The Palladium-Catalyzed Carbonylation of Nitrobenzene into Phenyl Isocyanate: The Structural Characterization of a Metallacylic Intermediate

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The synthesis and characterization of a family of metallacyclic complexes of palladium, that is, (N-N)PdC(O)ON(Ar′)C(O), are reported where N-N is a diimine ligand and Ar′ is a substituted aryl. The complexes were isolated from solutions during the catalytic carbonylation of nitroaromatics using palladium complexes and were proposed to be intermediates in the catalytic process. The X-ray structure determination of [(^{t}Bu)$_2$bipy]PdC(O)ON[*p*-C$_6$H$_4$-(^{t}Bu)]C(O) ((^{t}Bu)$_2$bipy = 4,4′-bis-*tert*-butyl-2,2′-bipyridyl) was carried out, the complex crystallizing in the triclinic space group $P\bar{1}$ $(C_{30}H_{37}N_3O_3Pd)_2 \cdot C_3H_6O$, $Z = 2$, $a = 15.626(4)$ Å, $b = 18.269(6)$ Å, $c = 12.067(3)$ Å, $\alpha = 107.34(2)°$, $\beta = 111.53(2)°$, $\gamma = 78.81(2)°$. The crystal structure contains two molecules in the asymmetric unit which are assembled in a quasi-dimeric form via stacking interactions. The previously assigned metallacyclic structure for these complexes was confirmed. A mechanistic pathway for the carbonylation process implicating a series of metallacycle intermediates is proposed without intervention of a metal−imido intermediate. Thermal decomposition studies of the metallacycle and some trapping experiments are also presented.

Introduction

Catalytic carbonylation of nitroaromatic compounds by various group VIII metal compounds is a reaction of great potential interest particularly for the industrial production of aromatic isocyanates, carbamates, and ureas.[1] Ruthenium-,[2,3] rhodium-,[4] and palladium-based[5,6] catalysts have proved to be the most effective for such transformations, and therefore several of these catalytic systems have been thoroughly investigated. In particular, we have studied homogeneous palladium catalyst systems composed of a Pd(II) precursor (usually $Pd(OAc)_2$), an aromatic diimine ligand (such as 1,10-phenanthroline or 2,2′-bipyridyl), in the presence of a Bronsted acid promoter.[5c,6c,d,7] These catalysts, which are among the most active and selective for such carbonylations, are effective at 130−180 °C under a pressure of 40−120 bar of carbon monoxide.

$$PhNO_2 + 3CO + EtOH \xrightarrow[180\ °C,\ 120\ bar]{[Pd] + 3phen + 8H^+} PhNHCO_2Et + 2CO_2 \quad (1)$$

In previous work we were able to isolate the metallacyclic complex **1a** (Ar = C_6H_5) by using milder conditions (80 °C, 30 bar CO) than those used catalytically and proposed a structure for **1a** on the basis of spectroscopic data (^{1}H and ^{13}C NMR, FABMS, and IR spectroscopy) as well as elemental analysis. Combining this evidence with our studies on the chemical reactivity

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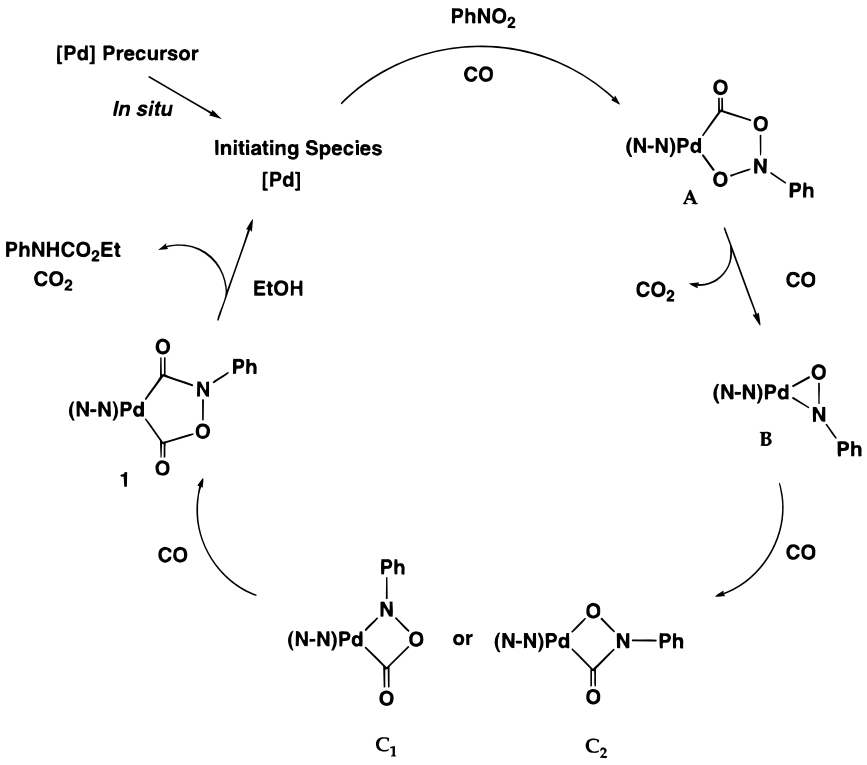
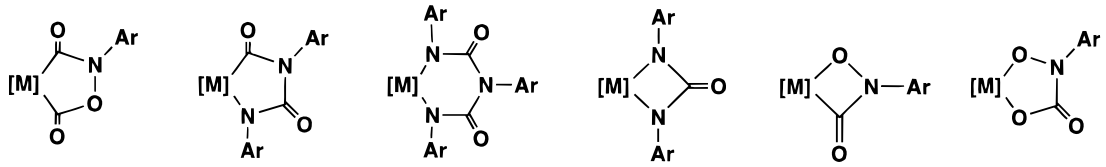
Scheme 1



Scheme 2



of **1a** led us to postulate this complex as a key intermediate in these Pd-catalyzed reactions.[8] Hence we proposed a mechanism by which the nitroaromatic substrate was converted into carbamate (Scheme 1) which involves a series of stepwise deoxygenation/carbonylation processes involving metallacyclic intermediates, **A**, **B**, $\mathbf{C_1}$, and $\mathbf{C_2}$.[8] Subsequently we were able to isolate and characterize (including X-ray structural determination) other similar five-, six-, and four-membered palladacycles **2**, **3**, and **4** (Scheme 2), which comforted (but by no means proved) our working hypothesis.[9−11]

However, these proposals, although feasible when made in 1990, remained strongly dependent on the precise structure of **1a**, for which an X-ray structure was not then available. After some effort, which involved the synthesis of a series of analogue complexes and attempts at their crystallization, eventually we were able to obtain suitable crystals of one such analogue for a structural determination.[11]

