracetic acid was performed at such a rate that the temperature was kept in the range 70−80 °C. The solution was stirred at 35 °C during 66 h, after which the excess of peracetic acid was destroyed with 9 mL of dimethyl sulfide. The solvent was evaporated, and the crude product was stirred in 200 mL of refluxing acetone for 3 h. The product was filtered off and dried under vacuum. Yield: 5.8 g of white powder (30.8 mmol, 96%). IR (KBr): 1250 (s) (N−O) cm^{-1}. ^{1}H NMR (D_2O): δ 8.46 (d, 2H, $H_6 + H_{6'}$), 7.8 (m, 6H, $H_5 + H_{5'}$, $H_4 + H_{4'}$, $H_3 + H_{3'}$) ppm.

4,4′-Dinitro-2,2′-bipyridine 1,1′-Dioxide (O_2N-bpy *N*-Oxide) (2). A solution of bpy *N*-oxide (**1**) (1.13 g, 6 mmol) in 4.8 mL of concentrated sulfuric acid was cooled to 0 °C and 1.9 mL of fuming nitric acid was added. The solution was stirred at 100 °C for 22 h. The solution was cooled to room temperature and poured onto 15 g of ice (−20 °C). The precipitate was filtered off and washed successively with 10 mL of a saturated aqueous Na_2CO_3 solution and 2 × 10 mL of H_2O. The product was treated twice with 5 mL of toluene, which was removed under vacuum. Yield: 0.7 g of yellow powder (2.5 mmol, 41%). IR (KBr): 1520 (s) (NO_2), 1350 (s) (NO_2), 1290 (s) (N−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.55 (d, 2H, $H_3 + H_{3'}$), 8.41 (d, 2H, $H_6 + H_{6'}$), 8.26 (dd, 2H, $H_5 + H_{5'}$) ppm.

4,4′-Dichloro-2,2′-bipyridine 1,1′-Dioxide (Cl-bpy *N*-Oxide) (3b). A suspension of 800 mg of O_2N-bpy *N*-oxide (**2**) (2.9 mmol) in 48 mL of acetyl chloride was refluxed under N_2 for 3 h. The solid product was filtered off, washed with 50 mL of diethyl ether, and dried under vacuum. Yield: 596 mg of pale yellow powder (2.3 mmol, 80%). IR (KBr): 1260 (m) (N−O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.27 (d, 2H, $H_6 + H_{6'}$), 7.73 (d, 2H, $H_3 + H_{3'}$), 7.36 (d, 2H, $H_5 + H_{5'}$) ppm.

4,4′-Dimethoxy-2,2′-bipyridine 1,1′-Dioxide (MeO-bpy *N*-Oxide) (3e). O_2N-bpy *N*-oxide (**2**) (1.14 g) was added to a freshly prepared solution of sodium methoxide (14 mmol) in 33 mL of methanol. The reaction mixture was refluxed during 3.5 h. The solution was neutralized with concentrated sulfuric acid. The precipitate was filtered off and washed with 3 × 10 mL of methanol. The combined methanol fractions were concentrated under vacuum. The crude product was refluxed in 150 mL of chloroform for 2 h. The remaining precipitate was filtered off. After treatment with Norit the solution was concentrated to ca. 70 mL. Hexanes (80 mL) was added, and the mixture was kept at −20 °C overnight. The precipitate was filtered off and dried under vacuum. Yield: 0.81 g of yellow powder (3.2 mmol, 80%). IR (KBr): 1220 (m) (C−O), 1205 (s) (N−O), 1010 (s) (C−O) cm^{-1}. ^{1}H NMR (CD_3OD): δ 8.32 (d, 2H, $H_6 + H_{6'}$), 7.36 (d, 2H, $H_3 + H_{3'}$), 7.26 (dd, 2H, $H_5 + H_{5'}$), 3.94 (s, 6H, CH_3) ppm.

4,4′-Bis(trifluoromethyl)-2,2′-bipyridine (F_3C-bpy) (4a). A solution of 1.18 g of nickel(II) chloride hexahydrate (5 mmol) and 5.2 g of triphenylphosphine (20 mmol) in 25 mL of DMF was stirred under N_2 at 60 °C for 2 h. At this temperature 0.32 g of zinc powder (5 mmol) was added. After another 2 h 0.91 g of 2-chloro-4-(trifluoromethyl)pyridine (5 mmol) was added. The reaction mixture was stirred at 60 °C for 2 h, after which it was poured into 100 mL of 12.5% aqueous ammonia. The ammonia solution was extracted with 3 × 50 mL of diethyl ether. The combined ether fractions were washed with 3 × 20 mL of water. After drying over $MgSO_4$ the solvent was evaporated. The crude product was purified by column chromatography, using 20% hexanes in dichloromethane as eluent. Yield: 0.24 g of white powder (0.83 mmol, 33%). IR (KBr): 1173 (m) (C−F) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.90 (d, 2H, $H_6 + H_{6'}$), 8.75 (s, 2H, $H_3 + H_{3'}$), 7.60 (d, 2H, $H_5 + H_{5'}$) ppm. ^{19}F NMR (DMSO-d_6): δ −63.17 (s, CF_3) ppm. Anal. Calcd for $C_{12}H_6F_6N_2$: C, 49.33; H, 2.07; N, 9.59. Found: C, 49.50; H, 2.20; N, 9.26. Mp: 75−76 °C.

