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Enhanced Catalytic Performance of Indenediide Palladium Pincer Complexes for Cycloisomerization: Efficient Synthesis of Alkylidene Lactams

Noel Ángel Espinosa-Jalapa,[†,‡] Diandian Ke,[†,‡] Noel Nebra,[†,‡] Lucas Le Goanvic,[†,‡] Sonia Mallet-Ladeira,[§] Julien Monot,[†,‡] Blanca Martin-Vaca,*[,†,‡] and Didier Bourissou*[,†,‡]

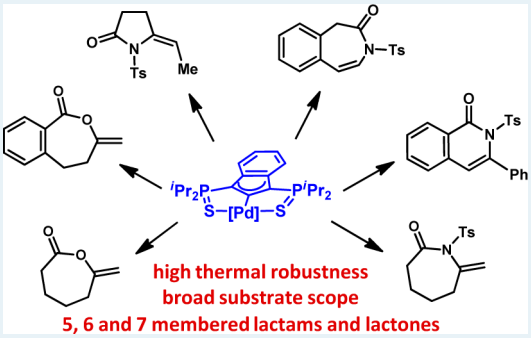
[†]Université de Toulouse, UPS, 118 route de Narbonne, F-31062 Toulouse, France

[‡]CNRS, LHFA UMR5069, F-31062 Toulouse, France

[§]Université de Toulouse, UPS, Institut de Chimie de Toulouse, FR2599, 118 Route de Narbonne, F-31062 Toulouse, France

Supporting Information

ABSTRACT: New SCS Pd pincer complexes featuring a noninnocent indenediide backbone show high catalytic activity in cycloisomerization. A variety of alkylidene lactams (five- to seven-membered rings) have been prepared efficiently from *N*-tosyl alkynylamides, and good results have also been obtained with challenging alkynoic acids.



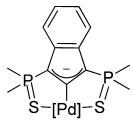
KEYWORDS: *pincer complexes, palladium, cycloisomerization, noninnocent ligand, lactams, metal−ligand cooperation*

Cycloisomerization reactions are extremely valuable transformations that give access to a broad range of cyclic products in great atom and step economy.[1,2] In particular, heterocycles can be readily prepared from unsaturated compounds bearing a tethered pro-nucleophile moiety (O−H, N−H functionalities).[2] A variety of transition metal complexes are known to catalyze these transformations. Typically, electrophilic metal centers activate unsaturated carbon−carbon bonds by π-coordination, thereby promoting nucleophilic attack and cyclization. These reactions may require the presence of an additive, most commonly a base, to activate simultaneously the pro-nucleophile.[2]

During the past two decades, spectacular progress has been achieved in bifunctional catalysis entailing metal/ligand cooperation.[3−8] In particular, pincer complexes featuring noninnocent ligands have been extensively used in transformations involving hydrogenation/dehydrogenation processes.[5−8] A few other reactions, including cycloisomerization, have also been occasionally promoted via metal/ligand cooperation.[9−12]

In this context, our group has developed a new SCS pincer framework featuring an electron-rich indenediide backbone flanked by two thiophosphinoyle side arms. Palladium complexes of type **I** (Chart 1) have been thoroughly investigated (preparation, bonding, and reactivity),[13] and first catalytic studies have shown their ability to catalyze the cyclization of alkynoic acids.[14] The reaction does not require any external base and works efficiently with a broad range of substrates. As an extension of this work, we have moved one step further and applied complexes of type **I** to more challenging transformations. Herein, we present the results we obtained in the cycloisomerization of *N*-tosyl alkynylamides[15,16] into alkylidene lactams.[17,18]

Chart 1. General Structure of Indenediide Pd Complexes I



I

Preliminary studies with the known indenediide catalysts prompted us to modulate slightly the structure of the ligand to increase the thermal stability of the Pd complexes. The phenyl rings at phosphorus were replaced with isopropyl groups. The corresponding complexes were prepared and successfully applied to the cycloisomerization of *N*-tosyl alkynylamides as well as challenging alkynoic acids. Accordingly, a broad variety of five-, six-, and seven-membered lactams and lactones have been obtained with high selectivities and in very good yields.

