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Palladium(0)-Catalyzed Trimerization of Arylisocyanates into 1,3,5-Triarylisocyanurates in the Presence of Diimines: A Nonintuitive Mechanism

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Abstract: We show here that palladium(0) (dibenzylideneacetone) complexes bearing 1,10-phenanthroline constitute efficient catalysts for the cyclotrimerization of aromatic isocyanates. For the first time, the mechanism of this reaction has been investigated experimentally and theoretically with group 10 catalysts. This investigation provides a very consistent picture of the catalytic cycle. Notably, we establish that the reaction does not proceed by stepwise cycloadditions or ring insertions involving metallacyclic intermediates, as might have been anticipated. Rather, in our proposal, the initial steps of the mechanism resemble the chain-growth process operative during the anionic polymerization of isocyanates and feature charge-separated intermediates. These steps are then followed by ring closure on the metal center of the last intermediate formed to yield a seven-membered metallacycle that reductively eliminates the cyclotrimer and re-forms the active species. In addition, we conclusively show that the (known) palladacycles that could be isolated during the experimental investigations are not catalytic intermediates but result from catalyst deactivation. Thus, with Pd(0) diimine catalysts, the actual trimerization mechanism appears to be a blend between the two types of mechanisms proposed thus far for the oligomerization of heterocumulenes with very different catalysts. In conclusion, this work contributes to a better understanding of the reactivity of arylisocyanates in the vicinity of late group 10 metal centers in low oxidation state and sheds some light on the detrimental self-poisoning processes observed during the reductive carbonylation of nitroaromatic substrates catalyzed by related catalysts in non-nucleophilic media.

Introduction

The reactivity of isocyanates in the coordination sphere of various group 10 metal centers was a field only partially explored by the early 1990s,[1] but some renewed interest for their reactivity has been shown more recently.[2] From an atom-economy perspective, such reactions are quite attractive since they can provide a very valuable access to various types of heterocycles,[3] as amply demonstrated not only by the seminal work of Hoberg with nickel complexes,[4,5] but also by other researchers later on.[6] Among these investigations, much fewer have focused on cyclotrimerization reactions of isococyanates,[7,8] especially with group 10 metal catalysts.[9] These reactions provide, however, an easy access to 1,3,7-isocyanurates (**3a**−**e**; Chart 1), which constitute important activators and additives for processing numerous urethane-based polymers and coatings.[7b,8,10] We have shown previously that such isocyanate oligomerization reactions are likely at the origin of self-

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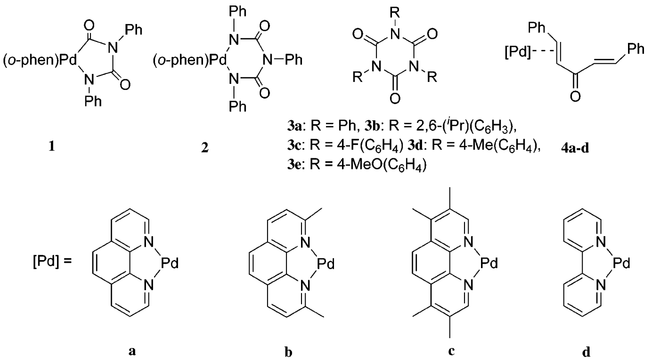
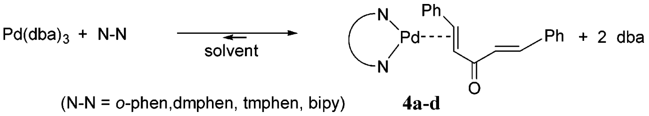
Chart 1. Structures of Selected Compounds



Scheme 1. Synthesis of Complexes **4a**−**d**



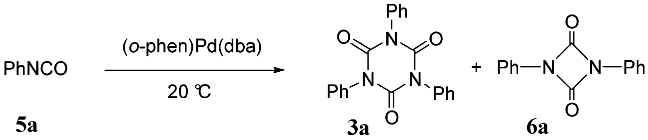
poisoning during the catalytic carbonylation of various nitroaromatic substrates when these transformations are conducted in non-nucleophilic/non-protic solvents.[11] Given that such carbonylation reactions have aroused an enormous industrial interest as potential means to replace the traditional phosgene-based processes in the production of isocyanates, a better understanding of the detrimental side processes was highly desirable, especially with (Pd/*o*-phen)-based catalytical systems (*o*-phen = 1,10-phenanthroline), which constitute the most active catalytic systems identified to date for this reaction.[12,13] With such catalysts, self-poisoning was often accompanied by the formation of palladacycles such as **1** or **2** (Chart 1).[11]

In the hope of getting additional clues on the way these palladacycles can form, we have studied the reaction of PhNCO with various Pd(0)−diimine precursors. At first, the reactivity of various (N−N)Pd(dba) complexes (**4a**−**d**) isolated from the Pd(dba)$_3$ precursor and the corresponding diimine was examined (Chart 1). Several among these complexes proved to constitute quite efficient catalysts for the trimerization reaction. The scope of this reaction was subsequently investigated experimentally and by density functional theory (DFT). Calculations carried out on this catalytic transformation allowed for the determination of a precise mechanism in full accordance with the experimental results.

Results

Synthesis of (N−N)Pd(dba) Complexes. The desired Pd(0) precursors **4a**−**d** were isolated from the known Pd(dba)$_3\cdot$C$_6$H$_6$ complex and various diimine ligands, following a procedure used by Ishii et al. in 1974 for the isolation of (bipy)Pd(dba) and more recently by Stahl and co-workers for the isolation of (bc)Pd(dba) (bc = bathocuproin) (Scheme 1).[14,15] Notably, the successful isolation of **4a**−**d** rests on their poor solubility in common organic solvents. Indeed, their precipitation in the reaction medium drives the various equilibria toward their quantitative formation. In accordance with the equilibrium situation, we have verified that the starting Pd(dba)$_3$ complex could be regenerated in solution when **4a** was exposed to a 10-fold excess of dba.

Scheme 2. Reaction of Phenylisocyanate (**5a**) with Complex **4a**



The pale orange air-sensitive Pd(0) complexes **4a**−**d** were obtained in good yields and were characterized by FABMS spectrometry. The low solubility of the complexes associated with the lability of the dba ligand which slowly generates palladium black in solution complicates any subsequent purification. As a result, only poor elemental analyses were obtained for these compounds. The strong fluxionality of the dba ligand is revealed by ^{1}H NMR. This fluxionality renders the diimine ligand symmetric at the NMR time scale and impedes observation of olefinic dba protons coordinated to the Pd(0) center at ambient temperature, but a one-to-one ratio between dba and phenanthroline ligands can be inferred from the ^{1}H NMR signals of complex **4a** at low temperatures (see Supporting Information). Infrared spectroscopy also clearly indicates that the dba ligand is monocoordinated in a π-fashion in the solid state, as suggested by the slight ν_{CO} shift to lower wavenumbers observed relative to free dba (ca. 15 cm^{-1}).[14]

Reaction of 4a−d with Aromatic Isocyanates. In line with the fluxionality observed by NMR, several studies have shown that the dba ligand was quite labile in **4a**−**d** and that these Pd(0) complexes could act as convenient sources of the (N−N)-Pd^0 fragment.[14−16] However, in our initial experiments, the inherent low solubility of **4a**−**d** severely restricted the available concentration of (N−N)Pd^0 precursor in solution and proved detrimental for obtaining clean stoichiometric reactions with aromatic isocyanates, due to the competitive decomposition of **4a**−**d** into palladium metal. To overcome this problem, we decided to use the isocyanate reactant in large excess (i.e., directly as solvent) to speed up the reaction kinetics.

Thus, when **4a** is suspended in neat PhNCO (**5a**), a slightly exothermic process takes place and large amounts of off-white product precipitate in the medium, rendering it viscous and completely heterogeneous after a few hours (Scheme 2).

