



HAL
open science

Palladium pincer complexes featuring an unsymmetrical SCN indene-based ligand with an hemilabile pyridine sidearm

Paul Brunel, Chloé Lhardy, Sonia Mallet-Ladeira, Julien Monot, Blanca Martin-Vaca, Didier Bourissou

► To cite this version:

Paul Brunel, Chloé Lhardy, Sonia Mallet-Ladeira, Julien Monot, Blanca Martin-Vaca, et al.. Palladium pincer complexes featuring an unsymmetrical SCN indene-based ligand with an hemilabile pyridine sidearm. Dalton Transactions, 2019, 48 (26), pp.9801-9806. 10.1039/C9DT00898E . hal-02398806

HAL Id: hal-02398806

<https://hal.science/hal-02398806v1>

Submitted on 8 Dec 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Palladium pincer complexes featuring an unsymmetrical SCN indene-based ligand with an hemilabile pyridine sidearm

Paul Brunel,^a Chloé Lhardy,^a Sonia Mallet-Ladeira,^b Julien Monot,^{*a} Blanca Martin-Vaca^{*a} and Didier Bourissou^{*a}

a. CNRS, Université Paul Sabatier, Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA, UMR 5069), 118 Route de Narbonne, 31062 Toulouse Cedex 09, France. Email: monot@chimie.ups-tlse.fr; bmvt@chimie.ups-tlse.fr and dbouriss@chimie.ups-tlse.fr

b. Université de Toulouse, UPS, Institut de Chimie de Toulouse, FR2599, 118 Route de Narbonne, F-31062 Toulouse, France.

Abstract: The new unsymmetrical indene-based pro-ligand featuring thiophosphinoyl and methylpyridine sidearms **2** was prepared. Coordination and cyclometalation in the presence of [PdCl₂(PhCN)₂] and PS-DIEA afforded three well-defined 2-indenyl SCN pincer complexes **3a-c**. The lability of the pyridine moiety has been evidenced upon treatment with triphenylphosphine and 2,6-dimethylphenylisocyanide. In addition, reversible C–Pd bond cleavage has been demonstrated under Brønsted acid/base conditions. The indenediide SCN pincer complex **4** was prepared by deprotonation of **3a** in the presence of triphenylphosphine. Preliminary catalytic tests on the cycloisomerization of 4-pentynoic acid have underlined the impact of the pyridine sidearm on catalytic activity.

Introduction

Over the last decades, metal/ligand cooperativity (MLC) has become a very active and flourishing domain in catalysis, in particular thanks to the progress of the chemistry of pincer complexes.¹ Starting from ruthenium pincer complexes, MLC has been developed with different late transition metals (Ru, Rh, Ir...),² and more recently first row transition metals (Fe, Mn, Ni...).³ Despite the forefront position of Pd in catalysis, scarce examples of MLC involve Pd pincer complexes so far.^{4,5} This is most likely due to the tridentate nature of pincer ligands and to the square-planar geometry of Pd(II) which result in only one available “working” site at Pd, limiting thereby the variety of possible transformations.

To overcome this limitation, the design of a hemilabile pincer ligand is appealing. According to the HSAB theory,⁶ the soft Pd(II) prefers soft donor atoms such as P or S over hard N donors. Accordingly, the incorporation of a N(sp²) lateral donor site into a tridentate ligand is attractive to achieve hemilability in pincer Pd(II) complexes. Wendt and coll.⁷ applied this strategy for the preparation of a hemilabile unsymmetrical PCN palladium pincer complex and demonstrated its efficiency in the catalytic decarboxylative cross-coupling of propiolic acids and aryl halides.

As part of our ongoing research program on indenediide pincer complexes (Chart 1, compound **A**),^{4b,c} we have demonstrated the high structural modularity of these systems and improved thereby their catalytic activity in cycloisomerization reactions. Seeking for further structural modifications, we reported last year the synthesis of a tridentate indene-based ligand with two pyridine sidearms. Coordination to Pd afforded the pincer complex **B** (Chart 1) with migration of the CC double bond.⁸

Here, we report the preparation of a new unsymmetrical indene-based ligand featuring thiophosphinoyl and methylpyridine sidearms as a fusion of models **A** and **B** (Chart 1, compounds **C**). Coordination to Pd leading to the corresponding indenyl and indenediide pincer complexes is described. The hemilability of the pyridine moiety and its impact on the catalytic activity of the indenediide pincer complex are discussed.