4,4′-dichloro-2,2′-bipyridine (Cl-bpy) (4b). A suspension of 843 mg of O_2N-bpy *N*-oxide (**2**) (3 mmol) in 50 mL of acetyl chloride (703 mmol) was refluxed under N_2 for 3 h. The reaction mixture was cooled to 0 °C, and 8.4 mL of phosphorus trichloride (96 mmol) was added. The suspension was refluxed under N_2 for another 3 h. After cooling to room temperature, the reaction mixture was poured into 150 mL of ice water and made alkaline with a saturated sodium hydroxide solution. The precipitate was filtered off and dissolved in 100 mL of dichloromethane. The solution was dried over $MgSO_4$, and the solvent was removed in vacuum. The crude product was purified by column chromatography, using 1% methanol in

(29) Maerker, G.; Case, F. H. *J. Am. Chem. Soc.* **1958**, *80*, 2745.
(30) Anderson, S.; Constable, E. C.; Sheddon, K. R.; Turp, J. E.; Baggott, J. E.; Pilling, M. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2247.
(31) Kharash, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

dichloromethane as eluent. Recrystallization from ethanol/water yielded 0.5 g of white product (2.2 mmol, 73%). ^{1}H NMR (DMSO-d_6): δ 8.71 (d, 2H, $H_6 + H_{6'}$), 8.38 (d, 2H, $H_3 + H_{3'}$), 7.69 (dd, 2H, $H_5 + H_{5'}$) ppm. Mp: 126–127 °C.

4,4'-Dimethoxy-2,2'-bipyridine (MeO-bpy) (4e). A suspension of 0.81 g of MeO-bpy *N*-oxide (**3e**) (3.2 mmol) in 35 mL of chloroform was cooled to 0 °C, and 5.6 mL of phosphorus trichloride (64 mmol) was added. The reaction mixture was refluxed for 3 h. The suspension was poured into 200 mL of ice water. The chloroform layer was washed with 2 × 50 mL of water. The combined water fractions were concentrated under vacuum to 100 mL, after which the solution was made alkaline with a saturated sodium hydroxide solution. The precipitate was filtered off and dissolved in 120 mL of dichloromethane. After treatment with Norit the solvent was evaporated. Recrystallization from refluxing ethanol yielded 0.48 g of pale pink product (2.2 mmol, 69%). IR (KBr): 1220 (m) (C–O), 1020 (s) (C–O) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.50 (d, 2H, $H_6 + H_{6'}$), 7.94 (d, 2H, $H_3 + H_{3'}$), 7.05 (dd, 2H, $H_5 + H_{5'}$), 3.92 (s, 6H, OCH_3) ppm. Mp: 167–168 °C.

4,4'-bis(dimethylamino)-2,2'-bipyridine (Me_2N-bpy) (4f). A suspension of 996.0 mg of Cl-bpy *N*-oxide (**3b**) (3.89 mmol) in 150 mL of DMF was refluxed under Ar for 40 h. The solvent was evaporated almost completely, and the resulting brown paste was dissolved in 100 mL of chloroform. Phosphorus trichloride (8.5 mL, 97 mmol) was added dropwise to the cooled solution (0 °C). The reaction mixture was refluxed for 3 h, after which it was poured into 250 mL of ice water. The chloroform layer was washed with 2 × 75 mL of water. The combined water layers were concentrated under vacuum to 100 mL and made alkaline with a saturated sodium hydroxide solution. The resulting precipitate was filtered off and purified by column chromatography, using 1% triethylamine and 10% methanol in dichloromethane as eluent. Recrystallization from water/methanol (1.5:1 v/v) yielded 212.5 mg of beige product (0.88 mmol, 23%). IR (KBr): 1069 (m) (C–N) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.21 (d, 2H, $H_6 + H_{6'}$), 7.68 (d, 2H, $H_3 + H_{3'}$), 6.65 (dd, 2H, $H_5 + H_{5'}$), 3.03 (s, 12H, CH_3) ppm. Anal. Calcd for $C_{14}H_{18}N_4 \cdot H_2O$: C, 64.59; H, 7.75; N, 21.52. Found: C, 64.29; H, 7.11; N, 21.01. Mp: 235–236 °C.

Pd(F_3C-bpy)Cl_2 (5a). A solution of 83.6 mg of F_3C-bpy (**4a**) (0.29 mmol) in 5 mL of acetone was added dropwise to a solution of 100 mg of Pd(benzonitrile)$_2Cl_2$ (0.26 mmol) in 10 mL of acetone. The reaction mixture was stirred for 3 h, after which 30 mL of hexanes was added. The solvents were removed by decantation, and the precipitate was washed with 2 × 40 mL of hexanes. The product was dried under vacuum. Yield: 111 mg of yellow powder (0.23 mmol, 89%). IR (KBr): 1183 (s) (C–F), 413 (w) (Pd–N), 345 (w) (Pd–Cl) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.40 (d, 2H, $H_6 + H_{6'}$), 9.32 (s, 2H, $H_3 + H_{3'}$), 8.29 (d, 2H, $H_5 + H_{5'}$) ppm. ^{19}F NMR (DMSO-d_6): δ −62.87 (s, CF_3) ppm. Anal. Calcd for $C_{12}H_6Cl_2F_6N_2Pd \cdot H_2O$: C, 29.56; H, 1.65; N, 5.75. Found: C, 29.54; H, 1.71; N, 5.75.