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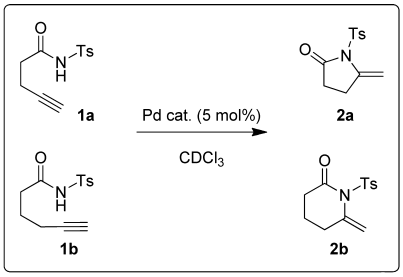
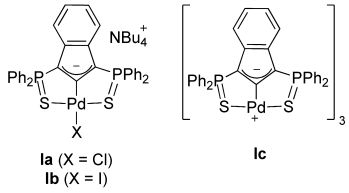
CYCLOISOMERIZATION OF *N*-TOSYL ALKYNYLAMIDES

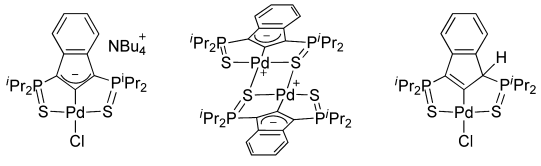
The previously described indenediide catalysts **Ia−c** were first evaluated for the cyclization of **1a** as a model reaction (Table 1). The cycloisomerization of *N*-tosyl alkynylamides is more challenging than that of the carboxylic acid counterparts and usually requires heating. The transformation of **1a** was conducted in deuterated chloroform (0.14 M) at 60 °C in the presence of chloropalladate **Ia** (5 mol %) without an external base. The reaction proceeds selectively via 5-exo-dig cyclization, and 5-alkylidene 2-pyrrolidinone **2a** was obtained quantitatively in <1 h (>99% conversion, entry 1). Replacement of chloride at palladium (**Ia**) for iodide (**Ib**) induces a slight decrease in activity (81% conversion, entry 2). With the neutral trimeric complex **Ic**, complete conversion of **1a** to **2a** is achieved within ∼50 min under the same conditions (entry 3). These first results demonstrate the ability of indenediide Pd pincer complexes to catalyze the cyclization of alkynylamides. A more challenging substrate, namely *N*-tosyl hex-5-ynamide **1b**, was then investigated. In this case, the reaction temperature had to be increased to 90 °C to achieve the cycloisomerization in a reasonable reaction time. 6-Exo alkylidene lactam **2b** was obtained in 67% conversion after 24 h using **Ia** as a catalyst. Increasing the substrate concentration (from 0.14 to 1 M) allows us to increase the conversion to 82% (entry 5), but the reaction failed to reach completion even after a prolonged reaction time. The same behavior was observed with iodopalladate **Ib** (entry 6), which was again less active than **Ia**.

Table 1. Evaluation of the Catalytic Properties of Indenediide Pd Complexes I−IV in the Cyclization of *N*-Tosyl Alkynylamides 1a and 1b





Ia (X = Cl)
Ib (X = I)
Ic



II **III** **IV**

entry[a]	substrate	catalyst	*T* (°C)	time	conversion (%)[b]
1	**1a**	**Ia**	60	1 h	>99
2	**1a**	**Ib**	60	1 h	81
3	**1a**	**Ic**	60	50 min	>99
4	**1b**	**Ia**	90	24 h	67
5	**1b**	**Ia**	90	24 h	82[c]
6	**1b**	**Ib**	90	24 h	49
7	**1b**	**Ic**	90	20 h	92
8	**1b**	**II**	90	12 h	>99
9	**1b**	**III**	90	12 h	>99
10	**1b**	–	90	24 h	nr
11	**1b**	**IV**	90	12 h	nr

[a]All catalytic tests were performed under an argon atmosphere starting from 0.1 mmol of alkynylamide (0.14 M in $CDCl_3$). [b]Conversions were determined by ^1H NMR. [c]Reaction conducted at 1 M alkynylamide.

To assess the impact of this structural modulation on catalytic activity, the cyclization of *N*-tosyl hex-5-ynamide **1b** was chosen as a benchmark. Using either **II** or **III**, the 6-exo alkylidene lactam **2b** is obtained in quantitative yield within one night at 90 °C (entries 8 and 9). In stark contrast with the reactions catalyzed by **Ia−c**, no sign of decomposition was observed with **II** and **III**. No signals corresponding to the free ligand could be observed by ^{31}P NMR over the whole reaction time, even when heating was prolonged for 6 h after full conversion (see Figure S2 of the Supporting Information).[19,21] Simple substituent exchange at phosphorus allow the significant enhancement of the robustness and thus the catalytic performance of indenediide Pd pincer complexes.