Analysis of the precipitate indicated that the latter was mostly composed of 1,3,5-triphenylisocyanurate (**3a**), the cyclic trimer of isocyanate, which evidently results from the catalytic cyclotrimerization of phenylisocyanate **5a** (40−45%) after 30 h (Table 1, entry 1). Traces of 1,3-diphenylene uretedione (**6a**), the cyclic dimer, were also characterized (0.6%), but no additional product could be identified apart from unreacted PhNCO (**5a**). In this reaction, the isolated yield of trimer **3a** corresponds to a catalytic turnover of ca. 120 cycles. Control experiments revealed that, under otherwise similar conditions, neither free dba, free *o*-phen, Pd adsorbed on charcoal (Pd/C),

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Table 1. Catalytic Trimerization of Phenylisocyanate by **4a**

entry	[**4a**]$_0$^{a}	[PhNCO]/[**4a**]	cosolvent (ratio vs PhNCO)	t (h)	T (°C)	isolated yield of **3a**
1	1.0×10^{-2}	800	/	30.0	25	45
2	2.4×10^{-2}	147	CH_2Cl_2 (2:1)	30.0	25	15
3	1.2×10^{-2}	350	CH_2Cl_2 (1:1)	120.0	25	46
4	1.2×10^{-2}	350	C_6H_6 (1:1)	120.0	25	3
5	1.2×10^{-2}	350	$(CH_3)_2CO$ (1:1)	120.0	25	65
6	1.2×10^{-2}	350	$PhNO_2$ (1:1)	120.0	25	80
7	1.2×10^{-2}	350	$PhNO_2$ (1:1)	14.0	25	99
8	1.2×10^{-2}	350	$PhNO_2$ (1:1)	0.5	25	80
9	1.2×10^{-2}	350	$PhNO_2$ (1:1)	0.2	140	10^b
10^c	2.2×10^{-2}	40	$PhNO_2$ (50:1)	7.0	140	0^d
11^c	2.2×10^{-3}	20	C_6H_6 (50:1)	1.0	80	0^e
12	2.4×10^{-2}	147	CH_2Cl_2 (2:1)	3.0	0	10^f
13	0.8×10^{-2}	350	$PhNO_2$ (2:1)	16.0	−10	67
14	0.8×10^{-2}	350	$PhNO_2$ (2:1)	0.3	25	25
15^g	0.8×10^{-2}	350	$PhNO_2$ (2:1)	0.3	25	22
16^h	0.8×10^{-2}	350	$PhNO_2$ (2:1)	0.3	25	16
17^i	0.8×10^{-2}	350	$PhNO_2$ (2:1)	0.3	25	20
18^j	0.8×10^{-2}	350	$PhNO_2$ (2:1)	0.3	25	7

[a] Initial concentration of **4a** in moles per liter. [b] Estimated after leaving the reaction medium 30 additional hours at 25 °C. [c] Five equivalents of *o*-phen also present in the medium. [d] Isolation of palladacycle **2** (95%: see Supporting Information). [e] Isolation of palladacycle **2** (28%) along with palladium black. [f] Estimated after leaving the reaction medium at 25 °C. [g] In the presence of a 10-fold excess of *o*-phen. [h] In the presence of a 5-fold excess of dba. [i] In the presence of a 5-fold excess of 1,9-dihydroanthracene. [j] In the presence of a 5-fold excess of duroquinone.

nor $Pd(dba)_3$ alone produced any visible reaction. Thus, the catalytic transformation must be imparted to **4a**. Accordingly, with such a hypothesis, when $Pd(dba)_3$ and excess *o*-phen are simultaneously introduced in the medium, or when another potential source of "(*o*-phen)Pd^0" such as (*o*-phen)Pd(PhNO)$_n$ is introduced in the medium,[17] the exothermic formation of isocyanurate is again observed. Thus, the "(*o*-phen)Pd^0" fragment appears as a constitutive structural unit of the active species.

The reaction observed in neat PhNCO is often incomplete, a fact that can be attributed to the heterogeneous nature of the reaction medium, rendering stirring inefficient after some time. To determine if the conversion of isocyanate (**5a**) in 1,3,5-triphenylisocyanurate (**3a**) could be improved, the use of a cosolvent was tested. With dichloromethane, no better conversions were obtained (Table 1, entries 2 and 3). Typically, using a 1:1 (volumic) mixture of PhNCO (**5a**) with dichloromethane delayed precipitation of the trimer (**3a**), but no higher yields were obtained even after 120 h (Table 1, entry 3). Further dilution of the phenylisocyanate substrate **5a** led to even lower conversions into **3a**, even when higher catalyst loadings are used (Table 1, entry 2). The medium apparently stays homogeneous, but the formation of metallic palladium is visible after several hours. We then realized that the nature of the cosolvent used could exert a strong influence on the catalyst turnover, with more polar cosolvents favoring higher conversions (Table 1, compare entries 3−6). Thus, when nitrobenzene was used as cosolvent, we observed a quite quantitative conversion of the starting isocyanate into isocyanurate after 14 h (Table 1, entry 7). Actually, monitoring of the reaction progress over time reveals that the conversion of the phenylisocyanate (**5a**) is quite complete already after 1 h in this solvent (Table 1, entry 8).

The temperature also appears to strongly influence the catalytic transformation (Table 1, entries 9−13). As can be seen from entries 9−11 in Table 1, heating of the reaction medium has a detrimental effect, since the isolated yield of **3a** drops to 10% after ca. 10 min of heating at 140 °C (entry 9). On the other hand, cooling of the reaction medium also results in a decrease of the catalytic activity, as qualitatively evidenced by the absence of visible precipitation after 3 h at 0 °C (entries 12 and 13). Clearly, the trimerization reaction appears to be favored at ambient temperature with **4a**.

Finally, the effect of various additives on the isolated yield of trimer **3a** was investigated under conditions for which the reaction is far from completion (Table 1, entries 14−18). First, the presence of excess of the catalysts ligands such as *o*-phen or dba was checked (entries 15 and 16). Thus, while the yield seems quite unaffected by excess *o*-phen, a 5-fold excess of dba seems to slightly hinder the reaction (compare entries 15 and 16 with entry 14). We also verified that additives such as 1,9-dihydroanthraquinone or duroquinone (Table 1, entries 17 and 18), well known to trap radicals, do not poison the reaction. This suggests that the mechanism does not proceeds via a radical pathway.

The fate of the palladium complex **4a** was examined next. The low yield in 1,3,5-triphenylisocyanurate (**3a**) in run 2 (Table 1) when dichloromethane was used as cosolvent allowed for selective precipitation of metal-containing species. Thus, the known palladacycle **1** (ca. 30−50% of starting **4a**) was isolated at the end of the reaction along with metallic palladium.[11,12] When the reaction was run at lower temperature in the same cosolvent (Table 1, entry 12), the formation of metallic Pd was not observed and **1** was again dominantly isolated (ca. 80% of **4a**) along with some palladacycle **2** (ca. 20% of **4a**) and trimer **3a** (10% of starting PhNCO). Yet, when **4a** is heated above 140 °C in nitrobenzene in the presence of a much slighter excess of phenylisocyanate (**5a**) and free *o*-phen in excess, the quasi-quantitative conversion of **4a** into **2** is observed along with traces of metallic palladium (Table 1, entry 10 and Scheme 3). Notably, the palladacycle **1** could never be isolated under these conditions.

We had previously established that both **1** and **2** were unreactive against phenylisocyanate (**5a**) at ambient temperature.[11] Thus, these complexes can by no means constitute intermediates in this transformation and correspond rather to

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(17) Paul, F. Ph.D. Thesis, Strasbourg 1, 1993.