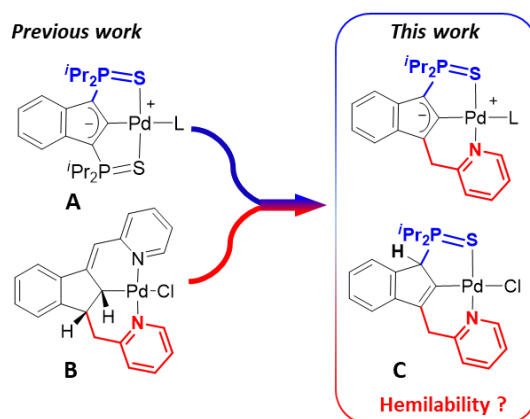
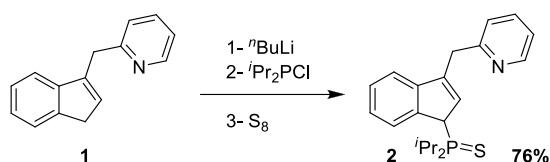


Chart 1. Bithiophosphinoyl-indenediide (**A**), bismethylpyridine-indenyle (**B**) and the new thiophosphinoyl-methylpyridine indenyl and indenediide (**C**) Pd pincer complexes.

Results and discussion

Preparation of the indenyl and indenediide complexes (3a-c, 4)

Starting from compound **1**,⁸ the pro-ligand **2** was readily prepared by deprotonation and addition of chlorodiisopropylphosphine followed by oxidation with an excess of elemental sulphur (scheme 1). After purification by flash chromatography, compound **2** was obtained in 76% yield as a brown viscous oil. The introduction of the thiophosphinoyl arm is confirmed by the appearance of a sharp singlet at 70 ppm in ³¹P NMR spectroscopy. The ¹H NMR signal for the C_{sp3}-H bearing the thiophosphinoyl sidearm appears with the expected multiplicity (dd, *J*_{HP} = 23.5 and *J*_{HH} = 1.8 Hz) at 4.26 ppm, similarly to what was observed for the bis(thiophosphinoyl) indene pro-ligand (Chart 1, **A**).^{4b}

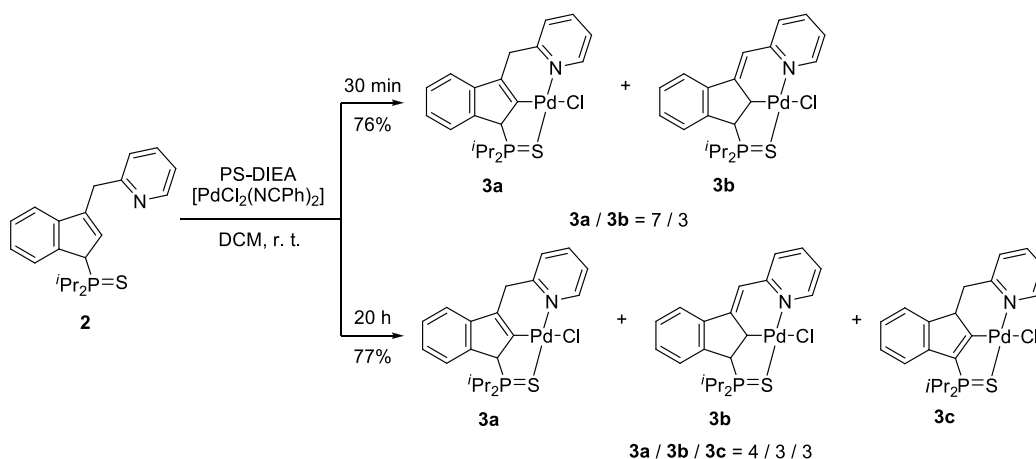


Scheme 1. Preparation of the pro-ligand **2** from **1**.

Then, pro-ligand **2** was reacted with [PdCl₂(PhCN)₂] in DCM at room temperature. After 30 min, an important precipitate was observed. The absence of ³¹P NMR signal indicated complete consumption of **2**. The high insolubility of the solid obtained after filtration prevented its characterization. Surmising that this precipitate results from the protonation of the pyridine sidearm upon activation of the C1-H bond, the reaction of **2** with [PdCl₂(PhCN)₂] was performed in the presence of polystyrene-supported diisopropylethyl amine (PS-DIEA) as an external base. After 30 min in DCM at room temperature, ³¹P NMR spectroscopy showed complete consumption of **2** and the apparition of two well-defined species giving rise to singlet signals at 81.9 and 82.5 ppm (in a 7 / 3 ratio, Scheme 2). Increasing the reaction time to 20 h in order to probe the interconversion between them, lead in fact to the formation of a third compound as apparent from the additional singlet observed at 84.9 ppm in the ³¹P NMR spectrum. These three species could be separated by flash chromatography with a good overall yield (76%). Stopping the reaction at 30 min allows to obtain **3a** as the major product.