Because very similar activities were observed with **II** and **III**, the study was continued with the neutral complex **III** (thereby, the noncrucial *n*-Bu_4N^+ counteranion was discarded) (Table 2). The cyclization of *N*-tosyl pent-4-ynamide **1a** was investigated first. The reaction proceeds readily at 60 °C and is substantially faster with **III** than with **Ia−c**. The desired 5-exolactam **2a** is obtained as unique product within only 10 min (98% isolated yield). The higher activity of **III** prompted us to decrease the catalyst load (entry 1). At 0.2 mol %, a longer reaction time and a higher concentration were required but the cyclization was completed in <7 h at 1.5 M [corresponding to a turnover number (TON) of 500].

The scope and functional group tolerance of the indenediide Pd catalytic system **III** were then explored. Different substituents were introduced at the α position of the amide function. The reaction is significantly accelerated by the Thorpe−Ingold effect, as indicated by the rapid cyclization of **1c** (featuring a ^{n}Hex group) at room temperature in only 30

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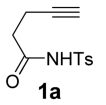
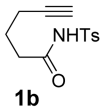
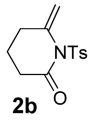
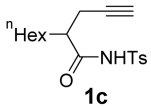
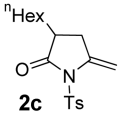
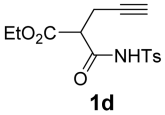
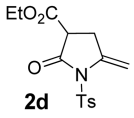
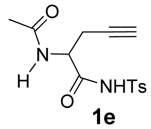
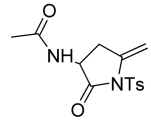
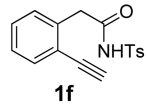
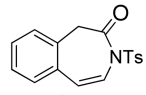
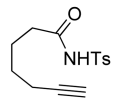
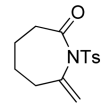
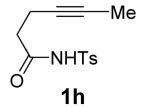
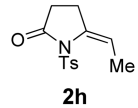
Table 2. Scope of the Cyclization of *N*-Tosyl Alkynylamides (1a–h) by Indenediide Pd Complex III

Entry[a]	Alkynylamide	Lactam	T (°C)	t (h)	Conv (%)[b]
1	 **1a**	 **2a**	60	10 min 7 h[c]	99 (98) 99[c]
2	 **1b**	 **2b**	90	12 h	99 (98)
3	 **1c**	 **2c**	25	30 min	99 (99)
4	 **1d**	 **2d**	25	30 min	99 (86)
5	 **1e**	 **2e**	25	30 min	99 (82)
6[d]	 **1f**	 **2f**	120	12 h	95 (51)[e]
7	 **1g**	 **2g**	90	130 h	70 (53)[e]
8	 **1h**	 **2h**	90	24 h	99 (83)[f]

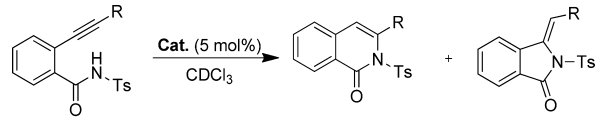
[a]Catalytic reactions performed under an argon atmosphere using 0.1 mmol of the corresponding alkynylamide **1a–h** (0.14 M in $CDCl_3$) and 5 mol % of the catalyst. [b]Conversions were determined by ^1H NMR analysis. Isolated yields are given in parentheses. [c]The catalyst load was decreased to 0.2 mol %, and the substrate concentration was increased to 1.5 M. [d]Reaction conducted at 0.2 M alkynylamide. [e]^1H NMR analysis of the reaction crude indicated formation of only one isomer (see Figures S3 and S4 of the Supporting Information). Differences between conversion and yield result from the loss of product during purification. [f]Reaction conducted at 0.3 M alkynylamide.

min (entry 3). Functional groups such as esters and protected amines are compatible with the cyclization, as exemplified with substrates **1d** and **1e** (entries 4 and 5, respectively). The aliphatic linker between the *N*-tosyl amide and alkyne moieties was then replaced with a benzyl group. Cyclization of **1f** occurs at 120 °C with endo instead of exo selectively to give the seven-membered product **2f** (entry 6, 95% conversion, 51% isolated yield). This transformation opens access to 3-benzazepin-2-ones, which are important motifs found in various biologically active compounds.[16a] As mentioned above, because of the ^{i}Pr groups at phosphorus, the catalyst is thermally robust, which allows us to target challenging substrates such as the flexible nonsubstituted *N*-tosyl hept-6-ynamide **1g**. Cyclization could be achieved within 6 days at 90 °C, yielding selectively the corresponding lactam **2g** (entry 7, 53% isolated yield). To the best of our knowledge, this is the first time a methylene ε-caprolactam is prepared by cycloisomerization.

