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Palladium Pincer Complex-Catalyzed Condensation of Sulfonimines and Isocyanoacetate to Imidazoline Derivatives. Dependence of the Stereoselectivity on the Ligand Effects

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This paper is dedicated to Professor Jan-E. Bäckvall on the occasion of his 60th birthday.

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: Palladium-catalyzed condensation reactions of sulfonimines with isocyanoacetate were performed using various PCP, SCS, SeCSe and NCN pincer complexes as catalysts. The reactions proceeded rapidly (2 h) at room temperature using only 1 mol% pincer complex catalyst without any additives. The electron-deficient and relatively bulky PCP complex provides imidazoline derivatives with a very high *syn* diastereoselectivity. The applied PCP catalyst proved to be very robust under the applied reaction conditions, as it could be recovered without any decomposition after the completed catalytic process. The stereoselectivity of the condensation reactions is reversed by employing the electron-rich SeCSe type of complexes. Simple palladium salts, such as palladium acetate, $Pd(OAc)_2$, catalyze the reaction with a poor stereoselectivity. The stereoselectivity of the PCP complex-catalyzed process does not depend significantly on the steric bulk of the sulfonimine component. Mechanistic studies revealed that the PCP complex-catalyzed reaction proceeds *via* an η^1-coordinated palladium isocyanoacetate pincer intermediate. This intermediate could also be isolated and its structure was determined by X-ray diffraction. The X-ray structure of this reaction intermediate indicates a surprisingly strong carbon-metal bond between the palladium atom and the coordinated isocyanoacetate molecule. Our mechanistic studies show that the pincer complex catalyst does not undergo redox reactions and, thus it retains a +2 oxidation state under the catalytic process.

Keywords: cyclization; imines; isocyanide ligands; palladium; pincer complexes; stereoselectivity

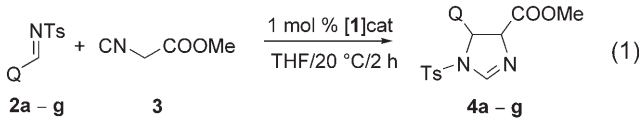
Introduction

Professor Jan-E. Bäckavall has exceptionally forwarded Swedish and world-wide research in organic chemistry and catalysis inspiring generations of young colleagues. Jan is a great friend and colleague and with this paper, we would like to congratulate him to the 60th birthday as well as show our appreciation of his great achievements in metal and bio-catalysis, in particular in palladium chemistry.[1–12]

Catalytic applications of palladium pincer complexes[13–19] (e.g., **1a–g**) have attracted considerable attention in the last couple of years,[20–39] since employment of pincer complex catalysts in place of the commonly used palladium salts often opens new and highly selective synthetic routes. Furthermore, palladium pincer complexes are highly stable and robust catalysts because of a tight terdentate coordination of the ligand to the metal center. One of the main application areas of palladium pincer complex catalysis is the aldol reaction of aldehydes with isocyanides affording oxazoline derivatives,[20,22,23,35,38–42] which can be hydrolyzed to amino acids. As far as we know, analogue pincer complex-catalyzed reactions employing imine substrates in place of aldehydes have never been reported. Notwithstanding, this reaction is particularly interesting, since condensation of imines with isocyanides leads to 2-imidazolines, which can easily be converted to α,β-diamino acids, which represent[43] a class of biologically important compounds. Although, this important condensation reaction could be performed using various sulfonimines (**2**) and isocyanoacetate (**3**) in the presence of gold,[44–46] ruthenium[47] and copper[48] catalysts, reports on palladium-

catalyzed reactions are very scarce.[44,47] This can be explained by the fact that the palladium-catalyzed coupling of imines with isocyanides was characterized as a slow and unselective process.[44,47]

We have now found that palladium pincer complexes show a relatively high catalytic activity in the coupling of sulfonimines with isocyanoacetate; and that the stereoselectivity of the process is highly dependent on the electronic properties of the applied pincer complex catalysts (Scheme 1). Therefore, we have studied the synthetic scope and selectivity of this reaction employing various sulfonimines (**2a**–**g**) and isocyanoacetate **3** in the presence of catalytic amounts of pincer complexes **1a**–**g** and a commonly employed palladium salt $Pd(OAc)_2$ (**1h**) affording 2-imidazoline products **4a**–**g** [Eq. (1)]. In addition to the synthetic studies we have also studied the mechanistic aspects of the condensation reaction.



2a – g **3** **4a – g** (1)

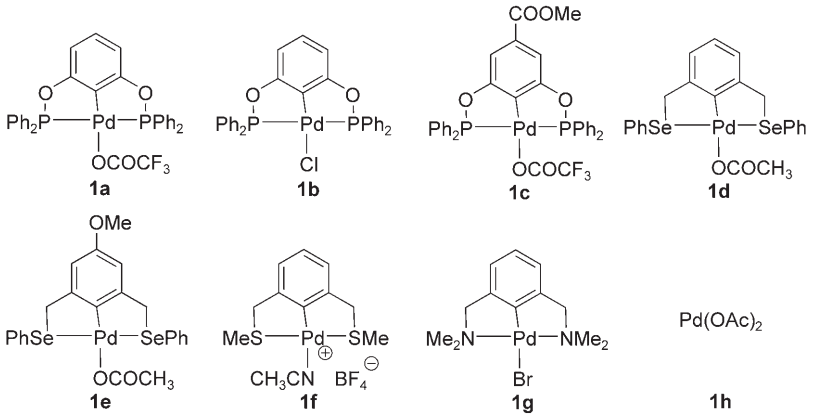
Results and Discussion

Synthetic Scope and Selectivity

The condensation reactions between various imines **2a**–**g** and isocyanoacetate **3** could easily be performed at room temperature in the presence of catalytic amounts (1 mol%) of pincer complexes **1a**–**g** affording 2-imidazoline derivatives **4a**–**g** with nearly quantitative yields [Eq. (1)]. In contrast to the palladium pincer complex-catalyzed condensation of aldehydes with isocyanoacetate **3**, the reactions with imine substrates **2a**–**g** could be achieved without base catalysis. The condensation reactions of **2a** with **3** in the presence of catalytic amounts of **1a** and **b** are completed within two hours indicating that the catalytic activity of **1a** and **b** in this process is much higher than in the corresponding allylation reaction of sulfonimines (such as **2a**), which requires at least 16 h to be completed.[33,34]