Scheme 3. Reaction of Phenylisocyanate (**5a**) with Complex **4a** under Heating

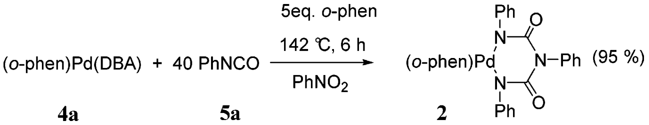
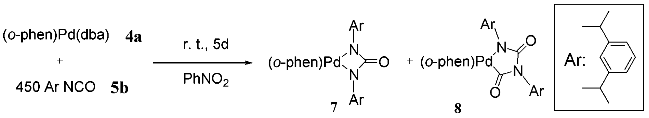


Table 2. Catalytic Trimerization of Various Arylisocyanates by **4a** at 25 °C in ArNCO/PhNO$_2$ (1:2) Mixtures[a]

entry	Ar	[ArNCO]/[**4a**]	*t* (min)	isolated yield[b]
1	Ph (**5a**)	350	15	17
2	2,6-(^{i}Pr)$_2$(C$_6$H$_3$) (**5b**)[c]	810	120	0
3	4-F(C$_6$H$_4$) (**5c**)[d]	350	15	49
4	4-Me(C$_6$H$_4$) (**5d**)	310	15	0
5	4-Me(C$_6$H$_4$) (**5d**)	310	1010	12
6	4-MeO(C$_6$H$_4$) (**5e**)	278	15	3
7	4-MeO(C$_6$H$_4$) (**5e**)	278	920	8

[a] Initial concentration of **4a**: 0.8 × 10^{-2} mol L^{-1}. [b] Of corresponding 1,3,5-triarylisocyanurate. [c] Initial concentration of **4a**: 2.9 × 10^{-2} mol L^{-1}. [d] Initial concentration of **4a**: 0.4 × 10^{-2} mol L^{-1}.

Scheme 4. Reaction of 2,6-Di(*iso*-propyl)phenylisocyanate (**5b**) with Complex **4a**



deactivated forms of the catalyst. We have now checked that neither **1** nor **2** can be obtained from insertion of an (*o*-phen)-Pd^0 fragment in **3a** and subsequent rearrangement. Indeed, when **4a** is refluxed with an excess of **3a** (i.e., 15 equiv), in the presence of an excess of free *o*-phen, the reaction leads mostly to decomposition of the compound **4a** in metallic Pd. Therefore, both **1** and **2** *do not* result from trapping of the (*o*-phen)Pd^0 fragment by the 1,3,5-triphenylisocyanurate (**3a**) catalytically generated during the catalysis.[18]

The reaction of **4a** with other arylisocyanates was also attempted (Table 2). Thus, when **4a** is reacted with a sterically crowded isocyanate such as the 2,6-di(*iso*-propyl)phenylisocyanate (**5b**), two palladacycles can be isolated instead of the corresponding 1,3,5-triarylisocyanurate (**3b**) (Scheme 4). The former (**7**) is a known four-membered metallacycle[11] and is essentially present as a side product (5%), while the other is a new five-membered palladacycle (**8**), analogous to **1**, which constitutes the dominant form (70%) of the Pd(0) precursor introduced.

Now, with less crowded arylisocyanates such as **5c** or **5e**, the catalytic reaction takes place and is significantly influenced by the para substituent (Table 2). Apparently, the reaction proceeds faster with electron-withdrawing groups.

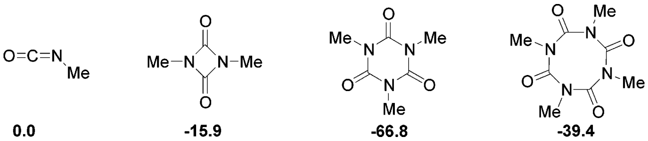
Finally, we have examined the reaction of phenylisocyanate (**5a**) with the other Pd(0) precursors **4b**−**d**. Except with the dmphen complex (**4b**), the catalytic trimerization takes place to a comparable extent (Table 3). With **4b**, no trimerization can be evidenced and only decomposition in metallic Pd is observed after several days. We believe that the steric strain introduced on the ortho positions of the dmphen ligand by the methyl groups is responsible for that lack of reactivity.

Table 3. Catalytic Trimerization of Phenylisocyanate by Various (N−N)Pd(dba) Precursors at 25 °C in ArNCO/PhNO$_2$ (1:2)[a]

entry	N–N	*t* (min)	isolated yield of **3a**
1	*o*-phen	15	17
2	dmphen	15	0
3	dmphen	1050	0
4	tmphen	15	18
5	bipy	15	9
6	bipy	995	57

[a] The initial concentration of the various (N−N)Pd(dba) complexes **4a**−**d** is 0.8 × 10^{-2} mol L^{-1} ([PhNCO]/[(N−N)Pd(dba)] = 350).

Chart 2. Relative Energies (kcal/mol) of Methylisocyanate Oligomers (*n* = 2, 3, 4) with Regard to Methylisocyanate



DFT Modeling of the Catalytic Transformation. DFT calculations were next carried out to determine the complete catalytic cycle and rationalize the experimental observations. All these calculations were carried out within the framework of DFT using the Gaussian 03W set of programs.[42−46] The structure of the 14 VE metallic fragment [(*o*-phen)Pd] was kept unmodified, but the phenylisocyanate was replaced by methylisocyanate to save computation time (see Supporting Information for further details). To take into account the role played by the polarity of the medium, single point calculations were realized using the polarized continuum model (PCM) method using dichloromethane as solvent. The choice of dichloromethane is not arbitrary and results from the fact that this solvent was used as cosolvent several times. Furthermore, the dielectric constant of CH$_2$Cl$_2$ (ϵ = 9.1) is close to that of phenylisocyanate (ϵ = 8.9), which was used as solvent in the initial experiments.

A first important point is the relative stability of the cyclic oligomers (R-NCO)$_n$ that may form during the process (n = 2, 3, 4). As expected, the trimer was found to be more stable than the dimer and the tetramer (Chart 2).

In the initial step, it was assumed that coordination of the isocyanate on the [(*o*-phen)Pd]^0 fragment (noted **I** hereafter) preferentially takes place at the C═N double bond. This preference can indeed be expected when one examines the MO scheme of the methylisocyanate. The HOMO and the HOMO−1 were found to be more developed on the C═N double bond, while the HOMO−2 and HOMO−3 are mostly located on the π-system of the C═O double bond (see Supporting Information). Furthermore, the LUMO and the LUMO+1 were also found to be more developed on the nitrogen atom. Note also that the same MO ordering is found for phenylisocyanate. This hypothesis was further confirmed by calculations of the possible 16 VE η^2-complexes **IIa** (coordination of methylisocyanate to fragment **I** through the C═N double bond) and **IIb** (coordination of methylisocyanate to fragment **I** through the C═O double bond) whose formation were found to be exothermic. As shown

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(18) Note that **2** and the known corresponding four-membered palladacycle could be isolated from **4a** and **6a** under similar conditions (see Supporting Information). However, this does not constitute a proof of reactivity of **4a** with the cyclodimer.[19]

(19) It is known that uretediones equilibrate with the corresponding isocyanates upon heating. It constitutes often the favored product under ambient conditions, but the kinetics of this reaction are very slow.[20]

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Scheme 5. Coordination of Methylisocyanate to Complex [(*o*-phen)Pd] **I** To Form **IIa** and **IIb**; NBO Charges Are Given in e Units