To extend further the scope of the reaction, we then turned our attention to internal *N*-tosyl alkynylamides, which are substantially more difficult to cyclize than terminal substrates.[16a,22] Cyclization of **1h** required heating at 90 °C (instead of 60 °C for the corresponding terminal alkyne **1a**), but reaction was complete within 24 h (entry 8). The alkylidene lactam **2h** was thereby obtained as a unique product in 83% isolated yield. Besides exo selectivity, the *Z* configuration of the exocyclic double bond (unambiguously deduced from NOE experiments)[19] is noteworthy. It is consistent with *trans* addition of the amide on the alkyne, which is activated by π-coordination to Pd (see below for more detailed mechanistic discussions).

Rigid internal substrates such as **1i** and **1j** were also investigated (Table 3) as an entry to isoquinoline skeletons that are present in many natural and pharmaceutical compounds of biological interest.[16b] Accordingly, complex **III** was found to

Table 3. Cyclization of *N*-Tosyl Alkynylamides 1i and 1j Catalyzed by Indenediide Pd Complexes Ia, Ic, and III



1i (R = Ph)
1j (R = Cy)

2i-endo (R = Ph)
2j-endo (R = Cy)

2i-exo (R = Ph)
2j-exo (R = Cy)

entry[a]	substrate	catalyst	*T* (°C)	rime	conversion (%)[b]	endo/exo
1	**1i**	**Ia**	50	5 h	53	92/8
2	**1i**	**Ic**	50	5 h	51	93/7
3	**1i**	**III**	50	5 h	87	84/16
4	**1i**	**III**	35	20 h	>99 (89)	86/14
5	**1j**	**Ia**	50	4 days	51	92/8
6	**1j**	**III**	50	3.5 days	>99 (92)	92/8

[a]Catalytic reactions performed under an argon atmosphere using 0.1 mmol of the corresponding alkynylamide **1i** or **1j** (0.2 M in $CDCl_3$) and 5 mol % catalyst. [b]Conversions were determined by ^1H NMR analysis. Isolated yields are given in parentheses.

efficiently promote the cycloisomerization of **1i** at 50 °C. The conversion is complete within 5 h and occurs preferentially via 6-endo cyclization, affording an 84/16 6-endo/5-exo product mixture. At a lower temperature (35 °C), the reaction requires 20 h to reach completion and the selectivity is approximately the same (86/14). The cyclohexyl-substituted substrate **1j** behaves very much like **1i** (entry 6). Here also, 6-endo cyclization is favored, and **2j-endo** is obtained as a major product (92/8 endo/exo ratio, 92% overall yield). The preferential formation of isoquinolines from **1i** and **1j** contrasts with the results obtained in the cyclization of alkynoic acids

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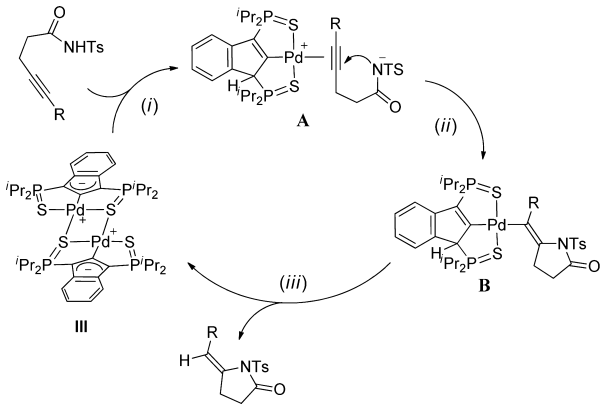
using **Ia** and **Ic** as catalysts.[14,23] In the latter case, the selectivity depends on the substrate. 6-Endo cyclization is favored when the alkyne bears a cyclohexyl substituent, while the substrate featuring a phenyl ring mainly undergoes 5-exo cyclization. To discard a potential catalyst effect, we conducted the cyclization of **1i** and **1j** with complexes **Ia** and **Ic**. Lower conversions were observed (~50%, entries 1, 2, and 5), and again, decomposition into free ligand was detected by ^{31}P NMR. However, the 6-endo/5-exo product ratios are comparable to those obtained with **III**, indicating only little influence of the catalyst structure on selectivity. Thus, 6-endo cyclization of **1i** and **1j** is intrinsically favored, and using **III** as a catalyst, isoquinolines can be efficiently prepared under mild conditions.