Pd(Cl-bpy)Cl_2 (5b). Pd(Cl-bpy)Cl_2 (**5b**) was prepared analogously to Pd(F_3C-bpy)Cl_2 (**5a**). However, 64.6 mg of Cl-bpy (**4b**) (0.29 mmol) needed to be dissolved in 10 mL of acetone/dichloromethane (1:1 v/v). Yield: 100 mg of yellow powder (0.25 mmol, 95%). IR (KBr): 419 (w) (Pd–N), 327 (w) (Pd–Cl) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.06 (d, 2H, $H_6 + H_{6'}$), 8.93 (d, 2H, $H_3 + H_{3'}$), 8.01 (dd, 2H, $H_5 + H_{5'}$) ppm. Anal. Calcd for $C_{10}H_6Cl_4N_2Pd$: C, 29.85; H, 1.50; N, 6.96. Found: C, 30.43; H, 1.76; N, 6.70.

Pd(bpy)Cl_2 (5c). The synthesis of Pd(bpy)Cl_2 (**5c**) is analogous to the synthesis of Pd(F_3C-bpy)Cl_2 (**5a**) with the following modifications. bpy (**4c**) (222 mg, 1.43 mmol) was dissolved in 10 mL of acetone and added to a solution of 500 mg of Pd(benzonitrile)$_2Cl_2$ (1.3 mmol) in 25 mL of acetone. Hexanes (50 mL) was added for complete precipitation. The solvents were removed by decantation, and the precipitate was washed with 2 × 80 mL of hexanes. Yield: 450 mg of orange-yellow powder (1.26 mmol, 97%). IR (KBr): 415 (w) (Pd–N), 335 (w) (Pd–Cl) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.14 (d, 2H, $H_6 + H_{6'}$), 8.59 (d, 2H, $H_3 + H_{3'}$), 8.37 (dd, 2H, $H_4 + H_{4'}$), 7.82 (dd, 2H, $H_5 + H_{5'}$) ppm. Anal. Calcd for $C_{10}H_8Cl_2N_2Pd \cdot H_2O$: C, 36.01; H, 2.42; Cl, 21.26; N, 8.40. Found: C, 36.06; H, 2.49; Cl, 21.22; N, 8.33.

Pd(Me-bpy)Cl_2 (5d). The synthesis of Pd(Me-bpy)Cl_2 (**5d**) was performed according to the synthesis of Pd(F_3C-bpy)Cl_2 (**5a**). However, 264 mg of Me-bpy (**4d**) (1.43 mmol) was dissolved in 15 mL of acetone/dichloromethane (2:1 v/v). The solution was added to 500 mg of Pd(benzonitrile)$_2Cl_2$ (1.3 mmol) in 25 mL of acetone. Hexanes (50 mL) was added for complete precipitation, and the solvents were removed by decantation. The precipitate was washed with 2 × 80 mL of hexanes. Yield: 460 mg of yellow powder (1.26 mmol, 98%). IR (KBr): 421 (w) (Pd–N), 330 (w) (Pd–Cl) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.91 (d, 2H, $H_6 + H_{6'}$), 8.45 (d, 2H, $H_3 + H_{3'}$), 7.63 (dd, 2H, $H_5 + H_{5'}$), 2.51 (s, 6H, CH_3) ppm. Anal. Calcd for $C_{12}H_{12}Cl_2N_2Pd$: C, 39.86; H, 3.35; N, 7.75. Found: C, 40.03; H, 3.42; N, 7.66.

Pd(MeO-bpy)Cl_2 (5e). Pd(MeO-bpy)Cl_2 (**5e**) was prepared analogously to Pd(F_3C-bpy)Cl_2 (**5a**), except that 62.3 mg of MeO-bpy (**4e**) (0.29 mmol) needed to be dissolved in 10 mL of acetone/dichloromethane (1:4 v/v). Yield: 98 mg of orange powder (0.25 mmol, 95%). IR (KBr): 1220 (m) (C–O), 1020 (s) (C–O), 435 (w) (Pd–N), 325 (w) (Pd–Cl) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.86 (d, 2H, $H_6 + H_{6'}$), 8.20 (d, 2H, $H_3 + H_{3'}$), 7.39 (dd, 2H, $H_5 + H_{5'}$), 4.06 (s, 6H, OCH_3) ppm. Anal. Calcd for $C_{12}H_{12}Cl_2N_2O_2Pd$: C, 36.62; H, 3.07; N, 7.12. Found: C, 36.01; H, 3.15; N, 6.88.

Pd(Me_2N-bpy)Cl_2 (5f). Pd(Me_2N-bpy)Cl_2 (**5f**) was synthesized analogously to Pd(F_3C-bpy)Cl_2 (**5a**). However, 80.3 mg of Me_2N-bpy (**4f**) (0.33 mmol) was dissolved in 10 mL of acetone/dichloromethane (1:1 v/v) and added to a solution of 114.7 mg of Pd(benzonitrile)$_2Cl_2$ (0.30 mmol) in 10 mL of acetone. Yield: 117.1 mg of yellow powder (0.28 mmol, 93%). IR (KBr): 1066 (m) (C–N), 437 (w) (Pd–N), 315 (w) (Pd–Cl) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.42 (d, 2H, $H_6 + H_{6'}$), 7.43 (s, 2H, $H_3 + H_{3'}$), 6.80 (dd, 2H, $H_5 + H_{5'}$), 3.19 (s, 12H, CH_3) ppm.