During this time in studies on the ruthenium/1,2-bis(diphenylphosphino)ethane catalyst system, Gladfelter isolated other potential intermediates for similar transformations.[2b,f] One of those was also the metallacyclic compound **5** (Scheme 2), which had a structure identical to that of the intermediate $\mathbf{C_2}$ proposed in our mechanism. However, from reactivity and kinetics studies, Gladfelter put forward a mechanism involving the intermediate formation of aniline.[2d−f] More recently, in the case of a rhodium/1,10-phenanthroline catalyst system, another metallacyclic complex **6**, possessing an isomeric structure of intermediate **A**, was crystallographically characterized by Cenini.[4b] This complex was also believed to be an intermediate in these reactions, and a mechanism involving a metal−imido species similar to that previously proposed by Gladfelter was preferred. Other metallacycles possessing isomeric or similar structures of intermediates **A**,[12,13] **B**,[2c,14] and **C**[2d,15] have also now been structurally characterized. However, in contrast to our original mechanistic proposal, a metal−imido intermediate has often been invoked as a key intermediate in these recent studies,

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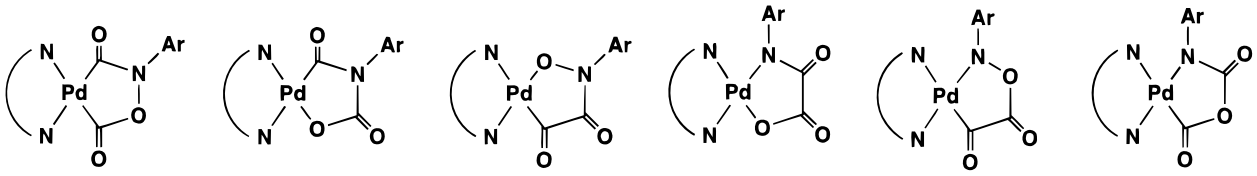
Scheme 3



1 2 3 4 5 6

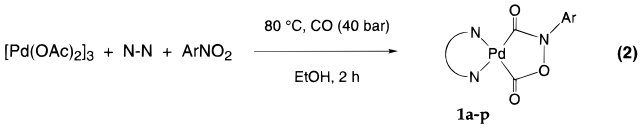
although an alternative proposal[6d] similar to that proposed by Gladfelter[2] has also been suggested.

The unambiguous structural determination of **1a** thus assumes a certain importance in these mechanistic discussions[1e,16] since the structure we have proposed could be seen to lead directly to the formation of a carbamate or isocyanate product without the necessity of passing through a metal−imido intermediate. Further, given the recent doubts[1e] cast upon our structural proposal for **1a**, we present here the X-ray structure of **1p**, an analogue of **1a**, and some additional studies on the reactivity of these metallacycles.

Results and Discussion

Complex **1a** was originally isolated from the reaction of $Pd(OAc)_2$, *o*-phenanthroline (3 equiv), and $PhNO_2$ (40 equiv) in ethanol under CO (30−40 bar) at 80 °C. The yellow complex precipitates out of solution over 2 h in ca. 80% yield (eq 2). IR, ^1H and ^{13}C-MAS NMR, and FAB mass spectrometric studies as well as elemental analysis led us to propose the five-membered metallacyclic structure for **1a**.[8] However, six isomeric structures (Scheme 3) had to be taken into consideration, and despite the strong evidence for **1a**, in particularly the FABMS spectrum and reactivity studies, certain of the other proposals could not definitively be excluded. **1a** was found to be of very low solubility in common organic solvents, and despite repeated attempts, crystals suitable for X-ray analysis were not obtained. Therefore, we undertook the systematic synthesis of various analogues of **1a** to resolve this problem.

A series of substituted nitrobenzenes, $XC_6H_4NO_2$, were studied under the conditions described above with *o*-phen as ligand, and the resultant complexes, **1b**−**1h** (with para substitution, X = OMe, *t*-Bu, Me, OH, OAc, F, Cl), **1i** (with *o*- $FC_6H_4NO_2$), **1k** (with *m*-$FC_6H_4NO_2$), and **1l** (with 3,5-$(CF_3)_2C_6H_3NO_2$), were isolated (eq 2).



(2)

The compounds presented IR and ^1H NMR spectroscopic features almost identical to those of **1a** except for substituent differences, but the solubilities of many of these analogues were also very low. We surmised that, given the expected planar structure of Pd(II) molecules of this type, strong intermolecular stacking interactions may be responsible for their low solubility behavior.

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Table 1. Crystallographic Data

formula	$2(C_{30}H_{37}N_3O_3Pd)\cdot C_3H_6O$
mol wt	1246.18
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	15.626(4)
b (Å)	18.269(6)
c (Å)	12.067(3)
α (deg)	107.34(2)
β (deg)	111.53(2)
γ (deg)	78.81(2)
V (Å^3)	3044(3)
Z	2
color	pale yellow
crystal dimens (mm)	0.35 × 0.30 × 0.25
D_{calc} (g cm^{-3})	1.36
F(000)	1296
μ(mm^{-1})	5.309
trans min and max	0.8080/1.0000
temp (K)	194
wavelength (Å)	1.54184
radiation	CuKα graphite monochromated
diffractometer	Philips PW1100
scan mode	$\theta/2\theta$
hkl limits	−13,13/−16,16/0,10
θ limits (deg)	3.0/47.05
no. of data measd	5332
no. of data with $I > 3\,\sigma(I)$	4223
weighting scheme	$4F_o^2/(\sigma^2(F_o^2) + 0.0036F_o^4)$
no. of variables	703
R	0.028
R_w	0.040
GOF	1.152
largest peak in final diff (e Å^{-3})	0.530

Accordingly, **1o** (X = H) and **1p** (X = *p*-*t*-Bu), which possessed bulky *tert*-butyl groups also on the bipyridyl ligand, were synthesized and found to be very soluble in organic solvents. Suitable crystals of **1p** could be grown by inverse diffusion of water into an acetone solution of the complex.

The complex crystallized in the $P\bar{1}$ space group with two molecules of **1p** (designated Pd_1 and Pd_2) in the asymmetric unit along with one molecule of acetone (Table 1). The structures of both molecules are shown separately in Figure 1. Most bond distances and angles of Pd_1 and Pd_2 are not significantly different. The bipyridine and the atoms of the metallacycle PdC(O)-ON are closely coplanar in both molecules with a somewhat larger deviation from the mean plane for the molecule Pd_1 than for Pd_2, that is, 0.034 and 0.082 Å, respectively. However, the ipso carbon atoms of the *t*-BuC_6H_4 groups are out of this plane by 0.944 Å in Pd_1 and 1.883 Å in Pd_2, leading to the angles Pd1−N3−C21 and Pd2−N103−C121 being 157.57° and 169.02°, respectively. As is shown in Figure 2, in the crystal Pd_1 and Pd_2 assemble so that the mean planes about each Pd are almost parallel, the angle between the planes of the two molecules being 5.87°, with a plane separation of only 2.942 Å. Hence relatively strong interactions