MECHANISTIC CONSIDERATIONS

A simplified catalytic cycle for the cyclization of *N*-tosyl alkynylamides catalyzed by complex **III** is proposed in Scheme 1.

Scheme 1. Simplified Catalytic Cycle Proposed for the Cyclization of *N*-Tosyl Alkynylamides Catalyzed by III



(i) The electron-rich indenediide backbone would deprotonate the *N*-tosyl amide, and the alkyne would be activated by π-coordination to palladium (intermediate **A**).

(ii) Cyclization by nucleophilic attack of the nitrogen atom on the C≡C bond would then give alkenyl complex **B**. *trans* addition is supported by the stereochemistry of the product **2h** obtained by 5-exo cyclization of the internal alkyne (see entry 8 of Table 2).

(iii) Finally, the alkylidene lactam would be released, and complex **III** would be regenerated.

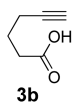
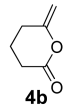
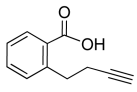
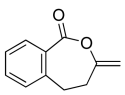
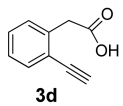
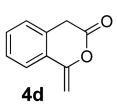
Some blank reactions were conducted to substantiate the role of the indenediide Pd complexes (Table 1). First, we checked that cyclization does not occur spontaneously upon heating. In the absence of the indenediide Pd complex, compound **1a** remained intact after prolonged heating for 24 h at 90 °C (Table 1, entry 10). Another control experiment was performed with the chloroindenyl complex **IV** (the protonated form of **II**). It is completely inactive toward **1a** (no reaction after 12 h, entry 11), demonstrating the necessity and active role of the indenediide moiety in the catalytic cycle.

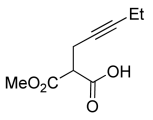
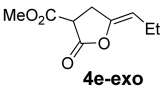
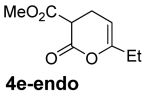
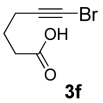
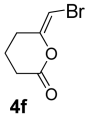
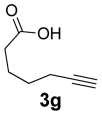
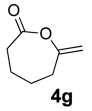
In addition, ^{31}P NMR monitoring during catalysis provided some insight into the resting state. Typically, upon cyclization of **1a** or **1b**, the two signals at δ 78.2 and 71.2 associated with complex **III** immediately disappear and a new pair of signals at δ 84.4 and 82.8 (1/1 integration) are observed (see Figure S5 of the Supporting Information).[19] This is consistent with the formation of an indenyl species (**A** or **B**) by protonation of the indenediide backbone.[24,25] Once the substrate is entirely consumed, the characteristic signals at δ 78.2 and 71.2 reappear, indicating regeneration of starting complex **III**. Thus, the acidic proton of *N*-tosyl alkynylamides is temporarily fixed on the indenediide backbone and transferred back to the organic product after cyclization.[26]

CYCLOISOMERIZATION OF ALKYNOIC ACIDS

Taking into account the catalytic performance of **III** in the cyclization of *N*-tosyl alkynylamides and its enhanced robust-

Table 4. Comparison of the Activities of Complexes Ib and III for the Cyclization of Alkynoic Acids 3a−g

Entry[a]	Alkynoic Acid	Lactone	Cat.	T (°C)	t (h)	Yield (%)[b]
1	 **3a**	 **4a**	**Ib**	25	1 h	99[14,c]
			III	25	30 min	99[c]
2	 **3b**	 **4b**	**Ib**	90	12 h	99[14]
			III	90	10 h	99 (98)
3	 **3c**	 **4c**	**Ib**	90	36 h	95
			III	90	9.5 h	95 (88)
4	 **3d**	 **4d**	**Ib**	90	3 h	99
			III	90	1 h	99 (94)