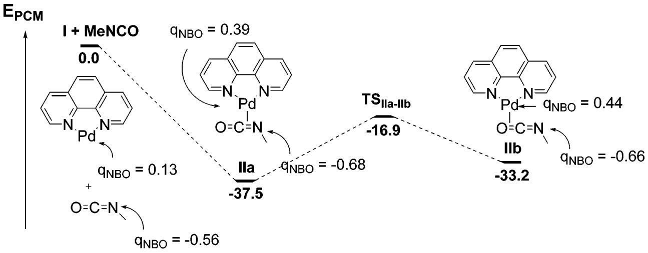

Table 4. Geometrical Data for C−O and C−N Bonds in Free Methylisocyanate and in Complexes **IIa** and **IIb**[a]

bond	CH_3NCO	IIa	IIb
C−O	1.18 (1.83)	1.22 (1.65)	1.26 (1.46)
C−N	1.20 (1.95)	1.28 (1.56)	1.26 (1.71)

[a] Distances are given in angstroms. Respective Wyberg bond indexes are given in parenthesis.

in Scheme 5, complex **IIa** was found to be 4.3 kcal/mol more stable than complex **IIb**. In both compounds, the C═O and C═N have lost their double bond character and a significant lengthening of bond distances is noted with respect to free methylisocyanate. This is also confirmed by calculation of Wyberg bond indexes (WBI), as summarized in Table 4. Also, NBO calculations indicate that the nucleophilic character of the nitrogen atom in **IIa** and **IIb** is slightly enhanced upon coordination, its charge increasing from q_{NBO}N = −0.56 e in methylisocyanate to −0.68 e in **IIa** and −0.66 e in **IIb**. This observation will prove important to rationalize the subsequent steps of the catalytic cycle. Note also that the positive charge on the palladium atom increases in **IIa** and **IIb** in comparison to that in **I** (Scheme 5).

A transition state $\mathbf{TS_{IIa-IIb}}$ connecting these two minima was found ($\Delta E^{\ddagger}_{\mathbf{IIa-IIb}}$ = 20.6 kcal/mol; Scheme 5; Figure 1a). The negative frequency characterizing this transition state corresponds to a rotation around the palladium carbon bond axis. These results where the two coordination modes lie close in energy resemble those reported for ketene on diphosphane Ni(0) and Pt(0) fragments.[21]

Having shown the preference for C═N coordination, we next examined the introduction of a second molecule of methylisocyanate. In a first series of calculations, we tried to coordinate two molecules of methylisocyanate to fragment **I** to see whether an 18 VE bisisocyanate complex such as [(*o*-phen)Pd(MeNCO)$_2$] could be obtained. Whatever the starting structure proposed, all attempts resulted in the re-formation of either complex **IIa** or **IIb**. This result prompted us to investigate a second sphere mechanism in which one molecule of methylisocyanate would react with the nucleophilic nitrogen atom. We logically focused our attention on complex **IIb** in which the nitrogen atom is not coordinated to the palladium center. Indeed, one may expect than coordination of nitrogen to Pd in **IIa** makes this complex less reactive toward nucleophilic attack on methylisocyanate. The reactivity of complex **IIa** will be discussed later. The new complex **III** was characterized as a local minimum on the potential energy surface (PES) and results from the attack of the uncoordinated nitrogen atom of **IIb** on a free molecule of isocyanate. The optimized geometry for the transition state ($\mathbf{TS_{IIb-III}}$) connecting **IIb** to **III** is shown in Figure 1b. This coupling reaction was found to be slightly exothermic ($\Delta E_{\mathbf{IIb-III}}$ = −4.4 kcal/mol) and requires a relatively weak activation energy of $\Delta E^{\ddagger}_{\mathbf{IIb-III}}$ = 14.2 kcal/mol (Scheme 6). It is noteworthy that the structure of complex **III** features a small interaction between the α-hydrogen atom of the *o*-phen ligand and the oxygen atom of the second molecule. The electronic structure of the second isocyanate is significantly disturbed by the attack of the nitrogen atom, the NBO charge of the nitrogen atom is increased (q_{NBO}N = −0.69 e **III** compared to q_{NBO}N = −0.66 e in **IIb** or −0.56 e in free methylsiocyanate), and the C═O and C═N bonds have partially lost their double bond character (C−O, 1.25 with WBI = 1.40; C−N, 1.29 with WBI = 1.58). The latter might be sketched by a zwitterionic valence bond mesomer ($\mathbf{III_z}$) which certainly possesses a non-negligible weight in the bonding description of **III**.

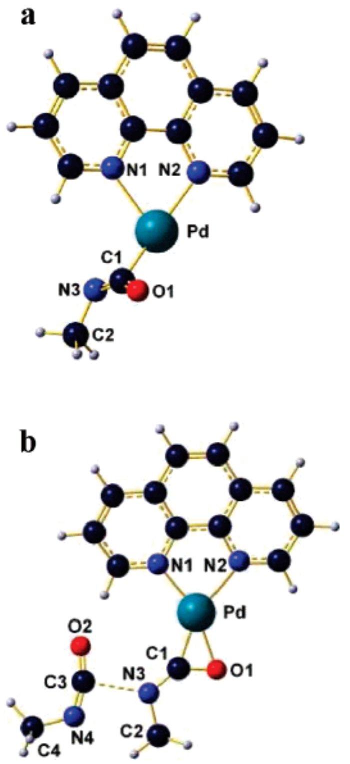

Figure 1. Views of the transition states $\mathbf{TS_{IIa-IIb}}$ (a) connecting complexes **IIa** and **IIb** and $\mathbf{TS_{IIb-III}}$ (b) connecting the two structures **IIb** and **III** as given by DFT. Most significant bond distances (Å) and bond angles (deg): $\mathbf{TS_{IIa-IIb}}$: Pd−N1, 2.298; Pd−N2, 2. 2.275; Pd−C1, 2. 1.953; Pd−O1, 2.636; Pd−N3, 2.511; C1−O1, 1.226; C1−N3, 1.270; C2−N3, 1.455; N1−Pd−N2, 73.8. $\mathbf{TS_{IIb-III}}$: Pd−N1, 2.105; Pd−N2, 2.228; Pd−C1, 2.269; Pd−O1, 2.053; C1−O1, 1.274; C1−N3, 1.270; C2−N3, 1.458; C3−N3, 2.215; C3−O2, 1.192; C3−N4, 1.232; C4−N4, 1.452; N1−Pd−N2, 76.8; C1−N3−C2, 116.9; O2−C3−N4, 161.1.

We next inquired about the formation of the five-membered metallacycle **1** which was isolated. Formation of this complex (corresponding to **IV** in our calculations) from complex **III** was found to be strongly exothermic (ΔE = −42.6 kcal/mol) and only involves a weak activation barrier ($\Delta E^{\ddagger}_{\mathbf{III-IV}}$ = 7.6 kcal/mol). An isomer (**V**) of complex **IV** featuring a Pd−O bond in place of the Pd−N bond of **IV** was also characterized as a local

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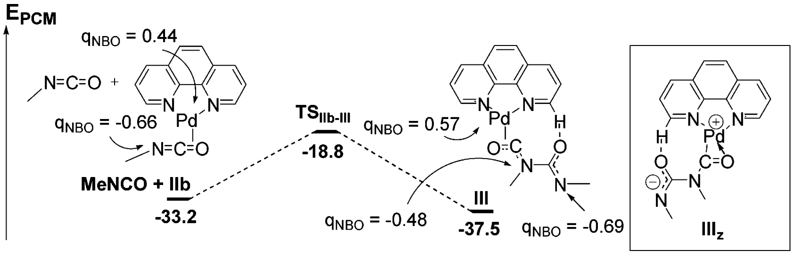
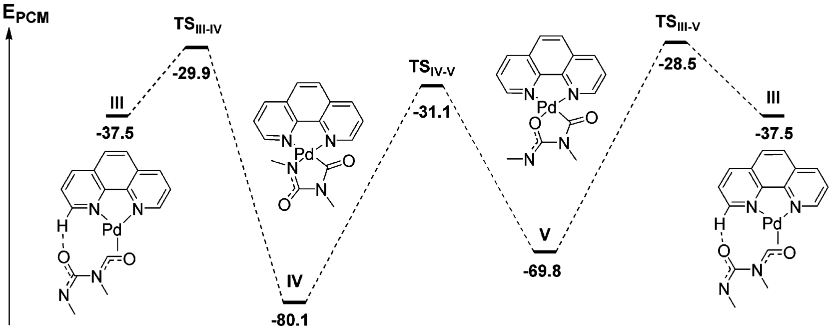
[21] (a) Hofmann, P.; Perez-Moya, L. A.; Steigelmann, O.; Reidel, J. *Organometallics* **1992**, *11*, 1167−1176. (b) Wright, C. A.; Thorn, M.; McGill, J. W.; Sutterer, A.; Hinze, S. H.; Prince, R. B.; Gong, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 10305−10306.