The 2-imidazoline products [Eq. (1), Table 1] are relatively stable in the absence of water, however they displayed some tendency for decomposition under silica gel or neutral alumina chromatography. In fact the corresponding diamino acid derivatives **5a** and **5b** could be easily obtained by stirring 2-imidazoline derivatives **4a** and **4b** in the presence of water and neutral aluminium oxide [Eq. (2)]. As silica and alumina chromatography leads to a partial ring opening [Eq. (2)], the final products were purified with quick flash chromatography on celite. We did not observe a condensation reaction between sulfonimines and **3** in the absence of a palladium catalyst.

Probably, the most interesting feature of the coupling reaction is the stereoselectivity for the formation of the imidazoline derivatives. The condensation reaction of **2a** and **3** proceeds with a high *syn* selectiv-



Scheme 1. Palladium pincer complexes **1a**–**g** employed in this study.

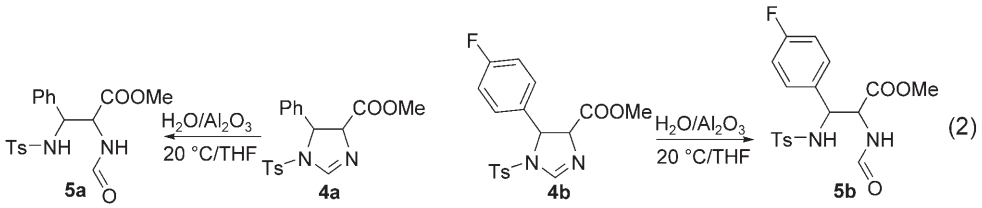
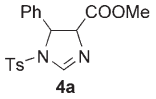
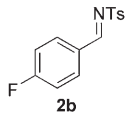
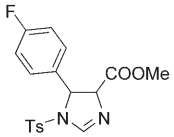
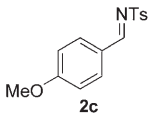
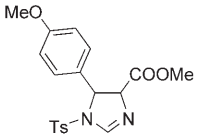
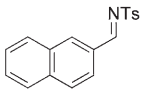
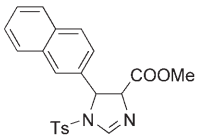
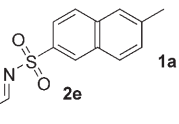
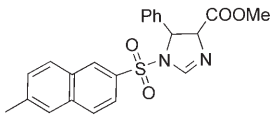
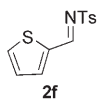
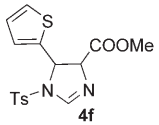
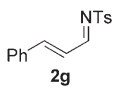
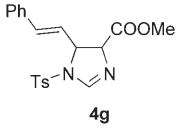


Table 1. Condensation of sulfonimines with isocyanoacetate in the presence of various palladium pincer complex catalysts.[a]

Entry	Imine	Catalyst	Product	Yield[b] [%]	dr[c] (*syn/anti*)
1	 **2a**	**1a**	 **4a**	98	10:1
2	**2a**	**1b**	**4a**	99	7:1
3	**2a**	**1c**	**4a**	99	8:1
4	**2a**	**1d**	**4a**	98	1:3
5	**2a**	**1e**	**4a**	99	1:4
6	**2a**	**1f**	**4a**	98	2:3
7	**2a**	**1g**	**4a**	99	2:3
8	**2a**	**1h**	**4a**	82	1:2
9	 **2b**	**1a**	 **4b**	98	9:1
10	**2b**	**1e**	**4b**	93	1:3
11	 **2c**	**1a**	 **4c**	98	11:1
12	 **2d**	**1a**	 **4d**	99	7:1
13	 **2e**	**1a**	 **4e**	98	8:1
14	 **2f**	**1a**	 **4f**	99	10:1
15	 **2g**	**1a**	 **4g**	99	8:1

[a] All reactions were performed using 1 mol% catalyst **1** at 20 °C in THF.
[b] Isolated yield.
[c] Ratio of the *syn* and *anti* products determined by ^{1}H NMR spectroscopy.

ity (*syn*/*anti* ratio 10:1) in the presence of the trifluoroacetate salt of PCP complex **1a** (entry 1). Change of the counterion on palladium to chloride (**1b**) leads to a slight decrease of the stereoselectivity (*syn*/*anti* ratio 7:1), however the *syn* selectivity is still maintained (entry 2). We have studied the effects of the electron-withdrawing methoxycarbonyl group on the stereoselectivity. However, using *para*-methoxycarbonyl-substituted complex **1c** in place of **1a** did not change significantly the stereoselectivity (entry 3). Surprisingly, employment of the SeCSe complex **1d**[37] instead of PCP complex **1a** led to the reversal of the stereoselectivity affording the *anti* stereoisomer of **4a** (*syn*/*anti* ratio 1:3) as the major product (entry 4). A further increase of the electron density on the complex can be achieved by applying a *para*-methoxy substituent[36] in the catalyst (**1e**). Compared to **1d** application of the methoxy-substituted SeCSe complex **1e** slightly increases (*syn/anti* ratio 1:4) the amount of the *anti* product in the condensation reaction (Entry 5). Furthermore, SCS (**1f**) and NCN (**1g**) complexes react with a low selectivity (*syn/anti* ratio 2:3), however the major product is still the *anti* form of **4a** (entries 6 and 7). Finally, we employed $Pd(OAc)_2$ (**1h**) as catalyst (entry 8), which afforded the imidazoline product (**4a**) with somewhat lower yield than the pincer complex-catalyzed reactions (entries 1–7). The $Pd(OAc)_2$-catalyzed process also provides the *anti* form as major diastereomer, however the selectivity is relatively low (*syn*/*anti* ratio 1:2). A similar reactivity and selectivity was reported for Pd(II) and Pd(0) salts applied as catalysts in the analogous condensation reactions.[44,47]