Entry[a]	Alkynoic Acid	Lactone	Cat.	T (°C)	t (h)	Yield (%)[b]
5	 **3e**	 **4e-exo**	**Ib**	90	8 h	99
			III	90	1.5 h	99 (97)
		 **4e-endo**	**exo/endo:** 1/1.2 with **Ib** & **III**			
6	 **3f**	 **4f**	**Ib**	90	5 h	52
			III	90	5 h	99 (94)
7	 **3g**	 **4g**	**Ib**	120	24 h	12
			III	120	22 h	69[d] (51)

[a]Catalytic reactions performed under an argon atmosphere using 0.1 mmol of the corresponding alkynoic acid **3a−g** (0.1 M in $CDCl_3$) and 5 mol % catalyst. [b]Conversions were determined by ^{1}H NMR analysis. Isolated yields are given in parentheses. [c]The high volatility of the compound prevented accurate determination of the isolated yield. [d]Reaction conducted at 1 M alkynoic acid.

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ness at high temperatures, we reconsidered the cycloisomerization of alkynoic acids that gave only modest results with **Ib** (Table 4). Preliminary catalytic assessments targeted the formation of simple five- and six-membered lactones **4a** and **4b** (entries 1 and 2, respectively). The corresponding reactions proceed slightly faster with **III** than with **Ia** (30 min and 1 h, and 10 and 12 h, respectively).[14]

The enhanced catalytic performance of **III** is better illustrated with more challenging substrates. For example, the reaction time for the cyclization of **3c** into the seven-membered lactone **4c** (entry 3) was reduced spectacularly (from 36 h with **Ib** to less than 10 h with **III**). Similarly, complex **III** significantly accelerated the 6-exo cyclization of **3d** to **4d** (entry 4). Improved catalytic results were also obtained with internal alkynoic acids as substrates. With **III**, cyclization of **3e** proceeded in 1.5 h (vs 8 h with **Ib**) to give again a 1/1.2 5-exo/6-endo product mixture (entry 5). Complete selectivity in favor of 6-exo cyclization is observed for the bromo-substituted hexynoic acid **3f** (entry 6), and here, complex **III** allows us to achieve complete conversion within 5 h (vs only 52% conversion with **Ib**).

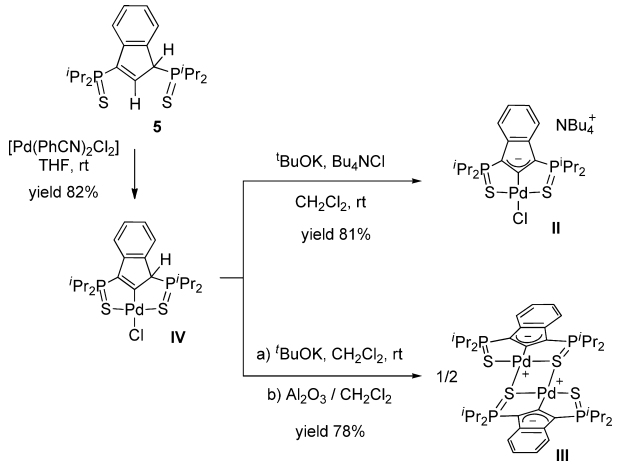
Finally, the ability of **III** to catalyze the cyclization of 6-heptynoic acid **3g** was evaluated (entry 7). The formation of flexible seven-membered ring lactones is extremely challenging and has only very little precedent with transition metal catalysts.[27] With complex **Ib**, the conversion reached barely 12%. Very harsh conditions are required (120 °C for 24 h in chlorobenzene), and the reaction is accompanied by catalyst degradation. Much better results were obtained with complex **III**. After optimization of the reaction conditions (substrate concentration increased to 1 M), ϵ-caprolactone **4g** could be obtained in 69% conversion (51% isolated yield) within 22 h at 120 °C. It is remarkable that no free ligand was observed by ^{31}P NMR under these drastic conditions, confirming that the catalyst modulation imparts very high thermal robustness. The catalytic performance of complex **III** in the cyclization of **3g** is among the best reported to date in terms of activity and selectivity. Common side reactions such as 8-endo cyclization[27b] and dimerization[27e] are absent, and to the best of our knowledge, the highest yield achieved so far is 28%, using a $PdMo_3S_4$ cluster.[27a]

Gratifyingly, the enhancement of catalytic performance observed in the cyclization of *N*-tosyl alkynylamides is also observed with alkynoic acids, and complex **III** stands as an efficient and general catalyst for the formation of alkylidene lactams and lactones.