Scheme 6. Energetic Pathway for the Transformation of **IIb** into **III**; NBO Charges Are Given in e Units



Scheme 7. Formation of Complexes **IV** and **V** from Complex **III**



minimum on the PES. Its formation also requires a weak activation energy starting from complex **III** ($\Delta E^{\ddagger}_{\mathrm{III-IV}} = 9.0$ kcal/mol) but appears to be less exothermic ($\Delta E = -32.3$ kcal/mol) than that of **IV**. Both **IV** and **V** are connected by a transition state (**TS$_{\mathrm{IV-V}}$**; $\Delta E^{\ddagger}_{\mathrm{IV-V}} = 49.0$ kcal/mol) which involves a rotation around the C3−N3 bond (Scheme 7). Given the energetic closeness of the two energy barriers, DFT predicts that the formation of both complexes can occur during the process. A view of the transition state **TS$_{\mathrm{III-V}}$** is presented in Figure 2a. Importantly, DFT confirms that complex **IV** behaves as a thermodynamic sink, in line with experimental observations.

Complex **V** turns out to be the only possible reactive intermediate to explain the formation of the cyclic trimer. As with **III**, complex **V** features one exocyclic nitrogen atom that is prone to react with a third molecule of methylisocyanate ($q_{\mathrm{NBO}}\mathrm{N} = -0.62$ e). As shown in Scheme 8, complex **VII** which results from the nucleophilic attack of **V** onto MeNCO was found to be a local minimum onto the PES and its formation is only slightly endothermic ($\Delta E = 4.5$ kcal/mol).

As with the transformation between **IIb** and **III**, complex **V** is connected to **VII** through **TS$_{\mathrm{V-VII}}$** (Figure 2b) whose formation requires an activation energy of $\Delta E^{\ddagger}_{\mathrm{V-VII}} = 16.4$ kcal/mol. Again the chain growth elementary process operative here is not a cycloaddition or an insertion but rather a nucleophilic attack of the corresponding terminal nitrogen atoms on the electrophilic carbonyl of the free methylisocyanate. Also, the new intermediate **VII** might be sketched by a zwitterionic valence bond structure (**VII$_z$**) which certainly possesses a non-negligible weight in its bonding description. This compound can then rearrange into the metallacyclic structure **VIII** in an exothermic fashion ($\Delta E = -13.8$ kcal/mol) via a nucleophilic attack of the external nitrogen atom on the palladium center with an activation barrier of $\Delta E^{\ddagger}_{\mathrm{VII-VIII}} = 23.0$ kcal/mol (see Supporting Information).

The last step of the process involves the formation of the cyclotrimer from complex **VIII**. This coupling process involves two distinct steps. The first is the reductive elimination that yields complex **IX** in which one molecule of trimer is coordinated to the 14 VE fragment **I** through one C−N bond (Scheme 9). This elimination process is slightly endothermic

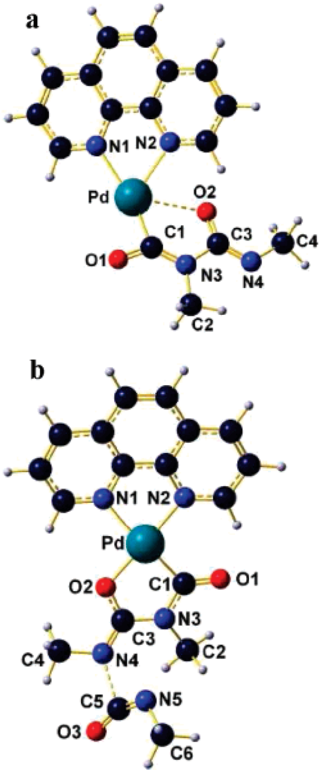
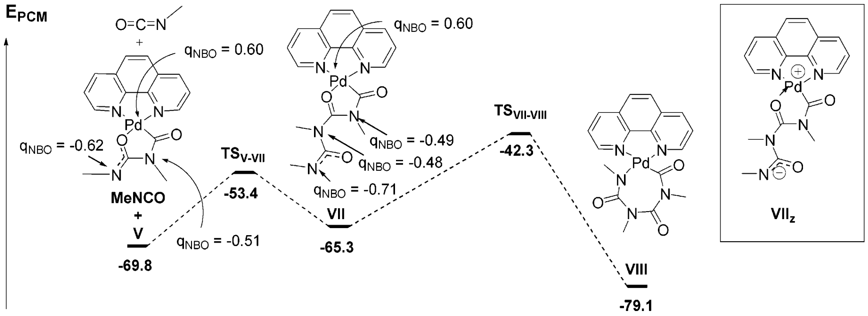
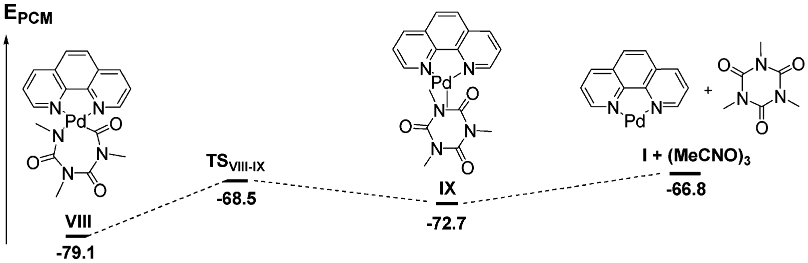


Figure 2. Views of the transition states **TS$_{\mathrm{III-V}}$** (a) connecting the two structures **III** and **V** and **TS$_{\mathrm{V-VII}}$** (b) connecting the two structures **V** and **VII** as given by DFT calculations. Most significant bond distances (Å) and angles (deg): **TS$_{\mathrm{III-V}}$**: Pd−N1, 2.229; Pd−N2, 2.309; Pd−C1, 1.891; Pd−O1, 2.319; Pd−O2, 2.647; C1−O1, 1.235; C1−N3, 1.317; C2−N3, 1.458; C3−N3, 1.477; C3−O2, 1.268; C3−N4, 1.289; C4−N4, 1.445; N1−Pd−N2, 73.5; O1−C1−N3, 132.3. **TS$_{\mathrm{V-VII}}$**: Pd−N1, 2.185; Pd−N2, 2.075; Pd−C1, 1.962; Pd−O2, 2.000; C1−O1, 1.122; C1−N3, 1.380; C2−N3, 1.458; C3−N3, 1.401; C3−O2, 1.301; C3−N4, 1.298; C4−N4, 1.449; C5−N4, 2.021; C5−O3, 1.196; C5−N5, 1.254; C6−N5, 1.458; N1−Pd−N2, 81.7.

Scheme 8. Energetic Pathway Explaining the Formation of Complex **VIII** from Complex **V**; NBO Charges Are Given in e Units



Scheme 9. Reductive Elimination Process Leading to 1,3,5-Trimethylisocyanurate and to Complex **I** Formation



($\Delta E_{\mathbf{VIII-IX}} = 6.4$ kcal/mol) and requires a quite weak activation barrier ($\Delta E^{\ddagger}{}_{\mathbf{VIII-IX}} = 10.6$ kcal/mol; Figure 3). It is therefore likely to occur under ambient conditions. The decomplexation of the cyclotrimer, which allows the re-formation of the active species **I**, is also slightly endothermic ($\Delta E_{\mathbf{IX-I}} = 5.9$ kcal/mol).