As mentioned above, the *syn/anti* selectivity of the condensation reaction of **2a** and **3** changes from 10:1 to 1:4 as one goes from catalyst **1a** to **1e**. Monitoring the progress of the catalytic reactions using ^{1}H NMR spectroscopy revealed that the catalytic activity of these complexes is also different (Figure 1). The con-

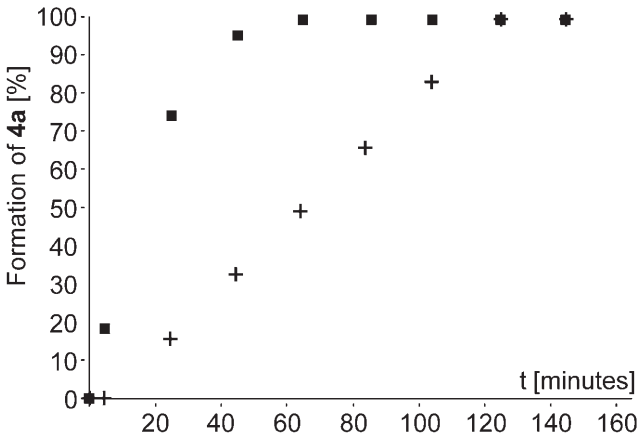


Figure 1. Formation of **4a** from **2a** and **3** catalyzed by 1 mol% of **1a** (■) or **1e** (+) in THF-d_8.

densation reaction catalyzed by PCP complex **1a** is faster than the corresponding process with SeCSe catalyst **1e**. It was found that the reaction with **1a** is completed in one hour, while the full conversion of **2a** and **3** to imidazoline product **4a** with the electron-rich SeCSe complex **1e** as catalyst required about twice as much time as with **1a**. These studies have also shown that the *syn*/*anti* ratio of **4a** was constant with both catalysts under the condensation reaction conditions.

Subsequently, we have studied the electronic effects of the aromatic substituents in the sulfonimine component. The fluoro substituted **2b** was reacted with **3** in the presence of **1a** (entry 9) with the same reactivity and about the same selectivity (*syn/anti* ratio 9:1), as the parent sulfonimine **1a**. Similar to the above condensation of **2a** and **3**, the stereoselectivity of the reaction was reversed (entry 10) when SeCSe complex **1e** was employed instead of PCP complex **1a** (*syn*/*anti* ratio 1:3). Application of **2c** with an electron-supplying *para*-methoxy group on the phenyl group (entry 11) gave somewhat higher selectivity (*syn/anti* ratio 11:1) than **2a**.

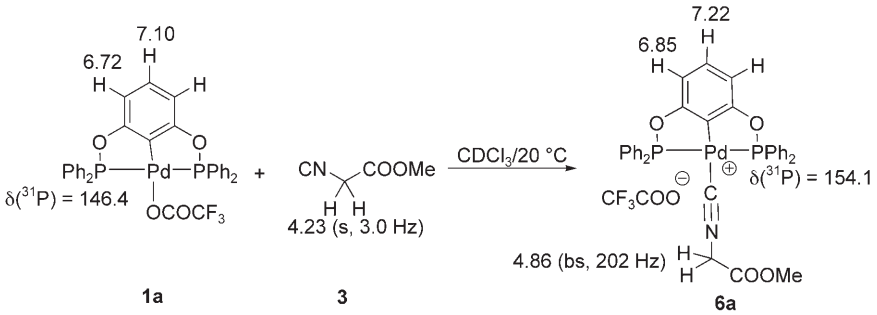
The steric effects of the aromatic rings of **2** are surprisingly small on the stereoselectivity of the reaction. Thus, the high *syn* selectivity (*syn*/*anti* ratio 7:1) of the condensation reaction was maintained even in the presence of the bulky naphthyl substituent (**2d**), in spite of the fact that the *syn* diastereomer of **4d** is thermodynamically probably less stable than the corresponding *anti* form (entry 12). The diastereoselectivity is also insensitive to the increase of the bulkiness of the sulfonyl substituent. For example, replacement of the tolyl group with a naphthyl one (**2e**) leads to a highly *syn* selective process (entry 13). The selectivity and reactivity of the palladium-catalyzed reaction is unchanged in the presence of sulfur-containing heterocycles, such as **2f** (entry 14). Furthermore, the catalytic reaction proceeds smoothly with high selectivity even with non-aromatic sulfonimines, such as **2g** (entry 15).

Stoichiometric Studies

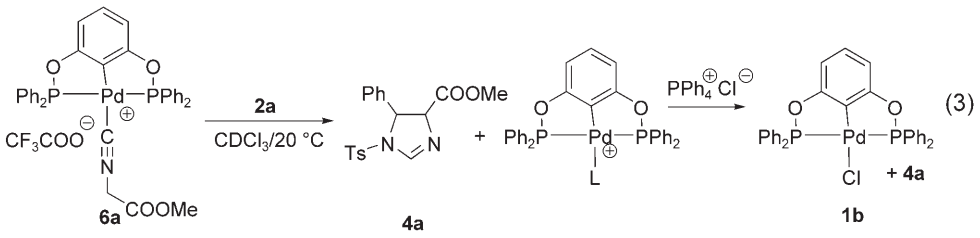
In order to get mechanistic insights to the above [Eq. (1)] catalytic condensation reactions, we have studied the stoichiometric reaction of PCP complex **1a** with isocyanoacetate **3**. Addition of a three-fold excess of **3** to the $CDCl_3$ solution of **1a** led to clearly observable changes in the ^1H NMR spectrum of these reagents (Scheme 2).