For the three complexes, the coordination of both the thiophosphinoyl and pyridine sidearms to the Pd center was confirmed by NMR spectroscopy in CDCl₃. For each species, the ³¹P NMR spectra displays a sharp singlet (at 81.9 and 82.5 ppm, respectively) shifted downfield by at least 10 ppm compared to that of the pro-ligand (70 ppm). In the ¹H NMR spectrum, the H_{ortho} of the pyridine ring is shifted downfield for all complexes **3** (9.61, 9.70 and 9.93 ppm) with respect to that of **2** (8.55 ppm).

In the case of compound **3b**, the carbon atom connecting the pyridine to the ligand backbone is no longer part of a CH₂ group but a C_{sp2}-H group, as indicated by the ¹H and ¹³C NMR signals at 6.94 and 115.5 ppm, respectively. This indicates migration of the C=C double bond, as in the case of the bis(pyridine)indenyl pincer complex **B**.⁸ Consistently, C1 and C2 display typical features for C_{sp3}-H moieties (¹³C NMR: 53.6 and 37.1 ppm, ¹H NMR: doublet of doublets at 4.63 and 5.12 ppm).



Scheme 2. Synthesis of the SCN Pd indenyle complexes **3**.

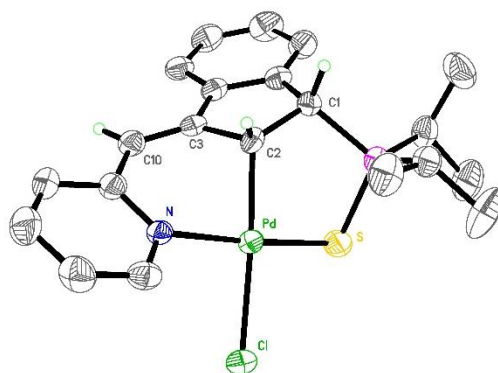
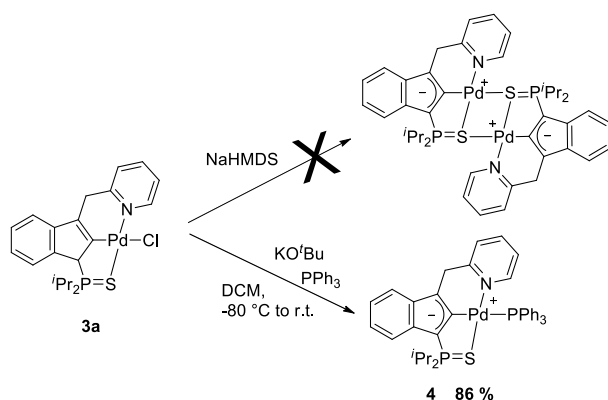


Figure 1. Ellipsoid drawings (50% probability) of the molecular structure of **3b**. For clarity, lattice solvent molecules and hydrogen atoms are omitted, except H1, H2 and H10.

Crystals were grown by slow diffusion of pentane in a saturated dichloromethane solution at room temperature. The structure of **3b** was definitely confirmed by X-ray diffraction analysis. As shown in Figure 1, the ligand is coordinated by N, C2 and S, and the Pd center in a slightly distorted square-planar environment. The C3 and C10 atoms are both in trigonal planar environment and form a CC double bond ($d_{C3-C10} = 1.345(6) \text{ \AA}$). Conversely, C1 and C2 are tetrahedral and the two respective H atoms (H1 and H2) are *syn* to each other.⁸

Assignment of complexes **3a** and **3c** as 2-indenyl Pd complexes, without migration of the CC double bond, was based on NMR spectroscopy. The ¹³C NMR spectra clearly shows the presence of an aliphatic CH₂ signal (at 37.48 and 39.45 ppm, respectively) for the methylpyridine sidearm. For **3c**, the CH₂ protons resonate in ¹H NMR as an AM system (2.74 and 3.46 ppm) due to the proximity of the asymmetric C3 center. The carbon of the indene directly bonded to P (C1) is quaternary and appears in the C_{sp2} zone (135.5 ppm, $J_{CP} = 92.0 \text{ Hz}$). For **3a**, the CH signal at 63.77 ppm displays a large coupling to phosphorus ($J_{CP} = 45.8 \text{ Hz}$), as the associated ¹H NMR signal at 4.78 ppm ($J_{HP} = 20.6 \text{ Hz}$).