Another experimental observation concerns the formation of metallacycle **2** upon thermolysis of [(*o*-phen)Pd(dba)] with excess PhNCO. A likely explanation for this experimental fact is to consider that metallacycle **VIII** undergoes a retro-CO insertion of the carbonyl group bonded to palladium. Actually, this process, which requires a rather large activation energy (50.1 kcal/mol; see Supporting Information for $\mathbf{TS_{VIII-X}}$), was found to be endothermic ($\Delta E = 24.9$ kcal/mol with regard to **VIII**), in line with the required heating of the reaction medium to isolate **2** (Scheme 10).

We then turned our attention again to the first step. As previously discussed, two η^2 complexes **IIa** and **IIb** can be formed, but the reactivity of complex **IIa**, which involves coordination of methylisocyanate through the C═N bond, had not been considered thus far. Two different attacks on this intermediate differing by the orientation of the incoming molecule of methylisocyanate were considered. In one case, the methyl group is directed toward the *o*-phen ligand, whereas in the second case the C═O groups of the incoming isocyanate point toward the ligand. These attacks lead, respectively, to complexes **IV** and **V**, which have been discussed earlier. The two corresponding transition states $\mathbf{TS_{IIa-IV}}$ and $\mathbf{TS_{IIa-V}}$ from **IIa** were computed (see Supporting Information). They also present weak activation barriers (19.2 kcal/mol for the formation of **IV** and 17.7 kcal/mol for the formation of **V**; Scheme 11).

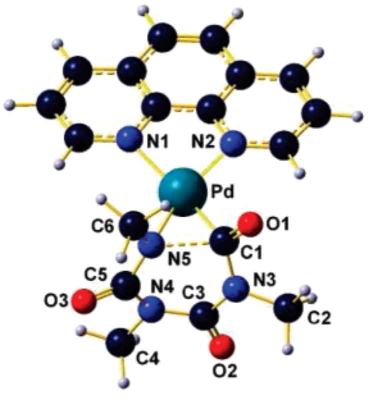
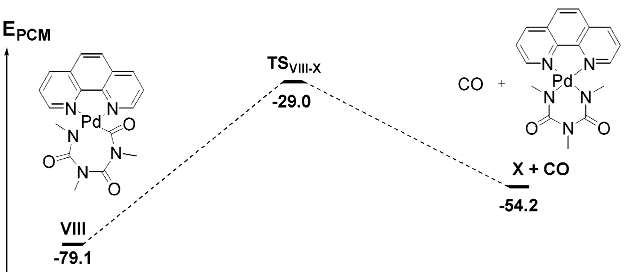
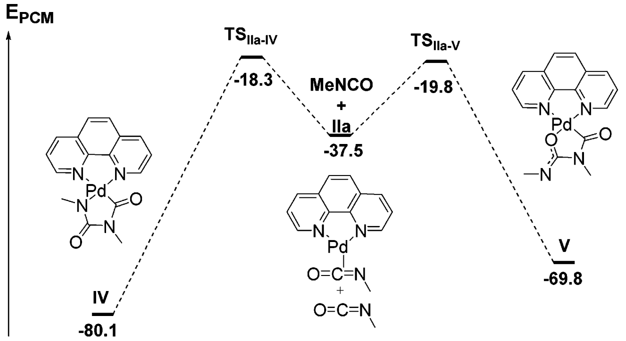


Figure 3. View of the transition state $\mathbf{TS_{VIII-IX}}$ connecting the two structures **VIII** and **IX** as given by DFT calculations. Most significant bond distances (Å) and angles (deg): Pd−N1, 2.282; Pd−N2, 2.125; Pd−C1, 1.971; Pd−O2, 2.253; Pd−N5, 2.076; C1−O1, 1.222; C1−N3, 1.419; C1−N5, 1.923; C2−N3, 1.459; C3−N3, 1.392; C3−O2, 1.225; C3−N4, 1.392; C4−N4, 1.459; C5−N4, 1.418; C5−O3, 1.225; C5−N5, 1.362; C6−N5, 1.450; N1−Pd−N2, 78.4.

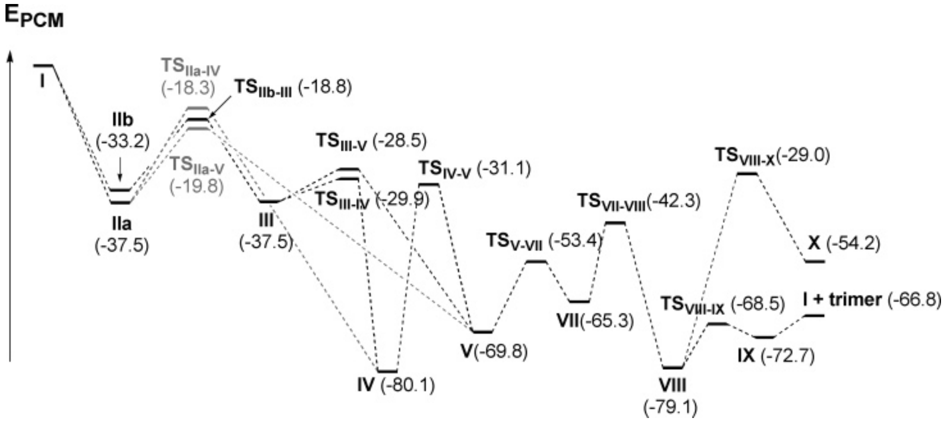
Scheme 10. Elimination of CO from Complex **VIII**



Scheme 11. Energetic Pathway Relative to the Formation of Complexes **IV** and **V** by Insertion of One Molecule of Methylisocyanate into Complex **IIa**



Scheme 12. Complete Energetic Pathway of the Catalytic Cycle Proposed; Energies Are Given in Kilocalories per Mole



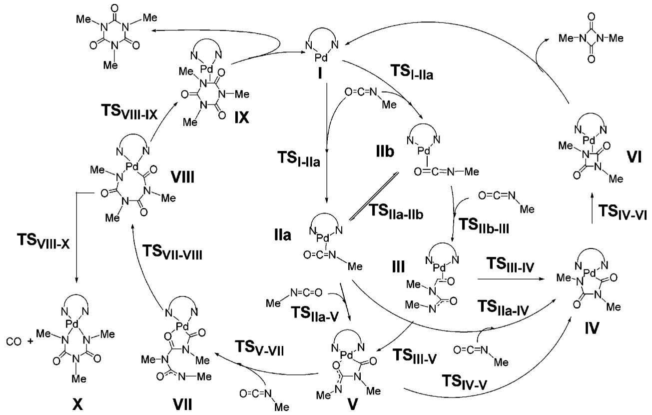
Obviously, an alternative entry in the catalytic cycle from **IIa** may be provided via **V**. This also shows that **IIa** will lead to the side formation of **IV** to a comparable extent in the catalytic process.

On the basis of these data and taking into account the level of theory considered, it is difficult to conclude which one is favored under the reaction conditions as both energetic pathways are comparable. However, it is important to keep in mind that steric factors have not been really taken into account since methylisocyanate was used in calculations instead of phenylisocyanate. One may propose that the presence of a phenyl group probably disfavors the formation of complex **IV** since in the transition state this phenyl group would strongly interact with the *o*-phen ligand. This reasoning emphasizes the formation of complex **V** as the first important intermediate in the catalytic cycle. The most significant information from these calculations is the fact that both complexes **IIa** and **IIb** can enter the cycle. The complete energetic pathway describing this trimerization process is presented in Scheme 12.