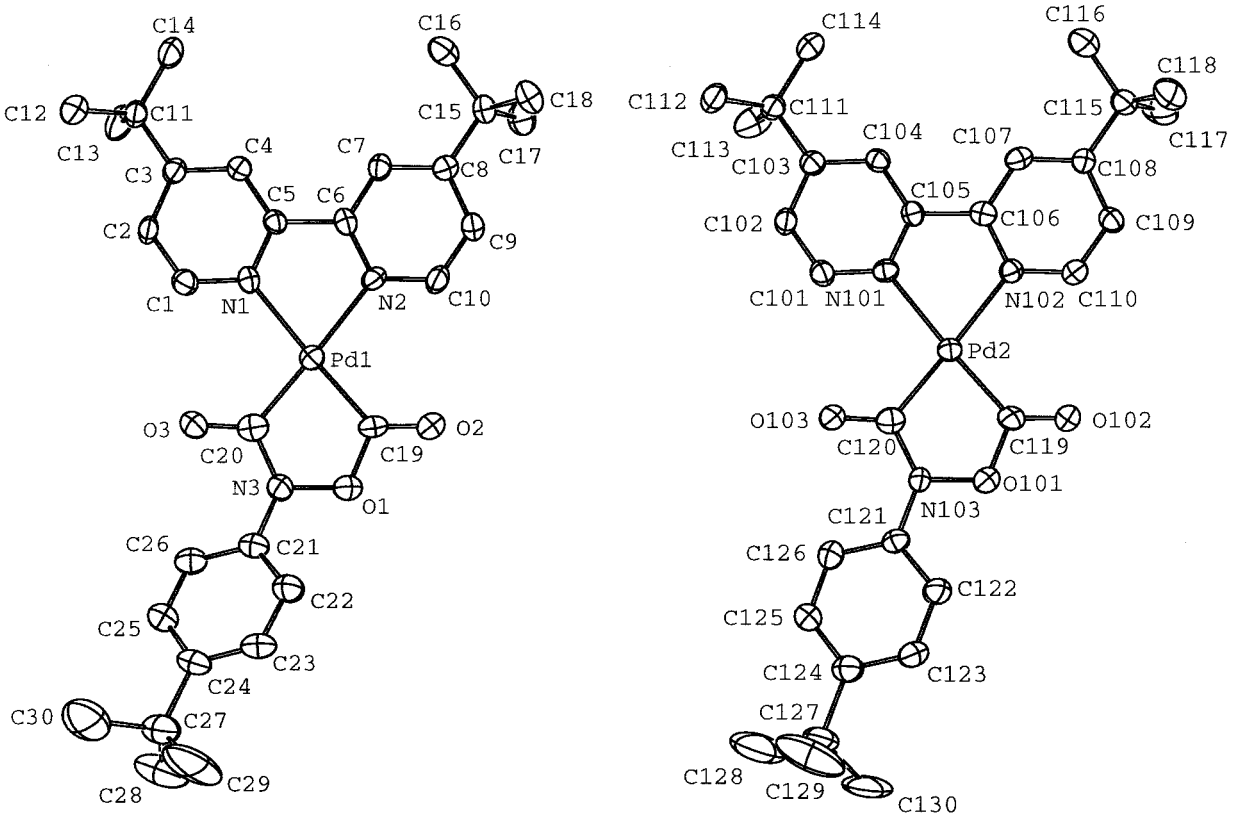

Figure 1. ORTEP drawing of the two molecules of **1p**. Selected bond lengths (Å) and angles (deg): Pd1−N1/Pd2−N101 2.124(4)/2.147(4), Pd1−N2/Pd2−N102 2.135(4)/2.132(4), Pd1−C19/Pd2−C119 1.950(6)/1.946(5), Pd1−C20/Pd2−C120 1.935(6)/1.965(5), C19−O1/C119−O101 1.398(6)/1.415(5), C19−O2/C119−O102 1.215(6)/1.204(5), C20−O3/C120−O103 1.239(6)/1.232(6), C20−N3/C120−N103 1.390(7)/1.385(6), N3−O1/N103−O101 1.419(5)/1.416(5), N1−Pd1−N2/N101−Pd2−N102 76.8(2)/76.8(2), N1−Pd1−C20/N101−Pd2−C120 101.2(2)/101.3(2), N1−Pd1−C19/N101−Pd2−C119 176.4(2)/176.6(2), N2−Pd1−C19/N102−Pd2−C119 100.8(2)/100.1(2), C20−Pd1−C 19/C120−Pd2−C119 81.1(3)/81.9(2).

between Pd_1 and Pd_2 are present which are undoubtedly a result of a mutual π-stacking type between the bipyridine ligands and the metallacycles. The two molecules are oriented in a quasi head to tail fashion and, although not identical, can be superimposed by a ca. 140° rotation about the Pd−Pd axis. If the substituents are ignored, the molecules can also be seen to be approximately related by a 2-fold axis perpendicular to the Pd−Pd vector. Although the two Pd atoms are also stacked in this structure, the Pd−Pd distance of 3.280 Å would seem to be too great for there to be a significant metal−metal bonding contribution. The existence of this assembled dimer structure supports our suspicions that the type of intermolecular interactions found herein may be responsible for the lack of solubility of most of the metallacycles of this type.

The geometry around the palladium is square planar, and the structure of the metallacycle is indeed that of the isomer we had previously proposed. The two carbonyl groups are linked directly to the metal with palladium to carbon bond lengths of 1.950(5) and 1.946(5) Å (Pd1−C19/Pd2−C119) and 1.935(5) and 1.965(5) Å (Pd1−C20/Pd2−C120). Hence the molecule formally contains a CO_2 unit linked by its carbon atom to the metal center in a five-membered metallacycle, a structural type which had been proposed only rarely[17−19] and which had not been previously fully established by X-ray methods. We note that the C−O bond distances are 1.398(6)/1.415(5) Å (C19−O1/C119−O101) and 1.215(6)/1.204(5) Å (C19−O2/C119−O102) for the CO_2 moiety and 1.239(6)/1.232(6) Å (C20−O3/C120−O103) for the other carbonyl group.