Pd(Cl-bpy)$_2$(OTf)$_2$ (6b). A suspension of 79.4 mg of Pd(Cl-bpy)Cl_2 (**5b**) (0.2 mmol), 45.0 mg of Cl-bpy (**4b**) (0.2 mmol), and 88.9 mg of silver triflate (0.4 mmol) in 25 mL of acetone was stirred in the dark for 3 h. A suspension of Norit in 25 mL of methanol was added, and the reaction mixture was stirred for another 2 h. The precipitate was filtered off, and the filtrate was concentrated under vacuum to circa 5 mL. Diethyl ether (50 mL) was added, resulting in precipitation of the product. The solvents were decanted, and the precipitate was washed with 2 × 25 mL of diethyl ether. The product was dried under vacuum. Yield: 67 mg of yellow powder (0.073 mmol, 36%). IR (KBr): 1260 (s) (−SO_2O−), 1170 (m) (C–F), 413 (w) (Pd–N) cm^{-1}. ^{1}H NMR (acetone-d_6, 200 K): δ 9.20 (m, 4H, $H_6 + H_{6'}$, $H_3 + H_{3'}$), 8.40 (br, 2H, $H_5 + H_{5'}$) ppm. ^{19}F NMR (DMSO-d_6): δ −77.3 (s, CF_3) ppm. Anal. Calcd for $C_{22}H_{12}Cl_4F_6N_4O_6S_2Pd \cdot H_2O$: C, 30.28; H, 1.62; N, 6.42. Found: C, 30.08; H, 1.55; N, 7.04.

Pd(bpy)$_2$(OTf)$_2$ (6c). A suspension of 140 mg of Pd(bpy)Cl_2 (**5c**) (0.42 mmol), 65.5 mg of bpy (**4c**) (0.42 mmol), and 216 mg of silver triflate (0.84 mmol) in 200 mL of methanol was stirred in the dark for 3 h. After addition of Norit the suspension was stirred for another 2 h. The precipitate was filtered off, and the filtrate was concentrated under vacuum to ca. 20 mL. Diethyl ether (150 mL) was added, and the product precipitated. The solvents were decanted and the precipitate was washed with 2 × 50 mL of diethyl ether. The product was dried under vacuum. The product was crystallized by suspending it in refluxing methanol/acetone (1:1 v/v). Methanol was added until a clear solution was obtained. Storage overnight at 4 °C gave pale yellow crystals. Yield: 293 mg (0.41 mmol, 97%). IR (KBr): 1260 (s) (−SO_2O−), 1157 (s) (−SO_2O−), 1142 (s) (C–F), 417 (w) (Pd–N) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.84 (d, 2H, $H_6 + H_{6'}$), 8.77 (d, 2H, $H_3 + H_{3'}$), 8.56 (dd, 2H, $H_4 + H_{4'}$), 7.99 (dd, 2H, $H_5 + H_{5'}$) ppm. ^{19}F NMR (DMSO-d_6): δ −77.3 (s, CF_3) ppm. Anal. Calcd for

$C_{22}H_{16}F_6N_4O_6S_2Pd$: C, 36.86; H, 2.25; N, 7.82; S, 8.96. Found: C, 36.43; H, 2.36; N, 7.67; S, 8.60.

Pd(Me-bpy)$_2$(OTf)$_2$ (6d). Pd(Me-bpy)$_2$(OTf)$_2$ (**6d**) was prepared analogously to Pd(bpy)$_2$(OTf)$_2$ (**6c**) with the following modifications. Pd(Me-bpy)Cl$_2$ (**5d**) (76.5 mg, 0.21 mmol), 38.9 mg of Me-bpy (**4d**) (0.21 mmol), and 109 mg of silver triflate (0.42 mmol) were suspended in 100 mL of methanol. After reaction the suspension was filtered and concentrated to ca. 10 mL; subsequently, 100 mL of diethyl ether was added. The solvent was decanted, and the precipitate was washed with 2 × 50 mL of diethyl ether. The product was crystallized by suspending it in refluxing methanol/acetone (1:1 v/v). Methanol was added until a clear solution was obtained. The solution was kept overnight at −20 °C, giving orange crystals. Yield: 146 mg (0.19 mmol, 90%). IR (KBr): 1274 (s) (−SO_2O−), 1166 (s) (C−F), 419 (w) (Pd−N) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.65 (d, 2H, $H_6 + H_{6'}$), 8.64 (s, 2H, $H_3 + H_{3'}$), 7.82 (d, 2H, $H_5 + H_{5'}$) 2.64 (s, 6H, CH_3) ppm. ^{19}F NMR (DMSO-d_6): δ −77.3 (s, CF_3) ppm. Anal. Calcd for $C_{26}H_{24}F_6N_4O_6S_2Pd{\cdot}H_2O$: C, 39.48; H, 3.31; N, 7.08. Found: C, 39.83; H, 3.12; N, 7.09.