Finally, a last point that remained to be examined was the possible palladium-promoted formation of uretediones, the isocyanate cyclodimer, which was also isolated once in the course of the previous investigations (**6a**), albeit in very low yields. One simple way to form this byproduct would be by reductive elimination from the intermediate **IV**. This mechanistic step, which would simultaneously regenerate the active species **I**, is akin to that previously computed from seven-membered palladacycle **VIII**. Likewise, we found that an intermediate complex (**VI**) might form during this process, which features an interaction between the formed four-membered ring and the fragment **I** (see Supporting Information). However, now the reductive elimination is much more strongly disfavored from a thermodynamic point of view, since the formation of **I** and of the dimer is highly endothermic ($\Delta E^{\ddagger}_{\mathbf{IV-I}} = 64.4$ kcal/mol). Notably, the intermediate **VI** is also found to be very high in energy ($\Delta E_{\mathbf{IV-VI}} = 44.1$ kcal/mol and $\Delta E^{\ddagger}_{\mathbf{IV-VI}} = 45.4$ kcal/mol), a fact that would be in line with the likely occurrence of the reverse reaction.

Overall, these results rationalize the inertness stated for palladacycle **1**, since neither the formation of the 14 VE complex **I** nor that of the isomeric palladacycle **V** is expected to occur from **IV** under ambient conditions. Thus, uretediones are certainly not catalytically generated as side products in this reaction. Most likely, when isolated, these products originate from the starting isocyanates.[19] A view of the whole catalytic cycle is shown in Scheme 13. Expectedly, the trimerization process is energetically downhill, and the various TS values computed have a lower energy than the initial state, in line with the spontaneous occurrence of this process under ambient conditions. It is also obvious that the most stable compound corresponds to **IV**, in line with the selective isolation of palladacycle **1**, after the death of the catalytic system, and to **VIII**, the seven-membered palladacycle (never experimentally observed) formed just before reductive elimination of the isocyanurate takes place.

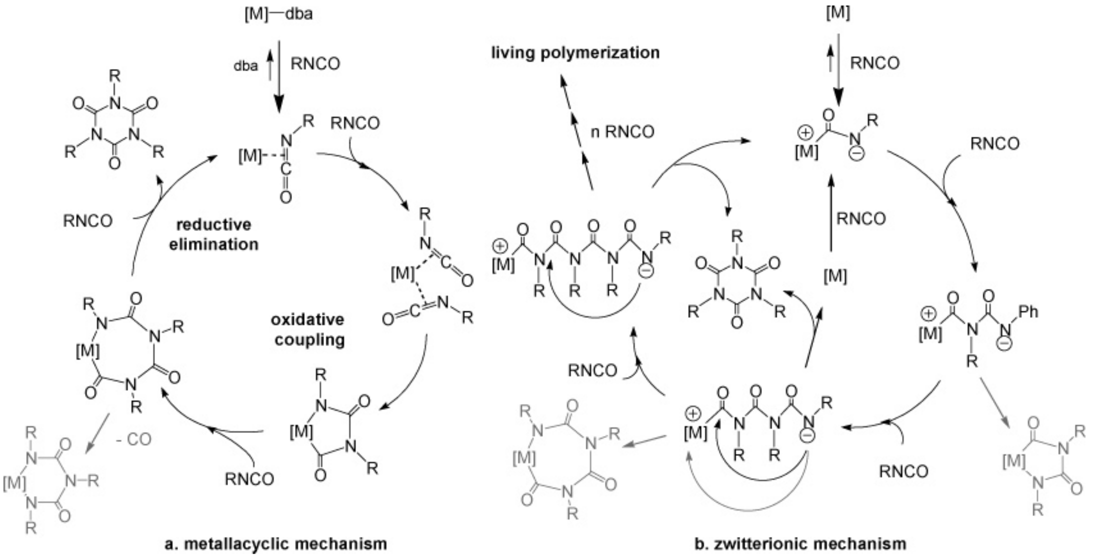
Scheme 13. Proposed Catalytic Cycle; Scheme Features the Different Complexes and Intermediates Calculated



Discussion

Mechanistic Proposal. In accordance with the working hypothesis previously made,[11a,12] we have evidenced now that **4a** can react with phenylisocyanate (**5a**) to form the known palladacycles **1** and **2**, the latter complex being obtained after subsequent decarbonylation. In addition, we have shown that the Pd(0) precursors **4a**−**c** catalyze the trimerization of various aromatic isocyanates into the corresponding 1,3,5-triphenylisocyanurates. Group 10 transition metal complexes are quite scarce for such a reaction, and the good activity reported for **4a** and **4c** is remarkable in this connection.[8,9] The present catalytic system bears a strong analogy with the (bipy)(Et)$_2$Ni (**9**) or (bipy)$_2$Ni (**10**) trimerization catalysts reported in 1975 by Kashiwagi et al.[22,23] A better turnover rate is presently obtained with **4a**.[25] However, in contrast with the first of these catalysts,

Scheme 14. Mechanisms Previously Envisioned for the Cyclotrimerization of Isocyanates



no linear polymer has ever been detected, even after running the reaction at lower temperatures, conditions that are supposed to favor the linear polymer.[26,27] Notably, with the present Pd(0) catalysts, the precipitation of the cyclotrimer during catalysis increases the viscosity of the reaction medium and certainly limits their efficiency. Several attempts to overcome this limitation by using a cosolvent resulted in decreased conversions and pointed out the importance of having a large isocyanate concentration present in the reaction medium.[7b,8a] This seems to be a general feature of related systems, since many outstanding catalysts recently reported were also used in neat isocyanate.[7a,8b,28]

Along with the heterogeneous reaction media, the incomplete solubilization of the complexes **4a**−**d** at the start of the reaction, especially when cosolvents are used, constitutes a severe limitation to obtain meaningful kinetic data on these systems. Nevertheless, we have shown that the simultaneous presence of a Pd(0) source and a given diimine ligand is needed for the catalysis to proceed, and most possibly it is the complex **4a** itself that initiates the catalysis. Indeed, Stahl and co-workers have shown that related (N−N)Pd(dba) precursors could exchange the dba ligand for an olefin via a tetrahedral-shaped 18 VE intermediate.[29] A similar intermediate with isocyanate instead of the olefin would presently constitute a convenient entry to the catalytic cycle and lead to a π-complex (of type **IIa** or **IIb**) analogous to known compounds.[30]

Regarding the mechanism of the catalytic transformation, we have experimentally shown that a mechanism involving radical intermediates could be disregarded,[31] since the catalysis proceeds in the presence of radical traps such as 9,10-dihydroanthracene or duroquinone (Table 1). Notably quinones, such as duroquinone, are known to form stable and insoluble adducts with **4c**.[14,15,32] This can explain the decrease in the yield observed in the presence of the latter additive. Moreover, one of the most important findings is that a "metallacyclic" mechanism, involving successive concerted oxidative coupling reactions, as shown in Scheme 14 and that resembles these often invoked for the cyclotrimerization of alkynes on metal centers,[33] is presently not operative. Indeed, we have previously clearly demonstrated experimentally that the palladacycle **1** *was not* an intermediate in this transformation, even under forcing conditions.[11a] The DFT calculations confirm that this type of compound (**IV**) constitutes a thermodynamic sink for the catalytic system. Quite clearly, this palladacycle constitutes a deactivated form of the catalyst. Note that similar complexes were previously isolated by other researchers from M(0) precursors (M = Ni, Pd, Pt) and ArNCO.[22,34]

Another mechanism often invoked in such a trimerization reaction is the so-called "zwitterionic" mechanism (Scheme 14b). This type of mechanism was initially proposed by Sashoua et al.[35] for the anionic polymerization of isocyanates.[10,20,26,36] It was then often extended to catalytic cyclotrimerization

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(22) Kashiwagi, T.; Hidai, M.; Uchida, Y.; Misono, A. *J. Polym. Sci., Part B: Polym. Phys.* **1975**, *8*, 173−175.