The crystal structure also revealed weak intramolecular interactions between the ortho hydrogen atoms of the diimine ligand (on C1, C10/C101, and C110) and the oxygen atoms (O2, O3/O102, and O103 respectively) of the α-carbonyl groups in the metallacycle. Similar hydrogen bond type interactions have been observed often in crystal structures.[20] However we also observe that in solution the ^{1}H NMR chemical shifts of the ortho protons of the diimine ligand in the metallacycles **1** are displaced 0.5 ppm to low field relative to the shifts measured in other Pd(II) complexes (Table 2). We suggest that the intramolecular interactions are probably maintained in solution aided by the rigidity of the coordination sphere around the metal. A similar ^{1}H shift was also observed for one of the diimine ortho protons of complex **2** and can also be related to the existence of an interaction with the proximal α-carbonyl.[9] Furthermore, in **2** the other α-proton of the diimine ligand is displaced toward high field by approximatively 3 ppm, which undoubtedly results from the proximity of the phenyl group of the NPh unit on

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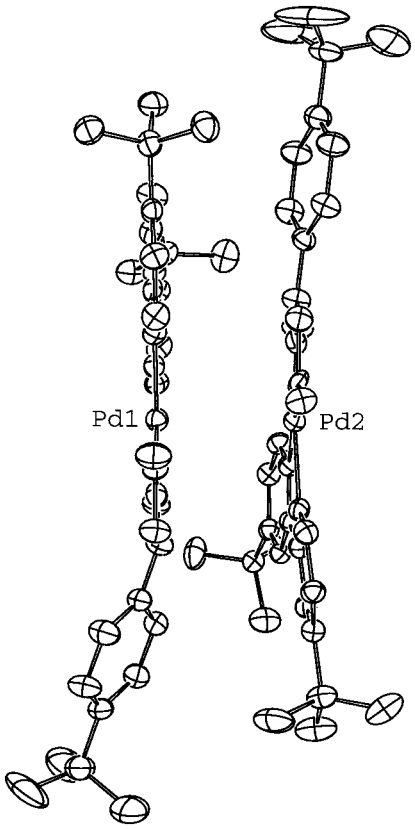


Figure 2.

Table 2. ^{1}H NMR Shifts of Ortho Protons of the Phenanthroline Ligand in Various Palladium(II)−Diimine Complexes

complex in CD_2Cl_2	H′ shift (ppm)	H″ shift (ppm)
[(^{t}Bu)$_2$bipy]PdCl$_2$[a]	9.19	9.19
[(^{t}Bu)$_2$bipy]Pd(OAc)$_2$[a]	8.17	8.17
1o	9.76	9.57
(phen)PdCl$_2$[a]	9.58	9.58
(phen)Pd(OAc)$_2$[a]	8.32	8.32
1a	10.13	9.94
2[b]	10.43	6.82

[a] See ref 11. [b] See ref 9.

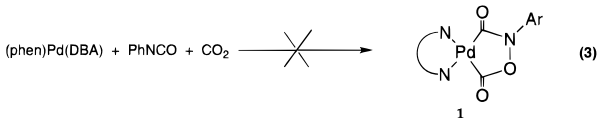
the metallacycle, the phenyl group being oriented perpendicular to the plane of the molecule, thereby deshielding this proton. Hence in five-membered palladacycles where carbonyl or phenyl imido units are directly linked to the metal center, α-hydrogens of coordinated diimine ligands should show characteristic chemical shifts in the ^{1}H NMR spectrum. This observation may be useful to distinguish between the various possible isomers in such systems, where crystallographic structural data is lacking. For instance, it can be seen that, if this criterion is applied to the isomers shown in Scheme 3, all except for structure **1** can be eliminated.

To confirm that **1p** was indeed an analogue of **1a**, we also showed that (a) the FABMS fragmentation patterns were analogous (except for the evident differences in ligand and the presence of *tert*-butyl groups) and (b) the catalytic reaction using the 4,4′-bis-*tert*-butyl-2,2′-bipyridine ligand proceeds typically under normal conditions.

We have found that, on heating of **1a** with excess maleic anhydride at 100 °C in an inert solvant, the palladium(0) diimine fragment arising from thermal decarboxylation and subsequent decomposition of **1a** could be trapped as the maleic anhydride adduct[8] (Scheme 4). We were unable to observe the supposed intermediate (phen)Pd(ArNCO) (**7**) since (in the absence of a trapping agent) decomposition of **1a** yields an intractable and insoluble black material (presumably mainly consisting of reduced metallic palladium), along with various organic products arising from phenyl isocyanate.[8,11]

However, we had previously shown that, on heating of **1a** with excess PhNCO at 140 °C, a six-membered palladacycle of the structural type **3** shown in Scheme 4 could be isolated in high yield.[9] Thus we carried out the same experiment using a labeled isocyanate hoping to observe the PhNCO group in the resultant metallacycle. Heating **1a** with excess *p*-tolyl isocyanate at 140 °C did not yield the mixed phenyl/tolyl derivative but instead only the isostructural tolyl-containing metallacycle **3**. We subsequently showed that such metallacycles readily exchange with excess aryl isocyanates under these conditions,[9] and thus our experiment was inconclusive. Incidentally this reaction proved to be much cleaner than the reaction involving phenyl isocyanate and (N-N)Pd(dba) (dba = dibenzylideneacetone), which has often been used as the source of (N-N)Pd(0).[10,11] Analogous decarboxylation processes have already been reported in five-membered rhodium metallacyles incorporating CO_2 units.[17,18]

Finally, we checked that complex **1a** was not formed when a palladium(0) precursor, (phen)Pd(dba), was heated together with carbon dioxide (20 bar) and phenyl isocyanate (eq 3) at 80 °C for 5 h. The palladacycle **3**

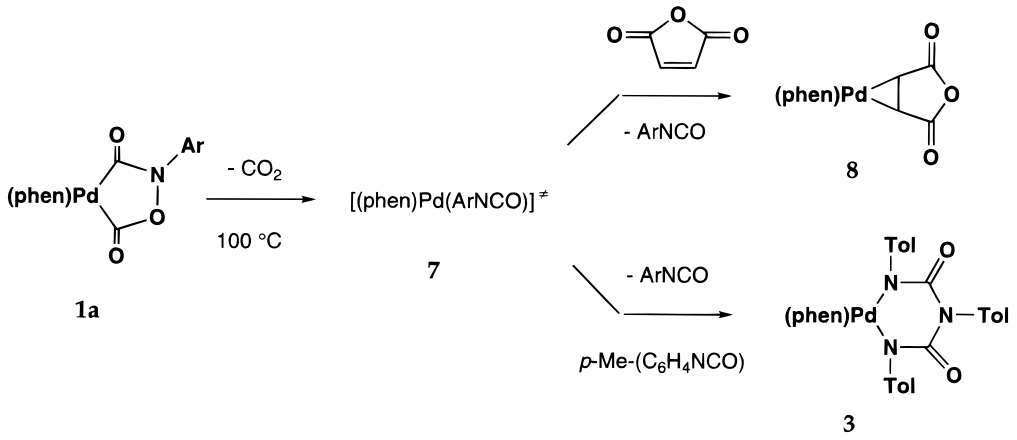


(3)

was again characterized as the main product, along with a new species and metallic palladium, but no evidence for the formation of **1a** was obtained. We have been unable to purify this new complex sufficiently to allow a definitive identification, but NMR data indicate the presence of a nonsymmetric phenanthroline ligand (ortho protons at δ 9.98 and 9.11) and carbonyl absorptions at 1620 and 1690 cm^{-1}. Tentatively we propose that this complex may possess the isomeric structure **2**, which would result indeed from coupling of phenyl isocyanate with CO_2. If this is correct then species of the structural type **2** (Scheme 3) could be resulting from postcatalytic reactions and may have no relevance as intermediates in the actual catalytic process. Attempts to characterize this complex in more detail are underway.