Having the palladium indenyl complexes **3** in hands, the preparation of the corresponding indenediide complex was attempted. First, a similar strategy to that applied for the synthesis of the bis(thiophosphinoyl) indenediide palladium dimer^{4b} was tested on **3a**, using NaHMDS as a base (Scheme 3, top). No deprotonation occurred but isomerization of **3a** into **3b** and **3c** was observed.



Scheme 3. Preparation of Pd indenediide complex **4**.

At this stage, we decided to target a chloropalladate type complex using the previously reported procedure.^{4b} Unfortunately, the addition of a base to **3a** in the presence of ammonium chloride salt did not lead to the desired compound. Using ^tBuOK as the base in the presence of a more strongly coordinating co-ligand such as triphenylphosphine proved more fruitful, leading to a unique well-defined compound (Scheme 3, down). Complex **4** was isolated as a dark red powder after precipitation with pentane in an excellent yield (86%). Two sharp doublet signals are observed in the ³¹P NMR spectrum at 76.6 and 17.8 ppm ($J_{CP} = 45.5 \text{ Hz}$) for the thiophosphinoyl sidearm and coordinated triphenylphosphine, respectively. Moreover, the disappearance of the H atom at C1 is clearly apparent from ¹H and ¹³C NMR (a Cq signal is observed for C1), confirming the formation of an indenediide moiety. Complex

4 is only moderately stable in solution. Its half-life time was estimated to ~10 h in CDCl_3 and 21 h in d^6 -benzene at room temperature.⁹ This poor stability prevented the obtention of crystals suitable for X-ray diffraction analysis.

Evaluation of the hemilability of the pyridine moiety.

The lability of the pyridine moiety of the pincer ligand was investigated next. Due to the low stability of **4** in solution, the study was carried out on the indenyl complexes **3**. The addition of increasing amounts of triphenylphosphine to a solution of **3a** in d^2 -DCM at room temperature was monitored by NMR spectroscopy (See Figure 2).

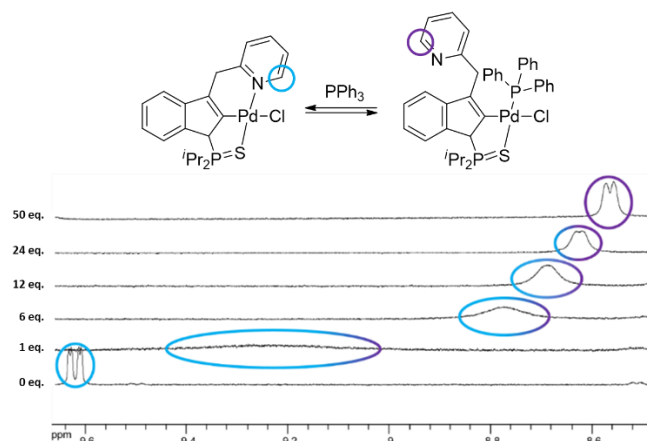
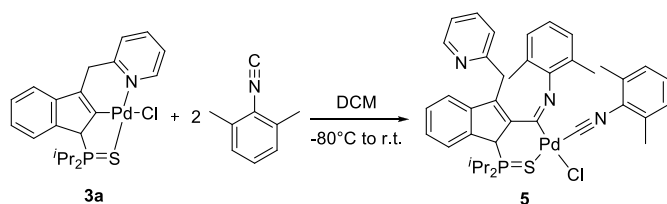


Figure 2. Stacking of ^1H NMR spectra for **3a** (region 9.70-8.50 ppm) with sequential additions of triphenylphosphine in d^2 -DCM at 293 K.