(23) It has been demonstrated that (bipy)$(Et)_2$Ni (**10**) reductively eliminates *n*-butane to generate the transient "(bipy)Ni(0)" species upon heating at ambient temperature.[24]

(24) Uchino, M.; Asagi, K.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* **1975**, *84*, 93−103.

(25) For (bipy)$(Et)_2$Ni (**10**), turnover = 10, and for $(bipy)_2$Ni (**9**), turnover = 22 in **3a** after 8 h. Note that 2,2′-bipyridine alone was also inactive.

(26) Parodi, F. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Vol. 5, pp 387−412.

(27) Bur, A. J.; Fetters, L. J. *Chem. Rev.* **1976**, *76*, 727−746.

(28) Nambu, Y.; Endo, T. *J. Org. Chem.* **1993**, *58*, 1932−1934.

(29) (a) Popp, B. V.; Thorman, J. L.; Morales, C. M.; Landis, C. R.; Stahl, S. S. *J. Am. Chem. Soc.* **2004**, *126*, 14832−14842. (b) Stahl, S. S.; Thorman, J. L.; de Silva, N.; Guzei, I. A.; Clark, R. W. *J. Am. Chem. Soc.* **2003**, *125*, 12−13.

(30) (a) Hoberg, H.; Korff, J. *J. Organomet. Chem.* **1978**, *150*, C20−C22. (b) Vasapollo, G.; Nobile, C. F.; Sacco, A. *Inorg. Chim. Acta* **1984**, *83*, 125−128.

(31) For an example of radicalar coupling involving alkynes, see: Yang, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1998**, *120*, 6834−6835.

(32) Popp, B. V.; Stahl, S. S. *J. Am. Chem. Soc.* **2006**, *128*, 2804−2805.

(33) (a) Canovese, L.; Visentin, F.; Chessa, G.; Uguagliati, P.; Levi, C.; Dolmella, A. *Organometallics* **2005**, *24*, 5537−5548. (b) Müller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1118−1123. (c) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, 1995; Vol. 12, pp 741−770. (d) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley: New York, 1992; pp 208−213. (e) Dieck, H.; Munz, C.; Müller, C. *J. Organomet. Chem.* **1990**, *384*, 243−255. (f) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245−281.

(34) (a) Hoberg, H.; Radine, K.; Milcherheit, A. *J. Organomet. Chem.* **1985**, *280*, C60−C62. (b) Hoberg, H.; Oster, B. W.; Krüger, C.; Tsay, Y. H. *J. Organomet. Chem.* **1983**, *252*, 365−373. (c) Beck, W.; Rieber, W.; Cenini, S.; Porta, F.; La Monica, G. *J. Chem. Soc., Dalton Trans.* **1974**, 298−304.

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reactions when nucleophilic organic catalysts were used,[7] but firm evidence for zwitterionic intermediates was only gathered recently with phosphane catalysts,[10] never with transition metal catalysts.[20] Our present computational results would actually be more in accordance with such a mechanism, at least concerning the initial steps. Note that although seldom encountered or isolated with transition metals,[37] zwitterionic intermediates were nevertheless sometimes invoked in related processes.[6b,38] Presently, DFT reveals that some intermediates, such as **V** for instance, cannot be envisioned as true zwitterions, since the charge is strongly delocalized. However, the important point according to the calculations is that reaction with incoming isocyanate molecules takes place on the pendant terminal nitrogen atom, with stepwise formation of bonds, in each case. Thus, except for the last steps, the actual mechanism differs markedly from the "metallacyclic" mechanism previously considered (Scheme 14a). In fact, when starting from type **II** intermediates, each incremental step is more accurately envisioned as a nucleophilic attack from the terminal nitrogen of the palladium complex, rather than as an insertion of the incoming isocyanate in the growing chain or as a metallacyclic rearrangement (Scheme 13). This readily explains the sensitivity to steric strain evidenced when diimine ligands bearing methyl groups in positions 2 and 9 (Table 3) or isocyanate substrates bearing isopropyl groups in positions 2 and 6 (Table 2) were used. In addition, such a mechanism would perfectly be in line with the previous finding of Stahl and co-workers, who evidenced that 16 VE (N−N)Pd(L)^0 complexes were quite nucleophilic.[29a,39] Also, the increased rate observed for isocyanates bearing electron-withdrawing groups as well as the higher yields of isocyanurate obtained in polar solvents are consistent with such a nucleophilic polymerization mechanism.[10,26,41]

In contrast to previous examples of related zwitterionic trimerizations (Scheme 14b), this transformation is not a "living" process, due to the absence of formation of linear isocyanate polymers. Indeed, a clear termination step takes place for the oligomerization process. Calculations indicate that the ring closure becomes favored over further chain extension (Scheme 13), the intermediate **VII** being much more prone to cyclize into **VIII** than to react further with free isocyanate. Also, with **VII**, no evidence for a transition state resulting from ring closure on the α-carbonyl could be obtained from our calculations. Apparently, with this intermediate, ring closure at the metal is energetically more favored over typical processes occurring following the zwitterionic mechanism. Then, depending on the temperature of the medium, the metallacyclic intermediate **VIII** can either regenerate the active species or eliminate carbon monoxide to form type **X** palladacycles, such as **2**, also inactive for the catalysis. All these steps are precisely these that would terminate a metallacyclic oligomerization process (Scheme 14a). Thus, the mechanism that we propose for these Pd(0) diimine catalysts is actually a blend of the "zwitterionic" and "metallacyclic" mechanisms. In addition, we also found that the formation of the very stable five-membered intermediate **IV** (corresponding to **1**) can occur competitively with that of **VIII** at earlier stages of the catalysis. This explains the slow deactivation of the catalyst under ambient conditions.

Conclusions

This work reveals that diimine−Pd(0) complexes constitute novel and efficient catalytic precursors for cyclotrimerizing aromatic isocyanates under ambient conditions without the occurrence of competing linear polymerization. The experimental and theoretical (DFT) mechanistic investigations conducted during this study demonstrate that the mechanism of this transformation does not proceed by successive cycloadditions on metallacyclic intermediates followed by the final reductive elimination of the isocyanurate, as might have been inferred by analogy with alkyne oligomerization reactions on group 10 metals, nor does the catalysis proceed by a typical zwitterionic process, which would lead to side formation of linear isocyanate polymers. Rather, our findings suggest that, at least in a formal sense, the trimerization mechanism on Pd(0) diimine complexes starts like an anionic polymerization mechanism, where the Pd(0) center plays the role of a nucleophilic initiator and gives rise to zwitterion-like intermediates. However, these charge-separated intermediates, upon lengthening, are prone to cyclize at the metal center and give rise to several metallacyclic intermediates of different stabilities. Eventually, a seven-membered metallacycle (**VIII**) is formed that generates the cyclotrimer and re-forms the active species upon reductive elimination. Notably, we have also evidenced here that, accordingly to our starting hypothesis, the known palladacycles **1** and **2** can be isolated from phenylisocyanate and the (*o*-phen)Pd(dba) precursor. Actually, these palladacycles are inactive for the trimerization reaction and constitute deactivated forms of the catalyst. Their formation is readily explained in light of the present investigation.

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Supporting Information Available: (i) Complete experimental section, (ii) VT ^{1}H NMR spectra of **4a**, (iii) complete ref 42, (iv) structures of selected transition states, (v) energetic pathway explaining the formation of the isocyanate dimer by reductive elimination, and (vi) computed Cartesian coordinates, thermochemistry, PCM energies, and lower frequencies of all theoretical structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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