The proton signal of **3** appearing at 4.23 ppm as a singlet (lb = 3.0 Hz) is shifted to 4.86 ppm and considerably broadened (lb = 202 Hz). At the same time, the doublet (6.72 ppm) and triplet shifts (7.10) of the aromatic ring of complex **1a** have also increased to 6.85 ppm and 7.22 ppm respectively (Scheme 2). A further significant change occurred in the ^{31}P NMR spectrum. The ^{31}P NMR shift of the phosphorus atom in the side arms in **1a** (146.2 ppm) was increased by eight ppm (154.1 ppm) on addition of **3**. In this process only a single phosphorus shift was observed indicating that the symmetrical tridentate pincer architecture of the resulted complex (**6a**) remained intact. Considering the above systematic changes we reasoned that **3** was coordinated to the palladium atom of the pincer complex affording complex **6a**. Formation of similar complexes was postulated in condensation reactions of **3** with aldehydes in pincer complex-catalyzed processes.[49,50]

After **1a** was completely converted to **6a** the solvent and the excess of **3** were evaporated. Complex **6a** proved to be surprisingly stable, as the NMR shift values of **6a** after evaporation and dissolution in $CDCl_3$ were identical to the corresponding data observed under the stoichiometric reaction. Subsequently, sulfonimine **2a** was added to the solution of **6a** and the reaction was monitored with ^1H NMR spectroscopy. It was found that the reaction of **2a** and **6a** leads to a rapid formation of the condensed product **4a** [Eq. (3)]. Thus, the stoichiometric reaction of **6a** and **2a** gives the same product as the catalytic transformation of **3** with **2a** in the presence of 1 mol% of **1a** (entry 1). Although several peaks appeared in the ^{31}P NMR spectrum of the reaction mixture indicating



Scheme 2. Change of the NMR shifts (in ppm) under the stoichiometric reaction of **1a** and **3**. Unless otherwise stated the ^1H NMR shift values are given.



that different ligands may have coordinated to the resulted pincer complex, addition of organic chloride salt PPh_4Cl led to appearance of only two ^{31}P NMR shifts. One of these shifts was assigned to the PPh_4^+ counterion, while the other one was assigned to chloro complex **1b**, which could also be isolated by chromatography and identified.

X-ray Structure of 6a

We were also able to isolate and crystallize catalytic intermediate **6a**. The obtained crystals were suitable for X-ray diffraction analysis of this species. The geometric parameters determined for the palladium-ligand bonding and for the coordinated isocyanoacetate molecule reveal some interesting features. The X-ray diffraction structure of **6a** clearly shows a pincer complex architecture with two palladacycles (Figure 2). The Pd–P and Pd–C1 bond lengths (2.27 and 2.00 Å) in **6a** are very close to the corresponding bond lengths in the parent **1a** reported by Bedford and co-workers.[30] As a typical feature of PCP pincer complexes, the PCP angle (159°) deviates from the linear alignment (180°), which would have been required for an ideal MO overlap in tetragonal planar complexes. Most interestingly, the palladium-carbon bond to the coordinated isocyanoacetate molecule (Pd–C2) is relatively short, 2.025 Å. This indicates that the palladium-carbon bonding to the aryl ring and to the carbon atom of the coordinated isocyanoacetate are about equally strong, Thus, the interaction between the isocyanide carbon and palladium can be classified as a strong covalent bond, instead of a donor-acceptor interaction between a Lewis acid (the pincer complex) and a Lewis base (**3**). This is probably an important structural feature, as in the aldol reaction of isocyanoacetates with aldehydes, the pincer complexes are often referred to as Lewis acid catalysts.[20] Other interesting structural features of the coordinated isocyanoacetate moiety are the bond lengths of the C3–C4 bond (1.532 Å) and the carbonyl carbon oxygen bond (C4=O1, 1.198 Å) bonds, which clearly indicate the presence of a typical carbon-carbon single bond and a carbon-oxygen double bond. Accordingly, coordination of isocyanoacetate **3** to palladium in **6a** does not induce spontaneous enolization, which is required to increase the nucleophilicity of the coordinated isocyanoacetate.[16,49]

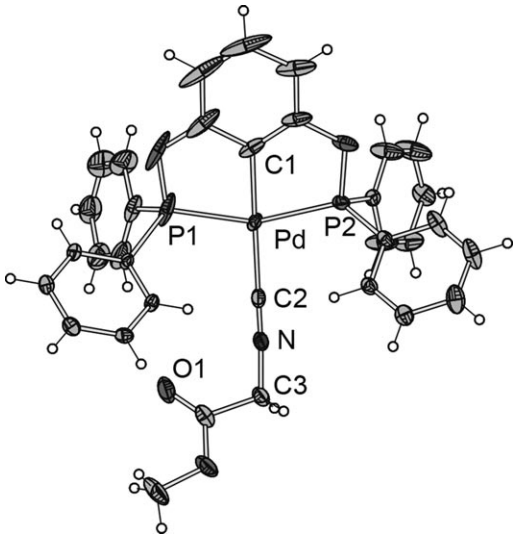


Figure 2. X-ray structure of **6a**. Selected bond lengths (Å) and angles: Pd–P1 2.2784(11); Pd–P2 2.2688(10); Pd–C1 2.004(5); Pd–C2 2.025(5); C2–N 1.123(6); N–C3 1.424(6); C3–C4 1.532(6); C4=O1 1.198(7); P2–Pd–P1 159.00(6); N–C2–Pd 173.3(4); N–C3–C4 108.8(4). For sake of clarity the trifluoroacetate counter ion and the included $CHCl_3$ molecule is not shown in the Figure. The displacement ellipsoids are drawn at the 30% probability level.

The Catalytic Cycle of the Reaction

The above stoichiometric studies clearly show two important mechanistic features of the catalytic reaction. The first step is formation of complex **6a** from catalyst **1a** and **3** followed by a reaction of **6** and sulfonimine **2a**. Under this process the tridentate coordination of the pincer complex catalyst was retained. A complete recovery of complex **1** clearly shows that the catalytic reaction does not involve palladium(0) species, since reduction of the palladium atom in **1** would have involved decomposition of the complex.[51–53] Furthermore, the X-ray structure of **6a** (Figure 2) clearly shows that the isocyanoacetate molecule is firmly coordinated to palladium without enolization of the substrate.