SYNTHESIS AND CHARACTERIZATION OF INDENEDIIDE COMPLEXES II AND III

Complexes **II** and **III** were prepared following the same strategy that was used to obtain **Ia**–**c** (Scheme 2).[13a,b] Indene was first derivatized in **5**.[19] Treatment with $PdCl_2(PhCN)_2$ then afforded the chloroindenyl palladium pincer complex **IV** (82% yield). Metalation of the central carbon of proligand **5** is clearly apparent as shown by NMR. The ^{1}H NMR signal for the central C_{sp^2}-H moiety of **5** disappears (δ 7.54), and the corresponding carbon atom resonates as a quaternary center in **IV** (δ 189.9). Reaction of **IV** with 1 equiv of ^{t}BuOK in the presence of tetrabutylammonium chloride led to the clean formation of chloropalladate **II** (81% isolated yield). Complex **II** is characterized by a sharp singlet at δ 75 in ^{31}P NMR. The ^{13}C NMR spectrum also simplifies, and a unique C_q signal is

Scheme 2. Synthesis of Pd Indenediide Complexes II–IV



observed for C1 and C3 at δ 100.1. The structure of **II** was confirmed crystallographically (Figure 1, left). The metric data of **II** very much resemble those of **Ia**. Replacement of the substituents at phosphorus has no visible geometric impact.

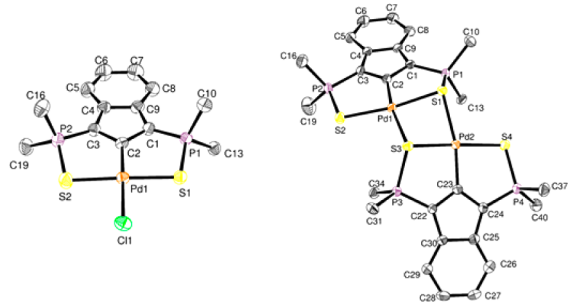


Figure 1. Ellipsoid drawings (50% probability level) of the molecular structures of **II** (left) and **III** (right). For the sake of clarity, lattice solvent molecules, hydrogen atoms, and counteranion were omitted and the isopropyl groups at phosphorus were simplified.

To obtain the corresponding neutral species, the chloroindenyl complex **IV** was deprotonated with ^{t}BuOK in the absence of tetrabutylammonium chloride. The ^{31}P NMR control indicates the formation of two species, the chloropalladate **II** and a new compound **III**. Elution of the crude mixture through an alumina pad induced the conversion of **II** to **III**. After precipitation in diethyl ether, complex **III** was isolated as a red powder in 78% yield. Its dimeric structure was unambiguously supported by X-ray diffraction analysis (Figure 1, right). Two indenediide Pd fragments are bridged by sulfur atoms. The central $(PdS)_2$ core is folded (butterfly geometry), and the bridging PdS bonds are slightly longer (2.45 Å) than those engaged in pincer chelation (2.35 Å). Overall, the structure of **III** resembles that of **Ic**. Only the nuclearity changes (dimeric vs trimeric), probably as the result of subtle stereoelectronic effects associated with the Ph/^{i}Pr substituents at phosphorus. According to NMR, complex **III** retains its dimeric structure in solution.[28] The ^{31}P NMR spectrum displays two signals at δ 78.2 and 71.2. The dissymmetrization of the ligand backbone is also apparent from the two doublets of doublets observed at δ 100.5 and 94.7 for C1 and C3.

To evaluate the electron donating character of the thiophosphinoyl arms and assess the influence of the

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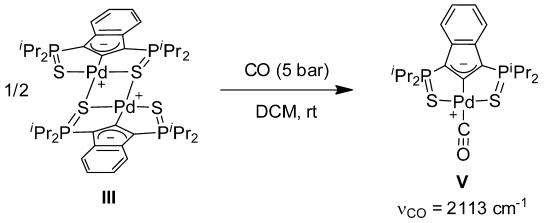
substituent exchange at phosphorus, we prepared carbonyl complex **V** (Scheme 3). To do so, a chloroform solution of