The addition of triphenylphosphine resulted in a broadening and upfield shift of the ^1H NMR signal attributed to the H_{ortho} atom of the pyridine group (Figure 2). The ^{31}P NMR signal related to the thiophosphinoyl sidearm disappeared, whereas a new broad signal at 80.9 ppm was observed. At the same time, the singlet signal corresponding to the free triphenylphosphine at -5.18 ppm significantly broadened and a second large signal appeared at 28.7 ppm. This is consistent with the coordination of PPh_3 to Pd with relatively fast exchange between free and coordinated phosphine. Adding 50 equivalents of PPh_3 resulted in a resolved doublet signal for H_{ortho} at 8.50 ppm in the region of the free ligand (8.55 ppm for pro-ligand **2**). All these observations are consistent with the displacement of the pyridine sidearm at Pd by PPh_3 in the presence of an excess of the phosphine. However, the isolation and characterization of the resulting complex was unsuccessful due to the high fluxionality of the system.

In order to further substantiate the decooordination of the N sidearm, we turned to a less hindered partner, namely 2,6-dimethylphenyl isocyanide (Scheme 4). We hypothesized an easier displacement of the pyridine and thus, the use of a lower amount of the external co-ligand.

The addition of one equivalent of 2,6-dimethylphenyl isocyanide to a solution of **3a** in DCM at -80°C led to half conversion into a new compound **5** displaying a singlet at 71.8 ppm in ^{31}P NMR. Two equivalents of isocyanide were necessary to convert quantitatively **3a** into **5**. The structure of **5** was determined by X-ray diffraction (crystals grown by slow diffusion of pentane in a saturated DCM solution at room temperature). A first observation confirms the decooordination of the pyridine sidearm and the coordination of an isocyanide to the Pd center. More surprising is the presence of a second unit of isocyanide inserted into the Pd- C_{sp^2} bond resulting in a 6-membered metallacycle with chair conformation. The palladium center is in a slightly distorted square-planar environment. The formation of **5** most likely results from displacement of the pyridine by an isocyanide, followed by its insertion into the Pd-C2 bond and coordination of a second isocyanide unit. This is the first time that an insertion process into the central Pd-C bond is observed with this kind of indenyl pincer complexes, but a similar process was previously reported by Gebbink and Szabó with $\text{SC}_{\text{sp}^2}\text{S}$ and $\text{PC}_{\text{sp}^2}\text{S}$ Pd pincer complexes.¹⁰



Scheme 4. Decoordination of the methylpyridine arm and insertion of an isocyanide unit.

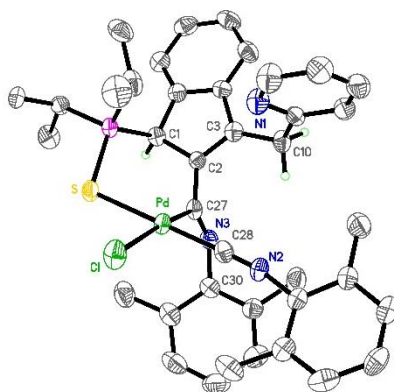
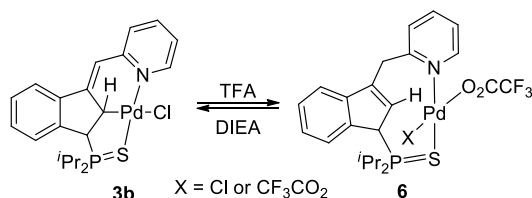


Figure 3. Ellipsoid drawings (50% probability) of the molecular structure of **5**. For clarity, lattice solvent molecules and hydrogen atoms are omitted, except H1 and H10.

Thus, reacting the indenyl complex with a phosphine and an isocyanide established the lability of the pyridine. We then studied its behaviour under Brønsted acid/base conditions. While no reaction was observed upon addition of an excess of acetic acid (> 10 equivalents) to a solution of complex **3b** in *d*²-DCM, a clean and complete reaction was observed upon addition of three equivalents of trifluoroacetic acid. Close inspection of the ¹H and ¹³C NMR data revealed the migration of the C=C double bond to reform an indene moiety and the cleavage of the C2–Pd bond (Scheme 5). The ¹H NMR signal at 6.94 ppm associated with the –CH= linker of **3b** disappeared to give an AM system integrating for 2 protons (5.1 and 3.83 ppm) and correlating in ¹³C NMR with an aliphatic CH₂ signal (40.19 ppm). Concomitantly, the ¹H and ¹³C NMR signals for the central C–H moiety are noticeably deshielded as the result of the change in C hybridization (from sp³ to sp²): from 5.12 to 6.39 ppm for H2, and from 37.05 to 93.71 ppm for C2. In addition, reactIR monitoring shows the appearance of bands at 1375 and 1610 cm⁻¹ upon formation of **6**. These data are diagnostic for κ¹ coordination of the trifluoroacetate group to the Pd center (see ESI, fig S2).¹¹ Attempts to isolate and crystallize **6** failed so far, thus the exact nature of the fourth ligand at Pd (X = Cl or CF₃CO₂) remains unknown.