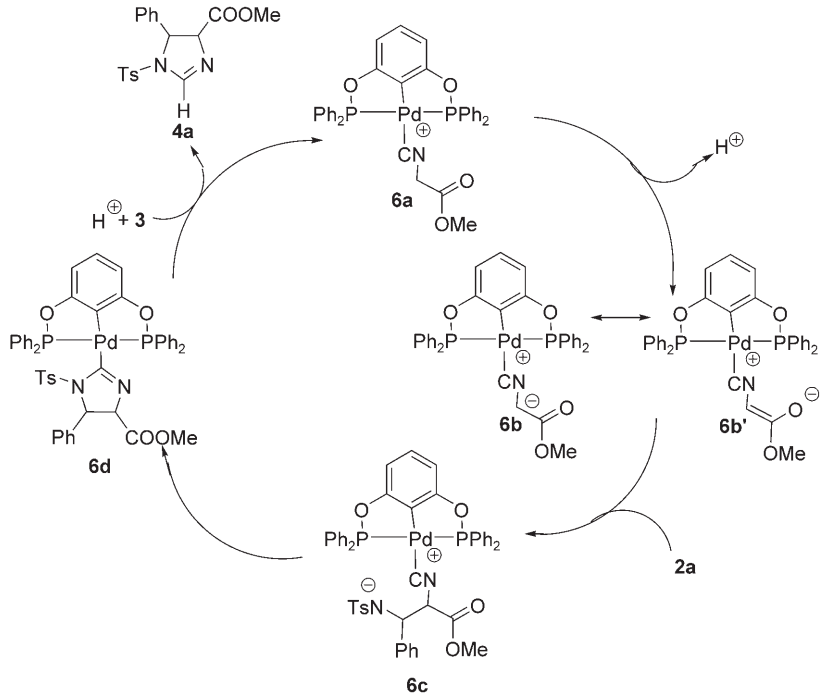
Considering the above studies a plausible catalytic cycle was constructed (Scheme 3). Accordingly, the catalytic reaction starts with deprotonation of **6a**. As we have pointed out, under catalytic conditions this proton dissociation takes place without added base. The deprotonated complex can be described by two resonance structures **6b** and the enolate form **6b′**. The next step is a nucleophilic attack of the electron-rich enolate moiety by the sulfonimine substrate to give **6c**. The condensation reaction is accomplished by a nucleophilic attack on the carbon atom of the isocyanate group, which is probably still coordinated to palladium affording complex **6d**. Protonation of the C2 carbon of the imidazoline ring leads decomplexation of the product (**4a**) and regeneration of the catalyst.

The stereoselectivity of the process is determined in the addition step of **2a** in the **6b**→**6c** process. Employing PCP complex **1a** as catalyst the *syn* selectivity is very high. Our studies indicate that using electron-supplying substituents, such as sulfur, nitrogen and selenium instead of phosphorus leads to an increase of the amount of the *anti* product (Table 1). Previous studies indicate that PCP complexes and pincer complexes[50,54] with sulfur or nitrogen atoms in the side arms (such as **1f** and **1g**) probably react by different mechanisms in aldol reactions. In addition, the difference in the geometric flexibility[55] of complexes **1a**–**g** may also influence the stereochemical outcome of the cyclization reactions.

It appears from the presented studies that application of PCP complexes **1a** and **b** leads to formation of *syn* isomers of **4a**–**g** according to the above mechanism (Scheme 3), while changing of the heteroatoms in side arms to selenium (**1d** and **e)**, sulfur (**1f**) or nitrogen (**1g**) may change the reaction mechanism shifting the stereoselectivity toward formation of the *anti* diastereomer. The highly different stereoselectivities obtained with palladium acetate (**1h**) and PCP complex **1a** also suggest a completely different mechanism for condensation of sulfonimines with isocyanoacetate **3**.

Conclusions

We have shown that condensation of sulfonimines with isocyanoacetate can be accomplished by using palladium pincer complexes in low (1 mol%) catalyst loadings. The reaction proceeds rapidly at 20 °C without addition of base or other additives. The stereoselectivity of the condensation reaction is strongly dependent on the applied pincer ligand. Using the electron-deficient and relatively bulky PCP complex **1a** the major product is the *syn* form, however the diastereoselectivity is reversed on applying SeCSe-based catalyst **1e**. The condensation reaction proceeds with a poor regioselectivity using common palladium salts[44,47] (such as **1h**), providing mainly the *anti* product. The synthetic scope of the condensation reaction using **1a** is relatively broad, as the reactivity and the selectivity of the reaction are not significantly dependent on the steric bulk of the sulfonimine component.



Scheme 3. Plausible catalytic cycle based on the mechanistic studies.

Our mechanistic studies show that the active intermediate of the reaction is an isocyanoacetate coordinated pincer complex (**6a**); and that the reaction proceeds without involvement of palladium(0) species. The pincer complex catalyst is very stable under the entire process and it can be recovered unchanged after the condensation reaction.

Experimental Section

All experiments were conducted under argon atmosphere employing standard manifold techniques. 1,3-Bis[(methylthio)methyl]benzene was prepared according to the procedure described by Furukawa and co-workers[56]. The palladium pincer complexes **1a**,[30] **1b**,[57] **1d**,[58] and **1g**[59] were prepared using published procedures. All solvents used in the reactions were freshly distilled prior to use. NMR spectra were recorded in $CDCl_3$ on Varian or Bruker spectrometers (^1H at 400 MHz, ^{13}C at 100.5 MHz, ^{31}P at 161.9 MHz, and ^{19}F at 376.3 MHz) using $CHCl_3$ ($\delta[^1H]=7.26$, $\delta[^{13}C]=77.0$), H_3PO_4 and α,α,α-trifluorotoluene as standards. Mass data (ESI) were obtained with a Bruker MicrOTOF spectrometer. For column chromatography, Merck silica gel 60 (230–400 mesh) was used.