In conclusion, the X-ray determination confirms our structural proposition for the metallacyclic complex isolated from the catalytic carbonylation process, such metallacycles being formed from differently functionalized nitroaromatics. The decomposition of **1a** is irreversible, indicating that the palladacycle is formed from the Pd-catalyzed reaction of nitrobenzene with CO and not from a later reaction of the products formed. Finally, although the precise mechanism for catalytic carbonylation of nitroaromatics by these palladium complexes is still unclear, especially for the initial steps

Scheme 4



of the catalysis,[11] the structure and the reactivity of **1**, as well as the very rich insertion−deinsertion behavior displayed by analogous palladium(0) complexes, provide support to a mechanistic pathway involving the interconversions of a series of metallacyclic intermediates (Scheme 1). Further investigations will be necessary to clarify the details of this fascinating and important catalytic reaction.

Experimental Section

General Comments. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Carbon monoxide (N-45 purity grade) and carbon dioxide (N-45 purity grade) were purchased from Air Liquide. The chelating 4,4′-bis-*tert*-butyl-2,2′-dipyridine was synthesized following the reported procedure of Belser.[21] Complexes (phen)Pd(OAc)$_2$,[22] (phen)PdCl$_2$,[23] and (phen)Pd(dba)[24] were also obtained following reported syntheses.

Reactions under pressure were performed in a 50 mL stainless steel SOTELEM reactor with a 750 W corresponding programmable oven. ^{1}H NMR spectra were obtained on a Brucker SY 200 (200 MHz) or SY 400 (400 MHz) Fourier transform spectrometer. ^{1}H NMR chemical shifts are reported in units of parts per million (ppm) relative to residual protiated solvent. Infrared spectra were recorded on a Perkin-Elmer 597 or IFS 66 fourier transform spectrometer in KBr windows. UV−visible spectra were recorded on a Cary 3 spectrometer, using quartz cells. GC analyses were performed on a Hewlett-Packard SII-5890 gas chromatograph, equipped with a 10 m methyl silicon semicapillary column (HP-1). Quantitative analyses were obtained by integrating peak areas versus appropriate external or internal standards. Response factors relative to the chlorobenzene standard were determined by using authentic samples of the products. Mass spectral studies and elemental analyses were obtained from the corresponding services of the Louis Pasteur University.

Crystallographic Study of [(^{t}Bu)$_2$bipy]PdC(O)ON[*p*-C$_6$H$_4$(^{t}Bu)]C(O) (1p). Pale yellow crystalline needles of **1p** were grown by slow diffusion (several weeks) of water in an acetone solution of the crude product isolated after reaction. Since the crystals desolvated slowly when separated from mother liquor at ambient temperature, data collection had to be performed at low temperature.

Diffraction data was collected at −100 ± 1 °C on a Philips PW1100/16 diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range corresponding to a triclinic cell. Packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure showed the space group to be $P\bar{1}$. Collection was achieved using the $\omega-2\theta$ scan to a maximum 2θ value of 47.0°. Scans of (0.90 + 0.14 tan θ)° were made at a speed of 0.02 °/s (in ω), and 5332 reflections were collected. Empirical absorption corrections and Lorentz and polarization corrections were applied to the data. The structure was solved by the Patterson method. All non-hydrogen atoms were located by the heavy-atom method and were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4223 observed reflections ($I > 3.00\sigma(I)$) and converged with unweighted and weighted agreement factors of R = 0.028 and R_w = 0.040, respectively. All computations used MOLEN on a VAX computer.[25] Crystal parameters, data collection details, and results of the refinements are summarized in Table 1.

Preparation of Compounds 1a−p: Typical Procedure. In the autoclave, 100 mg of palladium acetate (0.44 mmol), 3−10 equiv of the desired diimine ligand, and 3−40 equiv of nitroaromatic were added to 10 mL of ethanol. The autoclave was then flushed with carbon monoxide three times with stirring, pressurized to 40 bar, and heated to 80 °C (30 min). The stirring was further maintained for 2 h at this temperature. After subsequent cooling and depressurization, the pale suspension that formed in the medium was filtered and washed several times with ethanol and diethyl ether. Depending on the nitroaromatic used, the resulting yellow air-stable precipitate often contained metallic palladium but could be purified from hot ortho-dichlorobenzene (120 °C) by cooling and subsequent addition of *n*-pentane. Great care has to be exercised in controlling the temperature, since the complexes often undergo decomposition around 140 °C in solution. In many cases, crystalline needles of those complexes can be grown as well by slow diffusion of diethyl ether in a saturated dichloromethane solution.

(phen)Pd[C(O)N(C$_6$H$_5$)OC(O)] (1a): 80% yield; yellow. Mp: 238 ± 1 °C dec. IR (KBr, cm^{-1}): 3050 (w, C−H phen); 1698 (s, C═O), 1622 (s, C═O); 1585 (s, C═C arom); 1255 (m, N−O). NMR: ^{1}H (CD$_2$Cl$_2$) δ 10.13 (d, J = 5 Hz, 1 H, ortho/phenanthroline); 9.94 (d, J = 5 Hz, 1 H, ortho/phenanthroline); 8.56 (d, J = 8 Hz, 2 H); 8.00 (dd + s, 2 × 2 H); 7.71 (d, J = 8 Hz, 2 H, phenyl); 7.38 (t, J_{H-H} = 7 Hz, 2 H, phenyl); 7.14 (t,

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J_{H-H} = 8 Hz, 1 H, phenyl); ^{13}C (MAS) δ 191.0 (C═O); 185.4 (C═O); 151.9; 148.8; 145.9; 144.1; 138.8; 136.9; 136.0; 134.6;129.5 (phenanthroline); 126.4; 123.2; 119.9 (phenyl). FABMS (*m*-nitrobenzyl alcohol/*N*,*N*-dimethylacetamide): *m*/*z* 450 (M + 1), 422 (M + 1 − CO), 393 (M − 2CO), 378 (M + 1 − CO − NCO), 363 (M + 1 − CO_2 − NCO), 314 (M − CO − PhNO), 302 (M − CO − PhNCO), 286 (M − CO_2 − PhNCO). UV (CH_2Cl_2): λ (nm) (approximate ϵ in mol cm^{-1}); 275.0 (69 000); 293.5 (35 700); 330.5 (4900), 347.5 (4300). Anal. Calcd for $C_{20}H_{13}N_3O_3Pd$: C, 53.41; H, 2.91; N, 9.34; Found: C, 53.67; H, 2.91; N, 9.34.

(phen)Pd[C(O)N(*p*-MeOC_6H_4)OC(O)] (1b): 60% yield; yellow. Mp: 217 ± 3 °C dec. IR (KBr, cm^{-1}): 1700 (s, C═O), 1620 (s, C═O); 1240 (s, N−O). NMR: ^{1}H (CD_2Cl_2) δ 10.12 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 9.93 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 8.56 (d, *J* = 9 Hz, 2 H); 7.99 (dd + s, 4 H); 7.56 (d, *J* = 9 Hz, 2 H, phenyl); 6.93 (d, *J* = 9 Hz, 2 H, phenyl); 3.82 (s, 3 H, O*C*H_3). Anal. Calcd for $C_{21}H_{15}N_3O_4Pd$: C, 52.57; H, 3.15; N, 8.76; Found: C, 52.40; H, 3.08; N, 8.66.