Scheme 5. Equilibrium between **3b** and **6** under Brønsted acid-base conditions

Interestingly, the transformation of **3b** into **6** is reversible. Following the formation of **6** by reacting **3b** with 3 equivalents of TFA, 3 equivalents of a base (DIEA) were added. NMR showed instantaneous and quantitative reformation of **3b** (Figure 4). Thus, the cleavage / formation of the C2–Pd bond is reversible under Brønsted acid/base conditions. The protonation of the C2–metalated ligand likely represents the initial stage of ligand dissociation under strongly acidic conditions. Conversely, the formation of the C2–Pd bond from **6** is reminiscent of the formation of the SCS bis(thiophosphinoyl) methylindenyl Pd pincer complex.¹²

Despite the low stability of **4** in solution, we were curious about the impact that the pyridine sidearm may have on catalytic activity. Therefore, the activity of **4** was evaluated in the cycloisomerization of 4-pentynoic acid as a model reaction for which complete conversion was observed after 1 h with the palladium indenediide dimer [Ind(*i*Pr₂P=S)₂Pd]₂.^{4b,13} The reaction was carried out in CDCl₃ at room temperature, with 5 mol % of catalyst loading and in the absence of any external base (Scheme 6). The reaction proceeded readily and 62% conversion into the 5-*exo* lactone was observed after 1 h.¹⁴ In order to elucidate the potential role of the methylpyridine sidearm, we performed a few control experiments. First, complex **7** was prepared by adding 2 equivalents of triphenylphosphine to the

corresponding indenediide dimer and engaged in the catalytic cycloisomerization reaction. In this case, the catalytic activity was completely shut down (no reaction after 1 h at room temperature), most likely due to the saturation of the Pd coordination sphere by PPh₃. This control experiment is consistent with the need of a free coordination site for the π activation of the C \equiv C triple bond and thus suggests that the labile character of the methylpyridine is involved in the catalytic transformation. Given this, both the indenediide moiety and the pyridine moiety may contribute to the deprotonation (and activation) of the carboxyl acid group. A second control experiment was thus performed using the protonated chloroindenyl complex **3b**. In this case, no conversion was detected after 1 h, indicating that decoordination of pyridine is not enough for the cycloisomerization to occur, confirming thereby the necessity of the electron-rich indenediide moiety in addition to the free coordination site at Pd.