Pd(MeO-bpy)$_2$(OTf)$_2$ (6e). Pd(MeO-bpy)$_2$(OTf)$_2$ (**6e**) was synthesized according to the synthesis of Pd(bpy)$_2$(OTf)$_2$ (**6c**) except that 41.3 mg of Pd(MeO-bpy)Cl$_2$ (**5e**) (0.105 mmol), 22.7 mg of MeO-bpy (**4e**) (0.105 mmol), and 54 mg of silver triflate (0.21 mmol) were stirred in 50 mL of methanol. The filtrate was concentrated to ca. 5 mL, and 50 mL of diethyl ether was added. The resulting precipitate was washed with 2 × 25 mL of diethyl ether. Yield: 82 mg of light yellow powder (0.1 mmol, 93%). IR (KBr): 1274 (s) (−SO_2O−), 1220 (m) (C−O), 1142 (s) (C−F), 1020 (m) (C−O), 438 (w) (Pd−N) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.56 (d, 2H, $H_6 + H_{6'}$), 8.39 (s, 2H, $H_3 + H_{3'}$), 7.51 (d, 2H, $H_5 + H_{5'}$), 4.10 (s, 6H, OCH_3) ppm. ^{19}F NMR (DMSO-d_6): δ −77.3 (s, CF_3) ppm. Anal. Calcd for $C_{26}H_{24}F_6N_4O_{10}S_2Pd$: C, 37.31; H, 2.89; N, 6.69. Found: C, 37.37; H, 3.07; N, 6.65.

Pd(Me$_2$N-bpy)$_2$(OTf)$_2$ (6f). Pd(Me$_2$N-bpy)$_2$(OTf)$_2$ (**6f**) was prepared from freshly synthesized Pd(CH$_3$CN)$_4$(OTf)$_2$. Pd(CH$_3$CN)$_2$Cl$_2$ (129.8 mg, 0.5 mmol) was dissolved under Ar in 18 mL of acetonitrile. Silver triflate (256.94 mg, 1.0 mmol) was dissolved in 8 mL of acetonitrile, under Ar in the dark. The silver triflate solution was added to the solution of Pd(CH$_3$CN)$_2$Cl$_2$. The reaction mixture was stirred under Ar in the dark for 2.75 h. The yellow solution was decanted from the AgCl precipitate, and the solvent was evaporated. The resulting 284.3 mg of Pd(CH$_3$CN)$_4$(OTf)$_2$ (0.5 mmol) was dissolved in 15 mL of acetone and used for further synthesis immediately.

Me$_2$N-bpy (**4f**) (60.3 mg, 0.24 mmol) was dissolved under Ar in 8.5 mL of acetone. The Pd(CH$_3$CN)$_4$(OTf)$_2$ stock solution (3.8 mL, 0.033 M, 0.125 mmol) was added dropwise to the Me$_2$N-bpy (**4f**) solution. The reaction mixture was stirred under Ar for 1 h. The resulting precipitate was filtered off and washed with 2 × 10 mL of hexanes and dried under vacuum. Yield: 104.7 mg of yellow powder (0.12 mmol, 94%). IR (KBr): 1274 (s) (−SO_2O−), 1158 (s) (C−F), 1066 (w) (C−N) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.92 (br, 2H, $H_6 + H_{6'}$), 7.49 (s, 2H, $H_3 + H_{3'}$), 6.84 (br, 2H, $H_5 + H_{5'}$), 3.24 (s, 12H, CH_3) ppm.

Pd(Cl-bpy)Cl(OTf) (7b). Triflic acid (3.33 mL, 28.6 mmol) was added dropwise to 346 mg of Pd(Cl-bpy)Cl$_2$ (**5b**) (0.86 mmol). The solution was stirred under Ar at room temperature for 4 days. While the reaction mixture was cooled on an ice bath, 40 mL of diethyl ether was added. The product precipitated. The solvents were removed by decantation, and the precipitate was washed with 4 × 40 mL of diethyl ether. Yield: 164 mg of gray powder (0.32 mmol, 37%). IR (KBr): 1256 (s) (−SO_2O−), 1179 (s) (C−F), 414 (w) (Pd−N), 320 (w) (Pd-Cl) cm^{-1}. ^{1}H NMR (acetone-d_6, 200 K): δ 9.13 (d, 1H, H_6), 9.08 (d, 1H, H_3), 9.03 (d, 1H, $H_{3'}$), 8.67 (d, 1H, $H_{6'}$), 8.27 (dd, 1H, H_5), 8.16 (dd, 1H, $H_{5'}$) ppm. ^{19}F NMR (acetone-d_6): δ −77.1 (s, CF_3) ppm.

Pd(bpy)Cl(OTf) (7c). Pd(bpy)Cl(OTf) (**7c**) was prepared analogously to Pd(Cl-bpy)Cl(OTf) (**7b**) with the following modified amounts. Triflic acid (2.5 mL, 35.6 mmol) was added to 357 mg of Pd(bpy)Cl$_2$ (**5c**) (1.07 mmol). Yield: 460 mg of yellow-brownish powder (1.0 mmol, 93%). IR (KBr): 1259 (s) (−SO_2O−), 1177 (m) (−SO_2O−), 1162 (m) (C−F), 411 (w) (Pd−N), 340 (w) (Pd−Cl) cm^{-1}. ^{1}H NMR (acetone-d_6, 200 K): δ 9.15 (d, 1H, H_6), 8.84 (d, 1H, H_3), 8.79 (d, 1H, $H_{3'}$), 8.65 (m, 3H, $H_{6'} + H_4 + H_{4'}$), 8.11 (t, 1H, H_5), 8.00 (t, 1H, $H_{5'}$) ppm. ^{19}F NMR (acetone-d_6): δ −77.1 (s, CF_3) ppm. Anal. Calcd for $C_{11}H_8ClF_3N_2O_3SPd$: C, 29.55; H, 1.80; Cl, 7.93; N, 6.27; S, 7.17. Found: C, 29.27; H, 1.85; Cl, 7.82; N, 6.27; S, 7.16.