(phen)Pd[C(O)N(*p*-^{t}Bu-C_6H_4)OC(O)] (1c): 72% yield; yellow. Mp: 242 ± 1 °C dec. IR (KBr, cm^{-1}): 1705 (s, C═O), 1610 (s, C═O); 1270 (s, N−O). NMR: ^{1}H (CD_2Cl_2) δ 10.05 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 9.97 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 8.54 (d, *J* = 8 Hz, 2 H); 7.98 (dd + s, 4 H); 7.58 (d, *J* = 9 Hz, 2 H, phenyl); 7.40 (d, *J* = 9 Hz, 2 H, phenyl); 1.34 (s, 9 H, C(CH_3)$_3$). FABMS (*m*-nitrobenzyl alcohol): *m*/*z* 506 (M + 1), 448 (M − ^{t}Bu), 419 (M − 1 − CO), 393 (M + 1 − ^{t}Bu − 2CO), 362 (M + 1 − ^{t}Bu − CO_2 − NCO), 314 (M − CO − ^{t}Bu(C_6H_4)NO), 302 (M − CO − ^{t}Bu(C_6H_4)NCO), 286 (M − CO_2 − ^{t}Bu(C_6H_4)NCO). Anal. Calcd for $C_{24}H_{21}N_3O_4Pd$: C, 56.99; H, 4.18; N, 8.30; Found: C, 57.12; H, 4.17; N, 8.31.

(phen)Pd[C(O)N(*p*-Me-C_6H_4)OC(O)] (1d): 86% yield; yellow. Mp: 242 ± 3 °C dec. IR (KBr, cm^{-1}): 1700 (s, C═O), 1620 (s, C═O); 1260 (s, N−O). NMR: ^{1}H (CD_2Cl_2) δ 10.12 (d, *J* = 4 Hz, 1 H, ortho/phenanthroline); 9.93 (d, *J* = 4 Hz, 1 H, ortho/phenanthroline); 8.57 (d, *J* = 8 Hz, 2 H); 8.01 (dd + s, 4 H); 7.57 (d, *J* = 8 Hz, 2 H, phenyl); 7.20 (d, *J* = 8 Hz, 2 H, phenyl); 2.35 (s, 3 H, CH_3). Anal. Calcd for $C_{21}H_{15}N_3O_3Pd$: C, 54.39; H, 3.26; N, 9.06; Found: C, 54.62; H, 3.04; N, 8.79.

(phen)Pd[C(O)N(*p*-HOC$H_2C_6H_4$)OC(O)] (1e): 98% yield; yellow. Mp: 211 ± 2 °C dec. IR (KBr, cm^{-1}): 3340 (m, O−H), 1700 (s, C═O), 1615 (s, C═O); 1275 (s, N−O). NMR: ^{1}H ($C_6D_5NO_2$) δ 10.21 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 10.00 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 8.56 (d, *J* = 9 Hz, 2 H); 7.99 (dd + s, 4 H); 7.98 (d, *J* = 8 Hz, 2 H, phenyl); 7.53 (d, *J* = 8 Hz, 2 H, phenyl); 4.83 (d, *J* = 6 Hz, 2 H, CH_2OH); 2.15 (s, 1 H, CH_2O*H*). Anal. Calcd for $C_{21}H_{15}N_3O_4Pd$: C, 52.57; H, 3.15; N, 8.76; Found: C, 52.53; H, 3.33; N, 8.69.

(phen)Pd[C(O)N(*p*-OAcC_6H_4)OC(O)] (1f): 80% yield; red. Mp: 203 ± 4 °C dec. IR (KBr, cm^{-1}): 1740 (s, C═O/acetate); 1720 (s, C═O), 1620 (s, C═O); 1270 (s, N−O). NMR: ^{1}H (CD_2Cl_2) δ 10.13 (d, *J* = 5 Hz, 1 H ortho/phenanthroline); 9.94 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 8.58 (d, *J* = 8 Hz,2 H); 8.01 (dd + s, 4 H); 8.01 (d, *J* = 8 Hz, 2 H, phenyl); 7.73 (d, *J* = 8 Hz, 2 H, phenyl); 7.09 (d, *J* = 8 Hz, 2 H, phenyl); 2.28 (s, 3 H, O_2CCH_3). Anal. Calcd for $C_{22}H_{15}N_3O_5Pd$: C, 52.04; H, 2.98; N, 8.28; Found: C, 52.17; H, 3.01; N, 8.26.

(phen)Pd[C(O)N(*p*-FC_6H_4)OC(O)] (1g): 78% yield; yellow. Mp: 242 ± 2 °C dec. IR (KBr, cm^{-1}): 1705 (s, C═O), 1625 (s, C═O); 1265 (s, N−O); 1050 (m, C−F). NMR: ^{1}H (CD_2Cl_2) δ 10.09 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 9.91 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 8.57 (d, *J* = 8 Hz, 2 H); 8.00 (dd + s, 4 H); 7.68 (d, J_{H-H} = 9 Hz, J_{H-F} = 5 Hz, 2 H, phenyl); 7.13 (d, t, J_{H-H} = J_{H-F} = 9 Hz, 2 H, phenyl). Anal. Calcd for $C_{20}H_{12}N_3O_3FPd$: C, 51.36; H, 2.59; N, 8.98; Found: C, 51.12; H, 2.61; N, 8.22.

(phen)Pd[C(O)N(*p*-ClC_6H_4)OC(O)] (1h): 75% yield; yellow. Mp: 240 ± 5 °C dec. IR (KBr, cm^{-1}): 1695 (s, C═O), 1625 (s, C═O); 1265 (s, N−O); 670 (m, C−Cl). NMR: ^{1}H (CD_2Cl_2) δ 10.13 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 9.94 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 8.59 (d, *J* = 8 Hz, 2 H); 8.00 (dd + s, 4 H); 7.73 (d, *J* = 5 Hz, 2 H, phenyl); 7.35 (d, t, *J* = 5 Hz, 2 H, phenyl). Anal. Calcd for $C_{20}H_{12}N_3O_3ClPd$: C, 49.61; H, 2.50; N, 8.68; Found: C, 49.54; H, 2.48; N, 8.91.

(phen)Pd[C(O)N(*o*-FC_6H_4)OC(O)] (1i): 87% yield; light gray or yellow (H_2O solvate). Mp: 215 ± 5 °C dec. IR (KBr, cm^{-1}): 1705 (s, C═O), 1625 (s, C═O); 1265 (s, N−O); 1040 (m, C−F). NMR: ^{1}H ($C_6D_5NO_2$, 80 °C) δ 10.10 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 10.00 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 8.53 (d, *J* = 7 Hz, 2 H); 7.94 (dd + s, 4 H); 7.67 (m, 1 H, phenyl); 7.25 (m, 3 H, phenyl). Anal. Calcd for $C_{20}H_{12}N_3O_3FPd$: C, 51.36; H, 2.59; N, 8.98; Found: C, 51.16; H, 2.63; N, 8.47.