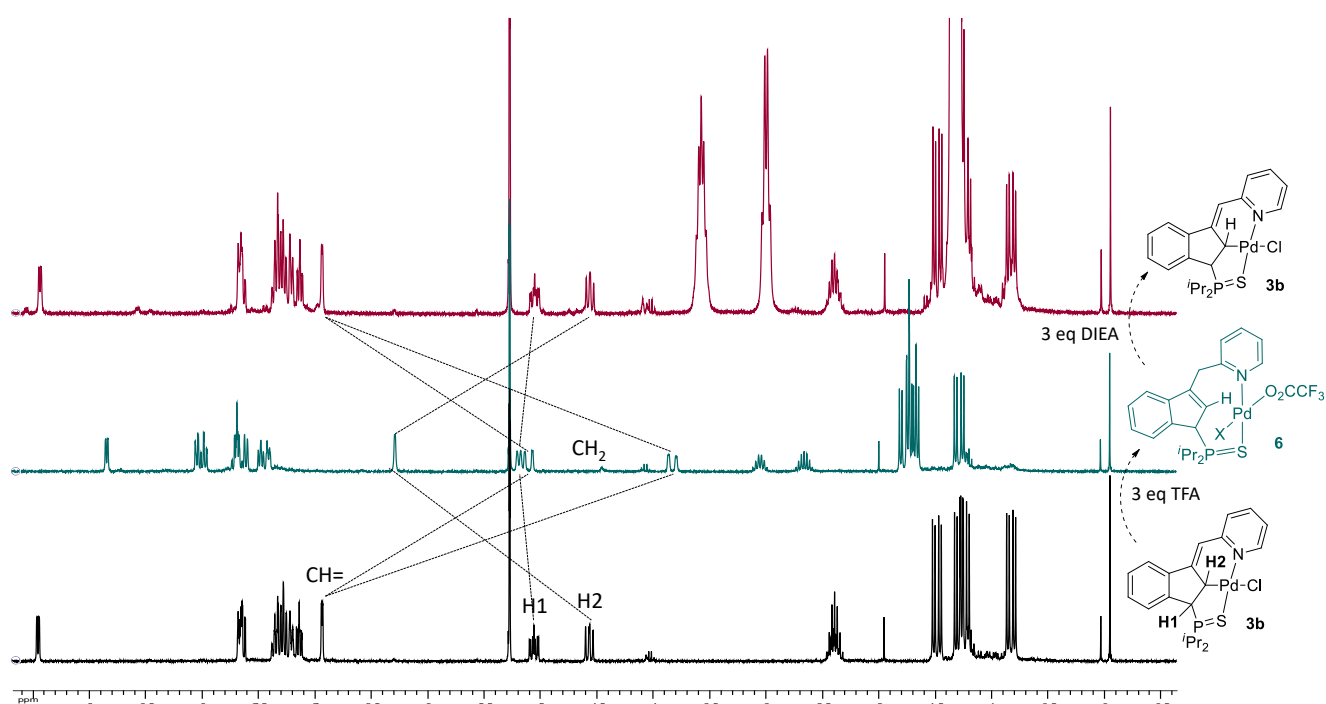
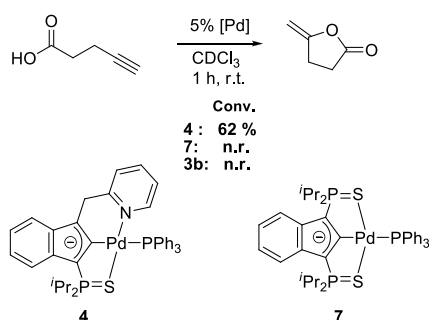


Figure 4. ¹H NMR monitoring of the addition of trifluoroacetic acid (3 equivalents, turquoise spectrum) and then *N,N*-diisopropylethylamine (3 equivalents, red spectrum).



Scheme 6. Evaluation of the catalytic performances of indenediide Pd complexes **4**, **7** and **3b** in the cyclization of 4-pentynoic acid. (Conversions estimated by ¹H NMR spectroscopy)

Conclusions

In summary, the new unsymmetrical indene based pro-ligand **2** featuring thiophosphinoyl and methylpyridine sidearms was prepared. Coordination to Pd afforded three isomeric complexes **3a-c** that

were separated and fully characterized. Competition experiments in the presence of Lewis bases demonstrate the lability of the methylpyridine sidearm of **3** while Brønsted acid/base conditions promotes reversible cleavage of the C2-Pd bond. A new SCN indenediide complex **4** stabilized by a triphenylphosphine co-ligand was also prepared. Preliminary catalytic tests underlined the impact of the methylpyridine sidearm on catalytic activity.

These results illustrate the interest and potential that hemilability may have on catalytic applications of indenediide pincer complexes. We have previously demonstrated that subtle structural modulations of the thiophosphinoyl sidearms can enhance greatly the robustness of indenediide Pd complexes.^{4b} Future work will aim to increase the stability of such unsymmetrical indenediide complexes by modification of the thiophosphinoyl sidearm, with the aim to take advantage of the hemilabile character of the pyridine moiety in catalysis.

Acknowledgements

Financial support from the Centre National de la Recherche Scientifique, the Université de Toulouse and the Agence Nationale de la Recherche (ANR CE6-CYCLOOP) is acknowledged. We thank Corinne Routaboul (ICT, Toulouse) for helpful assistance with the *in situ* infrared experiment with the ReactIR.