Pd(Me-bpy)Cl(OTf) (7d). The synthesis of Pd(Me-bpy)Cl(OTf) (**7d**) was performed according to the synthesis of Pd(Cl-bpy)Cl(OTf) (**7b**), except that 2.6 mL of triflic acid (29.6 mmol) was added to 322 mg of Pd(Me-bpy)Cl$_2$ (**5d**) (0.89 mmol). Yield: 322 mg of light brown powder (0.68 mmol, 76%). IR (KBr): 1265 (s) (−SO_2O−), 1179 (s) (C−F), 419 (w) (Pd−N), 337 (w) (Pd−Cl) cm^{-1}. ^{1}H NMR (acetone-d_6, 200 K): δ 8.79 (d, 1H, H_6), 8.59 (s, 1H, H_3), 8.56 (s, 1H, $H_{3'}$), 8.36 (d, 1H, $H_{6'}$), 7.89 (d, 1H, H_5), 7.78 (d, 1H, $H_{5'}$), 2.73 (s, 6H, CH_3) ppm. ^{19}F NMR (acetone-d_6): δ −77.1 (s, CF_3) ppm. Anal. Calcd for $C_{13}H_{12}ClF_3N_2O_3SPd{\cdot}2H_2O$: C, 30.54; H, 3.15; N, 5.48. Found: C, 29.70; H, 2.70; N, 5.23.

Methyl *N*-(2-Methoxyphenyl)carbamate. 2-Methoxyphenyl isocyanate (1.0 mL, 7.5 mmol) was added dropwise to 20 mL of methanol, while cooling on an ice bath. The reaction mixture was stirred under N_2 at 45 °C for 2 h. The reaction could be monitored by IR. The methanol was finally removed in vacuum. Yield: 1.31 g of yellow oil (7.2 mmol, 96%). IR (diethyl ether): 3441 (m) (N−H), 1747 (s) (C=O), 1605 (m) (N−H) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.44 (s, 1H, N−H), 7.67 (d, 1H, H_6), 7.11−6.90 (m, 3H, $H_3 + H_4 + H_5$), 3.80 (s, 3H, OCH_3), 3.66 (s, 3H, C(O)OCH_3) ppm.

Methyl *N*-(3-Methoxyphenyl)carbamate. The synthesis of methyl *N*-(3-methoxyphenyl)carbamate is analogous to the synthesis of methyl *N*-(2-methoxyphenyl)carbamate, except that the reaction is carried out at room temperature for 4 h. Yield: 1.44 g of yellow oil. IR (diethyl ether): 3295 (m) (N−H), 1737 (s) (C=O), 1609 (s) (N−H) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.65 (s, 1H, N−H), 7.22−7.17 (m, 2H, $H_2 + H_5$), 7.04 (d, 1H, H_6), 6.59 (d, 1H, H_4), 3.73 (s, 3H, OCH_3), 3.68 (s, 3H, C(O)OCH_3) ppm.

Methyl *N*-(4-Methoxyphenyl)carbamate. This carbamate was prepared analogously to the methyl *N*-(3-methoxyphenyl)carbamate. Yield: 1.40 g of white powder (7.7 mmol, 100%). IR (KBr): 3345 (m) (N−H), 1730 (s) (C=O), 1600 (m) (N−H), 1232 (m) (−O−CH_3), 1018 (m) (−O−CH_3) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.44 (s, 1H, N−H), 7.67 (d, 1H, H_6), 7.11−6.90 (m, 3H, $H_3 + H_4 + H_5$), 3.80 (s, 3H, OCH_3), 3.66 (s, 3H, C(O)OCH_3) ppm. Mp: 88−90 °C.

***N*-(2-Methoxyphenyl)-*N'*-(phenyl)urea.** Aniline (0.68 mL, 7.5 mmol) was dissolved in 15 mL of warm hexanes. At room temperature 1 mL of 2-methoxyphenyl isocyanate was added dropwise and the reaction mixture was stirred for 3.5 h. The resulting precipitate was filtered off, washed with 2 × 15 mL of hexanes, and dried under vacuum. Yield: 1.44 g of white powder (5.9 mmol, 79%). IR (KBr): 3331 (m) (N−H), 1645 (s) (C=O), 1254 (m) (−O−CH_3), 1026 (m) (−O−CH_3). ^{1}H NMR (DMSO-d_6): δ 9.35 (s, 1H, N−H), 8.26 (s, 1H, N−H), 8.13 (dd, 1H, H_6), 7.47 (d, 2H, $H_{2'} + H_{6'}$), 7.30 (t, 2H, $H_{3'} + H_{5'}$), 7.04−6.88 (m, 4H, $H_3 + H_4 + H_5 + H_{4'}$), 3.89 (s, 3H, OCH_3) ppm. Mp: 155−157 °C.

***N*-(3-Methoxyphenyl)-*N'*-(phenyl)urea.** Synthesis of *N*-(3-methoxyphenyl)-*N'*-(phenyl)urea is analogous to the synthesis of *N*-(2-methoxyphenyl)-*N'*-(phenyl)urea. Yield: 1.73 g of white powder (7.2 mmol, 94%). IR (KBr): 3295 (s) (N−H), 1638 (s) (C=O), 1232 (m) (−O−CH_3), 1033 (m) (−O−CH_3). ^{1}H NMR (DMSO-d_6): δ 8.74 (s, 1H, N−H), 8.72 (s, 1H, N−H), 7.46 (d, 2H, $H_{2'} + H_{6'}$), 7.29 (t, 2H, $H_{3'} + H_{5'}$), 7.20 (m, 2H, $H_2 + H_5$), 7.00−6.93 (m, 2H, $H_6 + H_{4'}$), 6.56 (d, 1H, H_4), 3.75 (s, 3H, OCH_3) ppm. Mp: 156−158 °C.