Scheme 3. Synthesis and IR Data of Pd Carbonyl Complex V



dimer **III** was pressurized with CO (5 bar) at room temperature. According to ^{31}P NMR, the S bridges are readily split under these conditions and complex **V** is formed quantitatively. It was unambiguously authenticated by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy.[19] The characteristic ν_{CO} band of **V** is found at 2113 cm^{-1}, vs a band at 2121 cm^{-1} for the corresponding carbonyl complex derived from **Ic**.[13f] The shift to a lower frequency upon replacement of the Ph rings with ^{i}Pr groups at phosphorus is consistent with a more electron-donating and stronger coordination of the SCS pincer ligand to Pd.[29] This is consistent with the enhanced thermal robustness observed during the cycloisomerization reactions and highlights how subtle modulation of the ligand framework can markedly influence the properties of the Pd complexes.

In conclusion, a simple structural modulation of previously described bis(thiophosphinoyle) indenediide Pd pincer complexes has been shown to markedly enhance their thermal robustness and catalytic performance in cycloisomerization reactions. The Ph rings at phosphorus have been replaced with ^{i}Pr groups. The corresponding chloropalladate **II** and dimeric neutral complex **III** stand as very efficient and general catalysts. Accordingly, a variety of alkylidene lactams (five- to seven-membered rings), including isoquinolines, 3-benzazepin-2-ones, and methylene ε-caprolactam, can be prepared in excellent yields (most often >90%) from the corresponding *N*-tosyl alkynylamides. Good results were also obtained with challenging alkynoic acids. In particular, complex **III** showed good activity and high selectivity in the cycloisomerization of 6-heptynoic acid into the corresponding methylene ε-caprolactone.

These results underline the great potential of indenediide pincer complexes in catalysis. Cooperation between the metal center and the electron-rich indenediide backbone holds much promise. Further structural modulations of the pincer complexes are currently being studied in our laboratory. We also seek to apply these systems to other catalytic transformations.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data, including crystallographic data for **II** (CCDC 1014581) and **III** (CCDC 1014580). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: bmv@chimie.ups-tlse.fr.

*E-mail: dbouriss@chimie.ups-tlse.fr.

Author Contributions

N.Á.E.-J. and D.K. contributed equally to this work.

Notes

The authors declare no competing financial interests.

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(19) See the Supporting Information.

(20) A control experiment in the absence of substrate showed that chloropalladate **Ia** is stable in $CDCl_3$ at 90 °C; no sign of decomposition was detected by ^{31}P NMR after 24 h.

(21) According to ^{31}P NMR, complex **II** is regenerated at the end of the reaction (see the Supporting Information).

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(23) A similar trend was reported for reactions catalyzed by $(Ph_3P)_2Pd(CH_2Ph)Cl/NEt_3$ (see ref 15c).

(24) The same intermediate is detected spectroscopically when the cyclization is catalyzed by chloropalladate complex **II**, suggesting that both catalytic systems operate similarly.

(25) This is further supported by preliminary mechanistic investigations: (i) reaction of **III** with 1 equiv of $HCl·Et_2O$ instantaneously leads to the formation of the corresponding chloroindenyl complex **IV** upon protonation of the indenediide backbone at C1, as demonstrated by ^{31}P and ^{1}H NMR (Figures S6 and S7 of the Supporting Information), and (ii) reaction of **III** with an excess of *N*-tosyl benzamide results in an equilibrium between **III** and an indenyl species (see Figures S8−S10 of the Supporting Information).

(26) This scheme is supported by D labeling studies using N-deuterated **1a**. Although some of the D labeling was lost during cyclization (N-deuterated sulfonamides are known to be labile, see: McKinney Brooner, R. E.; Widenhoefer, R. A. *Chem.—Eur. J.* **2011**, *17*, 6170−6178), the resulting lactam **2a** displays D labeling in the position *trans* to N (80%), but none in the position *cis* to N (see Figures S11 and S12 of the Supporting Information).

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(28) Complex **Ic** behaves differently. A single broad ^{31}P NMR signal is observed in solution, suggesting that the S bridges dissociate or reform rapidly on the NMR time scale.

(29) This is also apparent from the increased stability of **V** toward CO release. At 1 bar of CO, complex **V** remains the major species (3/1 **V**/**III** mixture according to ^{31}P NMR), while the corresponding Ph-substituted Pd carbonyl complex becomes minor (1/3 mixture in favor of trimer **Ic**). See also: Bolliger, J. L.; Blacque, O.; Frech, C. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 6514−6517.