Notes and references

- 1 J. R. Khusnutdinova and D. Milstein, *Angew. Chem. Int. Ed.*, 2015, **54**, 12236.
- 2 For selected examples, see: (a) C. Gunanathan and D. Milstein, *Acc. Chem. Res.*, 2011, **44**, 588; (b) C. Gunanathan and D. Milstein, *Chem. Rev.*, 2014, **114**, 12024; (c) T. Zweifel, J. V. Naubron, T. Büttner, T. Ott and H. Grützmacher, *Angew. Chem. Int. Ed.*, 2008, **47**, 3245; (d) T. Zweifel, J. V. Naubron and H. Grützmacher, *Angew. Chem. Int. Ed.*, 2009, **48**, 559; (e) D. Gelman and S. Musa, *ACS Catal.*, 2012, **2**, 2456; (f) S. Musa, L. Ackermann and D. Gelman, *Adv. Synth. Catal.*, 2013, **355**, 3077; (g) A. V. Polukeev and O. F. Wendt, *J. Organomet. Chem.*, 2018, **867**, 33.
- 3 For selected examples, see: (a) T. Zell and D. Milstein, *Acc. Chem. Res.*, 2015, **48**, 1979; (b) N. Gorgas and K. Kirchner, *Acc. Chem. Res.*, 2018, **51**, 1558; (c) F. Kallmeier and R. Kempe, *Angew. Chem. Int. Ed.*, 2018, **57**, 46; (d) A. Kumar, T. Janes, N. A. Espinosa-Jalapa and D. Milstein, *Angew. Chem. Int. Ed.*, 2018, **57**, 12076; (e) Y. K. Jang, T. Krücker, M. Rueping and O. El-Sepelgy, *Org. Lett.*, 2018, **20**, 7779; (f) C. Erken, A. Kaithal, S. Sen, T. Weyhermüller, M. Hölscher, C. Werlé and W. Leitner, *Nat. Commun.*, 2018, **9**, 4521; (g) D. Oren, Y. Diskin-Posner, L. Avram, M. Feller and D. Milstein, *Organometallics*, 2018, **37**, 2217; (h) T. Irrgang and R. Kempe, *Chem. Rev.*, 2019, doi:10.1021/acs.chemrev.8b00306.
- 4 (a) A. Scharf, I. Goldberg and A. Vigalok, *J. Am. Chem. Soc.*, 2013, **135**, 967; (b) N. Á. Espinosa-Jalapa, D. Ke, N. Nebra, L. Le Goanvic, S. Mallet-Ladeira, J. Monot, B. Martin-Vaca and D. Bourissou, *ACS Catal.*, 2014, **4**, 3605; (c) P. Brunel, J. Monot, C. E. Kefalidis, L. Maron, B. Martin-Vaca and D. Bourissou, *ACS Catal.*, 2017, **7**, 2652.
- 5 (a) L. C. Gregor, C. H. Chen, C. M. Fafard, L. Fan, C. Guo, B. M. Foxman, D. G. Gusev and O. V. Ozerov, *Dalton Trans.*, 2010, **39**, 3195; (b) C. C. Comanescu and V. M. Iluc, *Organometallics*, 2014, **33**, 6059; (c) C. C. Comanescu and V. M. Iluc, *Organometallics*, 2015, **34**, 4684; (d) C. C. Comanescu and V. M. Iluc, *Polyhedron*, 2018, **143**, 176.
- 6 (a) R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533; (b) R. G. Pearson, *J. Chem. Educ.*, 1968, **45**, 581; (c) R. G. Pearson, *J. Chem. Educ.*, 1968, **45**, 643.
- 7 (a) A. Fleckhaus, A. H. Mousa, N. S. Lawal, N. K. Kazemifar and O. F. Wendt, *Organometallics*, 2015, **34**, 1627; (b) A. H. Mousa, A. Fleckhaus, M. Kondrashov and O. F. Wendt, *J. Organomet. Chem.*, 2017, **845**, 157.
- 8 V. Vresch, J. Monot, B. Martin-Vaca and D. Bourissou, *Polyhedron*, 2018, **143**, 49.
- 9 Attempts to increase the stability of this indenediide complex by the introduction of other co-ligands were unsuccessful.
- 10 M. Gagliardo, N. Selander, N. C. Mehendale, G. Van Koten, R. J. Klein Gebbink and K. Szabó, *Chem. Eur. J.*, 2008, **14**, 4800.
- 11 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry, Sixth Edition*, Wiley-VCH, Weinheim 2014.
- 12 N. Nebra, J. Liséna, N. Saffon, L. Maron, B. Martin-Vaca and D. Bourissou, *Dalton Trans.*, 2011, **40**, 8912.
- 13 J. Monot, P. Brunel, C. E. Kefalidis, N. A. Espinosa-Jalapa, L. Maron, B. Martin-Vaca and D. Bourissou, *Chem. Sci.*, 2016, **7**, 2179.
- 14 No further conversion was observed after 1 h.