Synthesis of Complex 1c

To methyl 4-bromo-3,5-dihydroxybenzoate (0.2 g, 0.81 mmol) in THF (5 mL), Ph_2PCl (0.36 g, 1.62 mmol) was added, followed by dropwise addition of NEt_3 (0.18 g, 1.78 mmol) at room temperature. This reaction mixture was stirred for 5 h followed by filtration through a thin pad of Celite, and evaporation to give the crude pro-ligand. The pro-ligand was dissolved in toluene (1 mL) and added to $Pd_2(dba)_3$ (0.37 g, 0.4 mmol) followed by stirring for 3 h at 75 °C. Purification using silica gel chromatography (CH_2Cl_2 as eluent) afforded 0.29 g (50%) of the bromide of complex **1c**. To this bromide complex (0.29 g, 0.4 mmol) in CH_2Cl_2 (20 mL) AgTFA (0.26 g, 1.2 mmol) was added and then the resulting mixture was stirred for 3 h at room temperature. A subsequent filtration through a pad of silica yielded **1c** as a white solid in quantitative yield (0.3 g). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (m, 8H), 7.52 (m, 12H), 7.38 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 166.3, 164.5 (t, 8.0 Hz), 133.7, 133.0, 132.7, 132.5, 132.3, 132.2, 131.8 (t, J = 8.7 Hz), 131.6, 131.5, 128.9 (t, J = 6.0 Hz), 108.5 (t, J = 8.0 Hz), 52.2; ^{19}F NMR (376.3 MHz, $CDCl_3$): δ = −74.03; ^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 145.5.

Synthesis of Complex 1e

This complex was synthesized following a procedure by Yao and co-workers[37] described for similar species. A round bottomed flask was charged with (5-methoxy-1,3-phenylene)bis(methylene)bis(phenylselane) (0.3 g, 0.68 mmol) and glacial acetic acid (0.7 mL). To this mixture $Pd(OAc)_2$ and a further portion of glacial acetic acid (0.7 mL) was added. This mixture was refluxed for 3 h. After evaporation the residue was purified by silica gel chromatography (CH_2Cl_2/MeOH, 9:1) affording 1e (0.37 g, 89%). Complex **1e** is formed as a mixture of two diastereomers.[37,58] The ^1H NMR data were determined from the purified mixture of the diastereomers. Spectral data for the major diastereomer – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (dd, J = 2.0 and 7.8 Hz, 4H), 7.37–7.27 (m, 6H), 6.49 (s, 2H), 4.47 (d, J = 13.7 Hz, 2H), 4.19 (d, J = 13.9 Hz, 2H), 3.67 (bs, 3H), 1.69 (bs, 3H); spectral data for minor diastereomer – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 7.2 Hz, 4H), 7.37–7.27 (m, 6H), 6.45 (s, 2H), 4.47 (d, J = 13.7 Hz, 2H), 4.09 (d, J = 14.5 Hz, 2H), 3.65 (bs, 3H), 1.80 (bs, 3H); ^{13}C NMR data for the mixture of two diastereomers – ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 176.9, 176.7, 156.8, 156.6, 151.2, 150.6, 142.1, 141.6, 133.0, 132.95, 130.0, 129.7, 129.4, 129.35, 129.2, 109.7, 109.6, 55.1, 55.0, 42.7, 42.2, 23.5, 23.3.

Synthesis of Complex 1f

A suspension of $PdCl_2$ (0.1 g, 0.56 mmol) in anhydrous acetonitrile (30 mL) was refluxed under argon atmosphere until $PdCl_2$ was completely dissolved. Thereafter, $AgBF_4$ (0.22 g, 1.2 mmol) was added to the reaction mixture. The resulting mixture was refluxed for 2 h and subsequently cooled to room temperature. The precipitate was filtered off and the filtrate was added to 1,3-bis[(methylthio)methyl]benzene (0.11 g, 0.56 mmol), and then this mixture was refluxed for 4 h under argon atmosphere. After filtration the solvent was removed and the crude product was purified by chromatography (CH_2Cl_2:acetonitrile, 9:1) affording 0.268 g (82%) of **1f**. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.04–6.94 (m, 3H), 4.44 (bs, 2H), 4.06 (bs, 2H), 2.78 (s, 6H), 2.40 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 149.5, 126, 123.4, 47.1, 22.7, 2.9.

General Procedure for the Palladium Pincer Complex-Catalyzed Aldol Reaction with *N*-Sulfonylimines 2a–g

A mixture of *N*-sulfonylimine **2a–g** (0.2 mmol), methyl isocyanoacetate **3** (0.02 g, 0.2 mmol) and the corresponding catalyst **1a–h** (0.002 mmol, 1 mol%) was stirred in THF (1.0 mL) at 20 °C for 2 h. After filtration through a thin pad of Celite, the solvent was removed to yield a pure *cis/trans* mixture of 2-imidazoline derivative **4a–g**. The *cis/trans* ratio was determined from crude ^1H NMR spectra.

Methyl 1-[(4-methylphenyl)sulfonyl]-5-phenyl-4,5-dihydro-1*H*-4-imidazolecarboxylate (4a): The NMR data obtained for **4a** are identical with the literature values.[44,47] Spectral data for the *syn* isomer (entry 1) – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 2.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.21–7.08 (m, 5H), 6.99 (d, J = 8.0 Hz, 2H), 5.21 (dd, J = 11.5 and 2.0 Hz, 1H), 5.14 (d, J = 11.5 Hz, 1H), 3.13 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 168.3, 151, 144.7, 134.7, 133.9, 129.7, 128.5, 128, 127.5, 127.2, 76.2, 63.5, 51.7, 21.5; HR-MS: m/z = 381.0867, calcd. for $[M + Na]^+$, $C_{18}H_{18}N_2NaO_4S$: 381.0879. Spectral data for the *anti* isomer (entry 5) – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 2.1 Hz, 1H), 7.45 (d, J = 8.3 Hz, 2H), 7.25–7.11 (m, 7H), 5.06 (d, J = 7.5 Hz, 1H), 4.64 (dd, J = 7.5 and 2.1 Hz, 1H), 3.68 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 169.7, 150, 144.7, 138, 134.3, 129.7, 128.7, 128.4, 127.2, 126.8, 79.8, 63.7, 52.8, 21.5; HR-MS: m/z = 381.0871, calcd. for $[M + Na]^+$; $C_{18}H_{18}N_2NaO_4S$: 381.0879.