(phen)Pd[C(O)N(*m*-$CF_3C_6H_4$)OC(O)] (1j): 70% yield; yellow. Mp: 237 ± 2 °C dec. IR (KBr, cm^{-1}): 1705 (s, C═O), 1630 (s, C═O); 1265 (s, N−O); 1210 (m, C−F); 1160 (m, C−F); 1150 (m, C−F). NMR: ^{1}H ($C_6D_5NO_2$, 80 °C) δ 10.05 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 9.95 (d, *J* = 5 Hz, 1 H, ortho/phenanthroline); 8.60 (d, *J* = 7 Hz, 2 H); 8.45 (s, 2 H, phenyl); 7.99 (m + s, 5 H); 7.58 (s, 1 H, phenyl). Anal. Calcd for $C_{21}H_{12}N_3O_3F_3Pd$: C, 48.72; H, 2.34; N, 8.12; Found: C, 48.68; H, 2.52; N, 7.91.

(phen)Pd[C(O)N(*m*-$NO_2C_6H_4$)OC(O)] (1k): 75% yield; yellow. Mp: >250 °C dec. IR (KBr, cm^{-1}): 1725 (s, C═O), 1635 (s, C═O); 1520 (s, N═O); 1345 (s, N═O); 1265 (s, N−O). NMR: ^{1}H ($C_6D_5NO_2$, 115 °C) δ 10.07 (d, 1 H, ortho/phenanthroline); 9.93 (d, 1 H, ortho/phenanthroline); 8.82 (s, 1 H, phenyl); 8.62 (d, 2 H); 8.50 (d, 1 H, phenyl); 7.94 (dd + s, 4 H); 7.61 (m, 1 H, phenyl); 7.45 (m, 1 H, phenyl). Anal. Calcd for $C_{20}H_{10}N_4O_5Pd\cdot H_2O$: C, 46.82; H, 2.75; N, 10.93; Found: C, 46.82; H, 2.63; N, 10.66.

(phen)Pd[C(O)N(*m*-$(CF_3)_2C_6H_3$)OC(O)] (1l): 14% yield; yellow. Mp: 245 ± 5 (dec). IR (KBr, cm^{-1}): 1720 (s, C═O), 1630 (s, C═O); 1270 (s, N−O); 1190 (w, C−F), 1170 (w, C−F). NMR: ^{1}H ($C_6D_5NO_2$, 115 °C) δ 10.02 (d, 1 H, ortho/phenanthroline); 9.93 (d, 1 H, ortho/phenanthroline); 8.56 (d, 2 H); 8.44 (s, 2 H, phenyl); 8.07 (dd + s, 4 H); 7.61 (s, 1 H, phenyl). Anal. Calcd for $C_{22}H_{11}N_3O_3F_6Pd$: C, 45.11; H, 1.89; N, 7.17; Found: C, 45.18; H, 2.09; N, 6.97.

[3,4,7,8-(Me)$_4$(phen)]Pd[C(O)N(C_6H_5)OC(O)] (1m): 85% yield; light gray. Mp: 269 ± 1 (dec). IR (KBr, cm^{-1}): 1705 (s, C═O), 1620 (s, C═O); 1265 (s, N−O). NMR: ^{1}H ($C_6D_5NO_2$, 80 °C) δ 9.91 (s, 2 × 1 H, H, ortho/diimine); 9.72 (s, 2 × 1 H, H, ortho/diimine); 8.02 (s, 2 H); 8.01 (d, *J* = 7 Hz,2 H, phenyl); 7.43 (t, *J* = 8 Hz, 2 H, phenyl); 7.17 (t, *J* = 8 Hz,1 H, phenyl); 2.70 (s, 3 H, CH_3/diimine); 2.69 (s, 3 H, CH_3/diimine); 2.59 (s, 3 H, CH_3/diimine); 2.54 (s, 3 H, CH_3/diimine). Anal. Calcd for $C_{24}H_{21}N_3O_3Pd$: C, 56.99; H, 4.18; N, 8.31; Found: C, 56.27; H, 3.99; N, 8.30.

(bipy)Pd[C(O)N(C_6H_5)OC(O)] (1n). Eight equivalents of chelate was used in place of 3 in this case: yellow; 80% yield. Mp: 225 ± 5 °C dec. IR (KBr, cm^{-1}) 1705 (s, C═O), 1615 (s, C═O); 1270 (s, N−O). NMR: ^{1}H (CD_2Cl_2) δ 9.92 (d, *J* = 5 Hz, 1 H, ortho/bipyridine); 9.72 (d, *J* = 5 Hz, 1 H, ortho/bipyridine); 8.12 (dd + s, 4 H); 7.69 (d + t, 4 H, bipyridine and phenyl); 7.37 (t, *J* = 8 Hz, 2 H, phenyl); 7.13 (t, J_{H-H} = 8 Hz, 1 H, phenyl). FABMS (*m*-nitrobenzyl alcohol): *m*/*z* 426 (M + 1), 398 (M + 1 − CO), 369 (M − 2CO), 354 (M + 1 − CO − CO_2), 339 (M − NCO − CO_2), 290 (M − CO − PhNO), 262 (M − CO_2 − PhNCO). Anal. Calcd for $C_{18}H_{13}N_3O_3Pd$: C, 50.78; H, 3.08; N, 9.87; Found: C, 50.40; H, 3.11; N, 9.70.

[2,2′-(^{t}Bu)$_2$(bipy)]Pd[C(O)N(C_6H_5)OC(O)] (1o). Eight equivalents of chelating ligand and 40 equiv of nitroaromatic were used here. After 15 h, a suspension of metallic palladium was present in the reaction medium. This suspension was removed by filtration on Celite (Merck 545). Then 50 mL of acetone and 25 mL of H_2O were added to the yellow filtrate. After 5 days, the yellow precipitate (435 mg) was decanted and washed with *n*-pentane. This precipitate was a mixture of free ligand and the desired complex (80% by ^{1}H NMR) and was again recrystallized by slow diffusion of water in an

ethanolic solution of the crude precipitate: 13% yield; yellow needles. Mp: 224 ± 5 °C dec. IR (KBr, cm^{-1}) 1720 (s, C═O), 1620 (s, C═O); 1265 (s, N−O). NMR: ^1H (CD_2Cl_2) δ 9.75 (d, J = 6 Hz, 1 H, ortho/diimine); 9.56 (d, J = 6 Hz, 1 H, ortho/diimine); 8.07 (s, 2 H, diimine); 7.65 (m, 4 H, diimine and phenyl); 7.35 (t, J = 7 Hz, 2 H, phenyl); 7.12 (t, J = 7 Hz, 1 H, phenyl); 1.44 (s, 18 H, 2C(CH_3)$_3$). FABMS (*m*-nitrobenzyl alcohol): *m*/*z* 538 (M + 1), 510 (M + 1 − CO), 481 (M − 2CO), 567 (M + 1 − CO − CO_2), 451 (M − NCO − CO_2), 402 (M − PhNO − CO), 374 (M − CO_2 − PhNCO). Anal. Calcd for $C_{26}H_{29}N_3O_3Pd$: C, 58.05; H, 5.43; N, 7.81; Found: C, 57.80; H, 5.16; N, 7.81.