***N*-(4-Methoxyphenyl)-*N'*-(phenyl)urea.** This compound

Table 12. Crystallographic Data for $Pd(bpy)_2(OTf)_2$ (6c)

mol formula	$C_{22}H_{16}F_6N_4O_6S_2Pd$
mol wt.	716.9
cryst syst	monoclinic
space group	$P2_1/n$
temp	room
radiation (λ, Å)	Cu Kα (1.5418)
a, Å	8.0186(8)
b, Å	28.459(4)
c, Å	11.315(3)
β, deg	97.59(3)
V, Å^3	2559(1)
Z	8
D_{calcd}, g cm^{-3}	1.69
$F(000)$	1424
cryst dimens, mm	0.05 × 0.13 × 0.75
μ(Cu Kα), cm^{-1}	68.0
no. of unique tot. data	4330
no. of unique obsd data	3194 [$I > 2.5\sigma(I)$]
R	0.046
R_w	0.072

was prepared similarly to the *N*-(2-methoxyphenyl)-*N'*-(phenyl)urea. Yield: 1.79 g of white powder (7.4 mmol, 96%). IR (KBr): 3303 (m) (N—H), 1631 (s) (C=O), 1232 (m) (—O—CH_3), 1026 (m) (—O—CH_3). ^{1}H NMR (DMSO-d_6): δ 8.52 (s, 1H, N—H), 8.51 (s, 1H, N—H), 7.45 (d, 2H, $H_{2'} + H_{6'}$), 7.37 (d, 2H, $H_2 + H_6$), 7.28 (t, 2H, $H_{3'} + H_{5'}$), 6.69 (t, 1H, $H_{4'}$), 6.88 (d, 2H, $H_3 + H_5$), 3.73 (s, 3H, OCH_3) ppm. Mp: 190—192 °C.

***N,N'*-Bis(2-methoxyphenyl)urea.** 2-Methoxyaniline (0.42 mL, 3.8 mmol) was dissolved in 20 mL of diethyl ether. 2-Methoxyphenyl isocyanate (0.5 mL, 3.8 mmol) was added dropwise. The solution was refluxed under N_2 overnight. The product precipitated. The solvent was decanted, and the precipitate was washed with 2 × 15 mL of hexanes and dried under vacuum. Yield: 1.03 g of light purple crystals (3.8 mmol, 100%). IR (KBr): 3317 (m) (N—H), 1645 (s) (C=O), 1254 (m) (—O—CH_3), 1026 (m) (—O—CH_3). ^{1}H NMR (DMSO-d_6): δ 8.90 (s, 2H, N—H), 8.11 (d, 2H, $H_6 + H_{6'}$), 7.04—6.87 (m, 6H, $H_3 + H_{3'} + H_4 + H_{4'} + H_5 + H_{5'}$), 3.88 (s, 6H, OCH_3 + $OCH_{3'}$) ppm. Mp: 185—187 °C.

***N,N'*-Bis(4-methoxyphenyl)urea.** This synthesis was performed analogously to the synthesis of *N,N'*-bis(2-methoxyphenyl)urea, except that the reaction mixture could be stirred at room temperature for 3 h. Yield: 2.02 g of white powder (7.6 mmol, 97%). IR (KBr): 3317 (m) (N—H), 1645 (s) (C=O), 1239 (m) (—O—CH_3), 1026 (m) (—O—CH_3). ^{1}H NMR (DMSO-d_6): δ 8.45 (s, 2H, N—H), 7.36 (d, 4H, $H_2 + H_{2'} + H_4$ + $H_{4'}$), 6.87 (d, 4H, $H_3 + H_{3'} + H_5 + H_{5'}$), 3.73 (s, 6H, OCH_3 + $OCH_{3'}$) ppm. Mp: 239—240 °C.

***N*-(2-Methoxyphenyl)-*N'*-(4-methoxyphenyl)urea.** This urea compound was prepared similarly to *N,N'*-bis(4-methoxyphenyl)urea in 4.5 h. Yield: 0.49 g of white powder (1.77 mmol, 47%). IR (KBr): 3331 (m) (N—H), 1645 (s) (C=O), 1239 (m) (—O—CH_3), 1029 (m) (—O—CH_3). ^{1}H NMR (DMSO-d_6): δ 9.16 (s, 1H, N—H), 8.15 (s, 1H, N—H), 8.12 (d, 1H, H_6), 7.36 (d, 2H, $H_{2'} + H_{6'}$), 7.01—6.92 (m, 3H, $H_3 + H_4 + H_5$), 6.87 (d, 2H, $H_{3'} + H_{5'}$), 3.89 (s, 3H, OCH_3), 3.73 (s, 3H, $OCH_{3'}$) ppm. Mp: 143—146 °C.