Methyl 5-(4-fluorophenyl)-1-[(4-methylphenyl)sulfonyl]-4,5-dihydro-1*H*-4-imidazole-carboxylate (4b): The NMR data obtained for **4b** are identical with the literature values.[44] Spectral data for the *syn* isomer (entry 9) – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.75$ (d, $J = 2.0$ Hz, 1H), 7.41 (d, $J = 8.3$ Hz, 2H), 7.16 (d, $J = 8.3$ Hz, 2H), 7.0–6.95 (m, 2H), 6.79 (t, $J = 8.6$ Hz, 2H), 5.19 (dd, $J = 11.4$ and 2.0 Hz, 1H), 5.13 (d, $J = 11.4$ Hz, 1H), 3.18 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 168.2$, 163.8, 161.4, 150.9, 145, 134.6, 129.7, 129.4 (d, $J = 8.4$ Hz), 127.2, 115 (d, $J = 21.4$ Hz), 76, 62.7, 51.8, 21.5; HR-MS: $m/z = 399.0784$, calcd. for $[M + Na]^+$, $C_{18}H_{17}FN_2NaO_4S$: 399.0785.

Methyl 5-(4-methoxyphenyl)-1-[(4-methylphenyl)sulfonyl]-4,5-dihydro-1*H*-4-imidazole-carboxylate (4c): The NMR data obtained for **4c** are identical with the literature values.[44] Spectral data for the *syn* isomer (entry 11) – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.37$ (d, $J = 2.0$ Hz, 1H), 7.38 (d, $J = 8.2$ Hz, 2H), 7.11 (d, $J = 8.2$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 6.59 (d, $J = 8.7$ Hz, 2H) 5.15 (dd, $J = 11.3$ and 2.0 Hz, 1H), 5.10 (d, $J = 11.3$ Hz, 1H), 3.71 (s, 3H), 3.18 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 168.4$, 159.6, 150.8, 144.5, 134.8, 129.6, 128.8, 127.1, 125.7, 113.3, 75.9, 63.1, 55.1, 51.7, 21.4; HR-MS: $m/z = 411.0972$, calcd. for $[M + Na]^+$, $C_{19}H_{20}N_2NaO_5S$: 411.0985.

Methyl 1-[(4-methylphenyl)sulfonyl]-5-(2-naphthyl)-4,5-dihydro-1*H*-4-imidazolecarboxylate (4d): Spectral data for the *syn* isomer (entry 12) – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.83 (d, $J = 2.0$ Hz, 1H), 7.73–7.37 (m, 6H), 7.29 (d, $J =$ 8.3 Hz, 2H), 7.04 (dd, $J = 8.3$ and 2.0 Hz, 1H), 6.84 (d, $J =$ 8.3 Hz, 2H) 5.37 (d, $J = 11.3$ Hz, 1H), 5.31 (dd, $J = 11.3$ and 2.3 Hz, 1H), 3.03 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 168.3$, 150.8, 144.6, 134.8, 133, 132.5, 130.9, 129.4, 127.9, 127.8, 127.4, 127.3, 127, 126.4, 126.1, 124.7, 76.1, 63.7, 51.7, 21.2; HR-MS: $m/z = 431.1043$, calcd. $[M + Na]^+$; $C_{22}H_{20}N_2NaO_4S$: 431.1036.

Methyl 1-[(6-methyl-2-naphthyl)sulfonyl]-5-phenyl-4,5-dihydro-1*H*-4-imidazolecarboxylate (4e): Spectral data for the *syn* isomer (entry 13) – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.90 (d, $J = 2.0$ Hz, 1H), 7.87–7.36 (m, 6H), 7.14–7.00 (m, 1H), 6.99–6.92 (m, 4H), 5.22 (bs, 2H) 3.10 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 168.3$, 150.9, 139.8, 135.2, 133.5, 133.4, 129.9, 129.1, 129.0, 128.8, 128.6, 128.5, 127.9, 127.4, 126.7, 121.5, 76.1, 63.6, 51.6, 21.9; HR-MS: $m/z = 431.1027$, calcd. for $[M + Na]^+$, $C_{22}H_{20}N_2NaO_4S$: 431.1036.

Methyl 1-[(4-methylphenyl)sulfonyl]-5-(2-thienyl)-4,5-dihydro-1*H*-4-imidazolecarboxylate (4f): Spectral data for the *syn* isomer (entry 14) – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.69 (d, $J = 2.2$ Hz, 1H), 7.43 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J =$ 8.1 Hz, 2H), 7.09 (dd, $J = 4.6$ and 1.5 Hz, 1H), 6.75–6.70 (m, 2H) 5.49 (d, $J = 10.9$ Hz, 1H), 5.17 (dd, $J = 10.9$ and 2.2 Hz, 1H), 3.32 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 168$, 150.2, 144.7, 136.2, 134.8, 129.7, 127.6, 127, 126.5, 126.1, 75.9, 58.9, 52, 21.5; HR-MS: $m/z = 387.0435$, calcd. for $[M + Na]^+$, $C_{16}H_{16}N_2NaO_4S_2$: 387.0444.

Methyl 1-[(4-methylphenyl)sulfonyl]-5-[(*E*)-2-phenyl-1-ethenyl]-4,5-dihydro-1*H*-4-imidazolecarboxylate (4g): The NMR data obtained for **4g** are identical with the literature values.[44] Spectral data for the *syn* isomer (entry 15) – ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.66$ ($J =$ d, 2.0 Hz, 1H), 7.64 (d, $J = 8.2$ Hz, 2H), 7.30–7.23 (m, 2H), 7.15 (d, $J =$ 8.2 Hz, 2H), 7.12–7.06 (m, 3H), 6.52 (d, $J = 15.8$ Hz, 1H), 5.54 (dd, $J = 15.8$ and 9.5 Hz, 1H), 5.03 (dd, $J = 10.6$ and 2.0 Hz, 1H), 4.81 (dd, $J = 11.0$ and 9.5 Hz, 1H), 3.58 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 168.6$, 150.5, 144.9, 135.9, 135.5, 135.2, 129.8, 128.51, 128.48, 127.7, 126.6, 121.2, 74.6, 62.4, 52.2, 21.5; HR-MS: $m/z = 407.1036$, calcd. for $[M + Na]^+$, $C_{20}H_{20}N_2NaO_4S$: 407.1036.