[2,2′-(^{t}Bu)$_2$(bipy)]Pd[C(O)N(*p*-^{t}BuC_6H_4)OC(O)] (1p). The same experimental procedure was used as for **1o**. In this case, 50 mL of acetone was added to the crude reaction medium before filtration on Celite (Merck 545), and 25 mL of H_2O was subsequently added to the yellow filtrate. The pale precipitate formed was decanted and washed with *n*-pentane. This precipitate was a mixture of free ligand, traces of the corresponding urea, and the desired complex (70% by ^1H NMR). After extraction of the precipitate with three fractions of 3 mL of dichloromethane and subsequent evaporation of the solvent, yellow crystals were formed. Yield: 20%. Mp: 219 ± 5 °C dec. IR (KBr, cm^{-1}) 1699 (s, C═O), 1617 (s, C═O); 1268 (s, N−O). NMR: ^1H (CD_2Cl_2) δ 9.76 (d, J = 6 Hz, 1 H, ortho/diimine); 9.57 (d, J = 6 Hz, 1 H, ortho/diimine); 8.07 (s, 2 H, diimine); 7.66 (d, J = 5 Hz, 2 H); 7.56 (d, J = 7 Hz, 2 H, phenyl); 7.37 (d, J = 7 Hz, 2 H, phenyl); 1.44 (s, 9 H, C(CH_3)$_3$/diimine); 1.43 (s, 9 H, C(CH_3)$_3$/diimine); 1.32 (s, 9 H, C(CH_3)$_3$/phenyl). FABMS (*m*-nitrobenzyl alcohol): *m*/*z* 538 (M + 1 − 2CO), 537 (M + 1 − ^{t}Bu), 522 (M + 1 − CO − CO_2), 507 (M − NCO − CO_2), 480 (M + 1 − ^{t}Bu − 2CO), 402 (M − CO − (C_6H_4)NO), 374 (M − CO_2 − ^{t}Bu(C_6H_4)NCO). Anal. Calcd for $C_{30}H_{37}N_3O_3Pd$: C, 60.66; H, 6.28; N, 7.07; Found: C, 60.88; H, 6.11; N, 7.01.

Reaction of 1a and Maleic Anhydride. Complex **1a** (50 mg; 0.11 mmol) and 120 mg of 1,10-phenanthroline (0.66 mmol) were suspended in 15 mL of freshly distilled nitrobenzene, and 400 mg of maleic anhydride (4.08 mmol) was added. The reaction medium was heated at 100 °C with stirring. The heterogeneous medium became transiently homogeneous, giving rise to an orange solution, and a dark precipitate began to form. After 50 min, the medium was cooled, and the precipitate was filtered off and washed several times with diethyl ether. Elemental analysis, mP, and IR, after comparison with reported data, allowed its identification as being mainly (phen)Pd(maleic anhydride) (**8**) along with some metallic palladium. No other organometallic species could be identified.

Reaction of 1a with *p*-Tolyl Isocyanate. To 50 mg of complex **1a** (0.11 mmol) suspended in 5 mL of freshly distilled nitrobenzene was added 585 mg of *p*-tolyl isocyanate (4.40 mmol), and the reaction medium was heated at 142 °C with stirring. The heterogeneous medium became homogeneous (red) at 120 °C, while being heated. After 6 h, the medium was cooled and 2 mL of ethanol was added to neutralize the excess unreacted isocyanate. The complex **3** precipitated as an orange solid, which was filtered and washed several times with diethyl ether (80%). Mp: 301 ± 5 °C dec. IR (KBr, cm^{-1}) 1640 (s, C═O), 1615 (s, C═O). NMR: ^1H (CD_2Cl_2) δ 8.47 (d, J = 8 Hz, 2 H), 8.32 (d, J = 8 Hz, 4 H); 8.22 (d, J = 5 Hz 2 H); 7.96 (s, 2 H); 7,57 (dd, J_1 = 8 Hz, J_2 = 5 Hz, 2 H); 7.29 (d, J = 8 Hz, 2 H); 7.14 (d, J = 8 Hz, 2 H); 7.04 (d, J = 8 Hz, 4 H); 2.35 (s, 6 H, CH_3); 2.29 (s, 3 H, CH_3). FABMS (*m*-nitrobenzyl alcohol): *m*/*z* 658 (M + 1), 525 (M + 1 − TolNCO), 391 (M − 2TolNCO), 286 (M − 2TolNCO − NTol). Anal. Calcd for $C_{35}H_{29}N_5O_2Pd$: C, 63.88; H, 4.44; N, 10.64; Found: C, 63.72; H, 4.29; N, 10.62.

Reaction of (phen)Pd(dba) with PhNCO and CO_2. The complex (phen)Pd(dba) (50 mg; 0.10 mmol) and 100 mg of 1,-10-phenanthroline (0.55 mmol) in 15 mL of freshly distilled benzene under nitrogen were introduced in the autoclave. The autoclave was then flushed with carbon dioxide three times with stirring, pressurized to 20 bar, and heated to 80 °C (in 30 min). During heating, at 45 °C, 250 mg of phenyl isocyanate (2.10 mmol) was introduced into the medium by a mechanical device. The stirring was maintained for 5 h at 80 °C. After subsequent cooling and depressurization, the autoclave was opened in a glovebox. The orange-brown suspension that formed was decanted, washed several times with diethyl ether, and dried in vacuo (45 mg). No palladium complex could be further characterized in the mother solution. By IR and ^1H NMR spectroscopy, this air-stable precipitate proved to be a 1:1 mixture of complex **3** and another unknown compound presenting a dissymmetric phenanthroline (H_{ortho} at 9.98 and 9.11 ppm; J = 6 Hz). A sharp carbonyl absorption at 1690 cm^{-1} was clearly visible, whereas a second absorption at 1620 cm^{-1} appeared as a shoulder on the carbonyl absorption of **3**. Attempts to separate the new complex from **3** have as yet been unsuccessful since both complexes are sparingly soluble. Complex **1a** could not be detected either in the precipitate or in the mother solution.

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Supporting Information Available: Table S1 listing atomic coordinates for non-hydrogen atoms, Table S2 listing atomic coordinates for hydrogen atoms, Table S3 listing thermal parameters for anisotropic atoms, Table S4 listing bond lengths, and Table S5 listing bond angles (14 pages). Ordering information is given on any current masthead page.

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