X-ray Analysis. X-ray Structure Determination of $Pd(bpy)_2(OTf)_2$ (6c). X-ray data of the pale yellow crystal were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Cu Kα radiation. Crystallographic data are summarized in Table 12. Reflections were measured within the range $-9 \le h \le 0$, $0 \le k \le 33$, $-12 \le l \le 13$. The maximum value of $(\sin\theta)/\lambda$ was 0.59 Å^{-1}. Two reference reflections (170, 002) were measured hourly and showed no decrease during the 49 h of collection time. Unit cell parameters were refined by a least-squares fitting procedure using 23 reflections with $58 < 2\theta < 89°$. Corrections for Lorentz and polarization effects were applied. The asymmetric unit contains two independent molecules. The position of Pd was found by direct methods. The remainder of the non-hydrogen atoms were found in a subsequent ΔF synthesis. The hydrogen atoms were calculated. Full-matrix least-squares refinement on F, anisotropic 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 $R = 0.046$, $R_w = 0.072$, and $(\Delta/\sigma)_{max} = 0.94$. A weighting scheme $w = (6.1 + F_o + 0.0122F_o^2)^{-1}$ was used. An empirical absorption correction[32] was applied, with coefficients in the range 0.59—1.60. A final difference Fourier map revealed a residual electron density between −0.9 and +0.9 e Å^{-3}. Scattering factors were taken from refs 33 and 34. The anomalous scattering of Pd and S was taken into account. All calculations were performed with XTAL,[35] unless stated otherwise.

Table 13. Crystallographic Data for $Pd(Me\text{-}bpy)_2(OTf)_2$ (6d)

mol formula	$C_{26}H_{24}F_6N_4O_6S_2Pd$
mol wt	773.0
cryst syst	triclinic
space group	$P\bar{1}$
temp, K	258
radiation (λ, Å)	Cu Kα (1.5418)
a, Å	11.726(6)
b, Å	11.870(3)
c, Å	13.871(2)
α, deg	103.63(3)
β, deg	107.78(2)
γ, deg	113.32(3)
V, Å^3	1542(1)
Z	2
D_{calcd}, g cm^{-3}	1.67
$F(000)$	776
cryst dimens, mm	0.15 × 0.40 × 0.75
μ(Cu Kα), cm^{-1}	69.7
no. of unique tot. data	5838
no. of unique obsd data	5462 [$I > 2.5\sigma(I)$]
R	0.147
R_w	0.204

X-ray Structure Determination of $Pd(Me\text{-}bpy)_2(OTf)_2$ (6d). X-ray data for the orange crystal were collected with the same procedure as for $Pd(bpy)_2(OTf)_2$ (**6c**). Crystallographic data are summarized in Table 13. Reflections were measured within the range $-13 \le h \le 14$, $-13 \le k \le 14$, $-16 \le l \le 0$. The maximum value of $(\sin\theta)/\lambda$ was 0.61 Å^{-1}. Two reference reflections (101, 021) were measured hourly and showed a 6% decrease during the 66 h of collecting time, which was corrected for. Unit cell parameters were refined by a least-squares fitting procedure using 23 reflections with $76 < 2\theta < 83°$. The two CF_3SO_3 moieties were not stable during refinement and therefore were refined isotropically, while restraining the C—F distance to approximately 1.28 Å and the S—O distance to approximately 1.35 Å. Full-matrix least-squares refinement on F converged to $R = 0.147$, $R_w = 0.204$, and $(\Delta/\sigma)_{max} = 0.24$. A weighting scheme $w = (5.7 + F_o + 0.0059F_o^2)^{-1}$ was used. An empirical absorption correction[32] was applied, with coefficients in the range 0.75—1.17. A final difference Fourier map revealed a residual electron density between −3.7 and +6.2 e Å^{-3} in the vicinity of the CF_3SO_3 moieties.

Catalysis. Pd(acetate)$_2$/Ligand/*p*-Toluenesulfonic acid. In a typical experiment using the in situ prepared catalyst system the autoclave was charged with 10 mL of methanol and 1.5 mL of nitrobenzene (14.6 mmol). $Pd(OAc)_2$ (9 mg, 0.04 mmol), 0.64 mmol of the ligand (16 equiv to Pd), and 190 mg of *p*-tsa (0.4 mmol, 10 equiv to Pd) were dissolved in this mixture. The autoclave was pressurized with 60 bar of CO

(32) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(33) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1986**, *A24*, 321.
(34) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, p 55.
(35) Hall, S. R.; Stewart, J. M., Eds. *XTAL3.0 User's Manual*; Universities of Western Australia and Maryland: Perth, Australia, and College Park, MD, 1990.

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 and the pressure was released.

Pd(ligand)$_2$(OTf)$_2$/Ligand or Pd(ligand)Cl(OTf)/Ligand. Experiments with the preformed complexes were carried out as described for the in situ combination, with 0.04 mmol of complex and 0.12 mmol of ligand (5 equiv to Pd). No *p*-tsa was added.

Acknowledgments. We thank Innovation Oriented Research Programme (IOP-katalyse) for their financial support of this research. Dr. E. Drent from Shell, Amsterdam, is thanked for the helpful discussions about the catalysis. We are grateful to Dr. W. M. A. Niessen, R. A. M. van der Hoeven, and J. J. van Houte from the Leiden/Amsterdam Center for Drug Research, Division of Analytical Chemistry at the University of Leiden, for their help with the LC–MS measurements.

Supplementary Material Available: Tables S1–S6, listing the fractional atomic coordinates for the non-hydrogen and the hydrogen atoms and the anisotropic thermal parameters for Pd(bpy)$_2$(OTf)$_2$ (**6c**) and Pd(Me-bpy)$_2$(OTf)$_2$ (**6d**), are available as supplementary material (10 pages). Ordering information is given on any current masthead page.

OM940386K