General Procedure for the Preparation of Diamino Esters 5a and b from the Hydrolysis of 2-Imidazolines 4a and b

To the 2-imidazoline **4** (0.195 mmol) in $CHCl_3$ (2 mL) was added water (0.007 g, 0.39 mmol) followed by neutral aluminum oxide (0.20 g, 1.96 mmol). The mixture was stirred at room temperature for 16 h and thereafter, filtered and purified by chromatography using pentane/EtOAc (1:1) as eluent.

Methyl 2-formylamino-3-[(4-methylphenyl)sulfonyl]amino-3-phenylpropanoate (5a): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.17$ (bs, 1H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.10–7.20 (m, 5H), 7.01–6.96 (m, 2H), 6.64 (d, $J = 8.6$ Hz, 1H), 6.42 (d, $J =$ 6.6 Hz, 1H), 5.04 (dd, $J = 8.6$ and 3.3 Hz, 1H), 4.89 (dd, $J =$ 7.6 and 3.3 Hz, 1H), 3.70 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 169.6$, 161.8, 143.2, 137.2, 135.3, 129.2, 128.3, 127.9, 127, 126.5, 59.2, 55.9, 52.7, 21.3; HR-MS: $m/z = 399.0983$, calcd. for $[M + Na]^+$, $C_{18}H_{18}N_2NaO_5S$: 399.0985.

Methyl 3-(4-fluorophenyl)-2-formylamino-3-[(4-methylphenyl)sulfonyl]amino-propanoate (5b): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.21$ (s, 1H), 7.58 (d, $J = 8.2$ Hz, 2H), 6.74–6.15 (m, 6H), 6.76 (d, $J = 7.8$ Hz, 1H), 6.46 (d, $J =$ 8.8 Hz, 1H), 5.0 (dd, $J = 8.8$ and 3.5 Hz, 1H), 4.95 (dd, $J =$ 7.8 and 3.5 Hz, 1H), 3.68 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 169.4$, 161.8, 143.5, 137.3, 131.2, 129.4, 128.4, 128.3, 127.0, 115.2, 115.4, 58.8, 56.2, 53.0, 21.4; HR-MS: $m/z = 417.0890$, calcd. for $[M + Na]^+$, $C_{18}H_{19}FN_2NaO_5S$: 417.0891.

Stoichiometric Reaction with Pincer Complex 1a and Methyl Isocyanoacetate 3

Complex **1a** (0.008 g, 0.012 mmol) and methyl isocyanoacetate **3** (0.003 g, 0.036 mmol) were dissolved in $CDCl_3$ (0.5 mL). The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy at 25 °C. After consumption of **1a** the reaction mixture was evaporated. After re-dissolving the residue in $CDCl_3$ the NMR shift values for **6a** were found to be identical to the corresponding data recorded under the catalytic reaction. After addition of sulfonimine **2a** (0.003 g, 0.012 mmol) to the solution of **6a**, the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. Change of the NMR shifts clearly showed formation of **4a**, which was also the product of the condensation of **2a** and **3** catalyzed by **1a** (entry 1). After the stoichiometric reaction of **6a** and **2a** was completed, PPh_4Cl (0.005 g, 0.012 mmol) was added and formation of catalyst **1b** could be detected by ^{1}H and ^{31}P NMR spectroscopy. The identity of complex **1b** could be confirmed after purification of the reaction mixture by silica gel chromatography using CH_2Cl_2/pentane (2:1) as eluent.

Monitoring the Pincer-Complex Catalyzed Condensation of 3 with 2a

In an NMR tube **2a** (0.2 mmol) and the corresponding catalyst **1a** or **1e** (0.002 mmol, 1 mol%) were dissolved in THF-d_8 (0.5 mL) at 25 °C. Thereafter, methyl isocyanoacetate **3** (0.02 g, 0.2 mmol) in THF-d_8 (0.5 mL) was added and this reaction mixture was monitored by ^{1}H NMR spectroscopy (Figure 1).

Isolation of Complex 6a

Complex **1a** (0.05 g, 0.07 mmol) and methyl isocyanoacetate 3 (0.015 g, 0.146 mmol) were dissolved in $CDCl_3$ (1.5 mL). Formation of 6a could be observed in 10 min by ^{1}H, ^{31}P and ^{13}C NMR spectroscopy. Then, the $CDCl_3$ solution of **6a** was transferred to a vial followed by addition of diethyl ether (0.5 mL), and then this mixture was stored at 5 °C affording crystalline form of **6a** suitable for X-ray structure determination. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.82$–7.74 (m, 8H), 7.62–7.55 (m, 12H), 7.22 (t, $J = 8.2$ Hz, 1H), 6.85 (d, $J = 8.2$ Hz, 2H), 4.86 (bs, lb = 202 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): $\delta = 165$ (t, $J = 7$ Hz), 164.4, 160.75 (apparent q, $J = 33$ Hz), 133.3, 131.6 (t, $J = 8.4$ Hz), 130.9 (t, $J = 28.6$ Hz), 129.6 (t, $J = 6.4$ Hz), 107.7 (t, $J = 8.4$ Hz), 53.4, 47.2 (bs, lb = 34 Hz); ^{19}F NMR (376.3 MHz, $CDCl_3$): $\delta = -74.6$; ^{31}P NMR (161.9 MHz, $CDCl_3$): $\delta = 154.1$.

X-ray Analysis of Complex 6a

The diffraction data were measured at 100 K with an Oxford Diffraction Xcalibur-2 kappa-diffractometer with a Sapphire-III CCD-detector.[60] The structure was solved with direct methods using SHELXS-97[61] and refined with conventional full matrix least square methods using SHELXL-97.[61] File CCDC 645985 contains the supplementary crystallographic data for complex **6a** in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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