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Dinuclear pincer-palladium(II) complexes and their use as homogeneous or heterogeneous catalyst for the aldol reaction of methyl isocyanoacetate

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Abstract

Two new bimetallic Pd complexes have been synthesized and characterized and their catalytic activity checked for the aldol reaction of aldehydes with methyl isocyanoacetate. Each palladium atom is coordinated to an SCS-type ligand and the two pincer units are linked by a chiral spacer. The catalytic aldol reaction of methyl isocyanoacetate with aldehydes proceeds quickly but no significant diastereoselectivity and enantioselectivity is found. The comparison with a homologous mononuclear Pd complex shows no differences with the bimetallic compounds, concluding that there is no cooperativity between the metal centers. Two silica-supported catalysts prepared with a bimetallic compound show catalytic activity with very minor enantioselectivity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Aldol-condensation; Homogeneous catalysis; Heterogeneous catalysis; Bimetallic complex; Silica-supported catalyst

1. Introduction

The aldol-condensation of isocyanoacetates and aldehydes or ketones provides oxazolines, which can be hydrolyzed to yield β-hydroxy-α-amino acids. The latter are biologically interesting compounds and important building blocks in organic synthesis. The fact that this reaction can be catalyzed by metal complexes makes it a candidate for enantioselective synthesis [1]. The catalytic mechanism likely involves metal coordination to the isocyanide group, which enhances the acidity of the adjacent methylene group. This feature creates a challenge for chiral induction since one needs to induce asymmetry at a point three bonds removed from the metal center (Fig. 1).

Effective stereochemical induction has been achieved with gold-ferrocenyl bisphoshines that incorporate an amino functionality and planar chirality. However, gold complexes with other more prototypical chiral phosphine ligands such as (*S*,*S*)-chiraphos, (−)-DIOP and *p*-(+)-TolBINAP were ineffective at inducing significant enantioselectivity (see references in [2]).

Chiral PCP pincer-palladium and platinum complexes are effective catalysts for the aldol-condensation of methyl isocyanoacetate and aldehydes [3–4]. It has been proposed that the chiral pocket in these pincer ligands is deeper than those of other chiral phosphines, [4] which leads to a moderate to good enantioselectivity in the catalyzed aldol reaction of methyl isocyanoacetate with aldehydes. Similar chiral palladium complexes with NCN-type ligands have been explored for asymmetric catalytic reactions like aldol, Michael addition or Diels–Alder [5].

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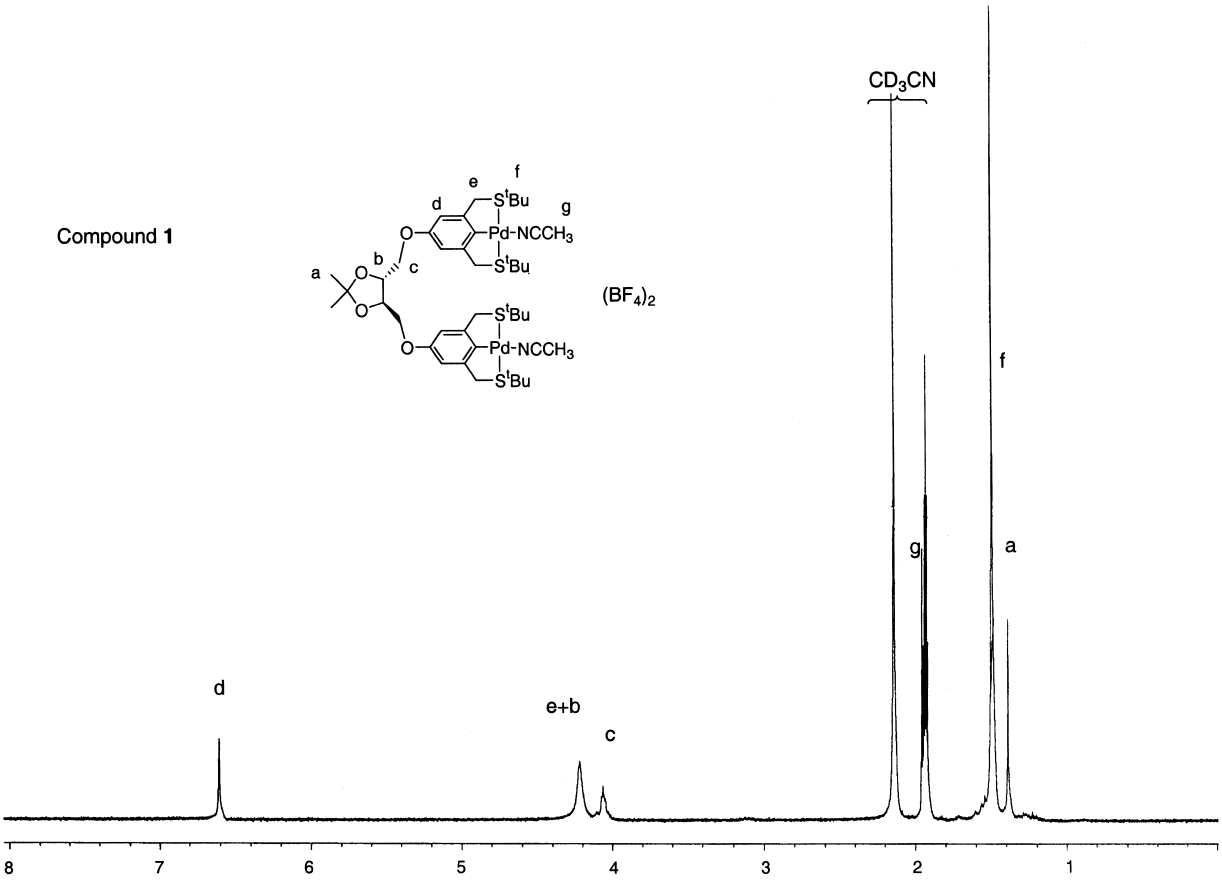
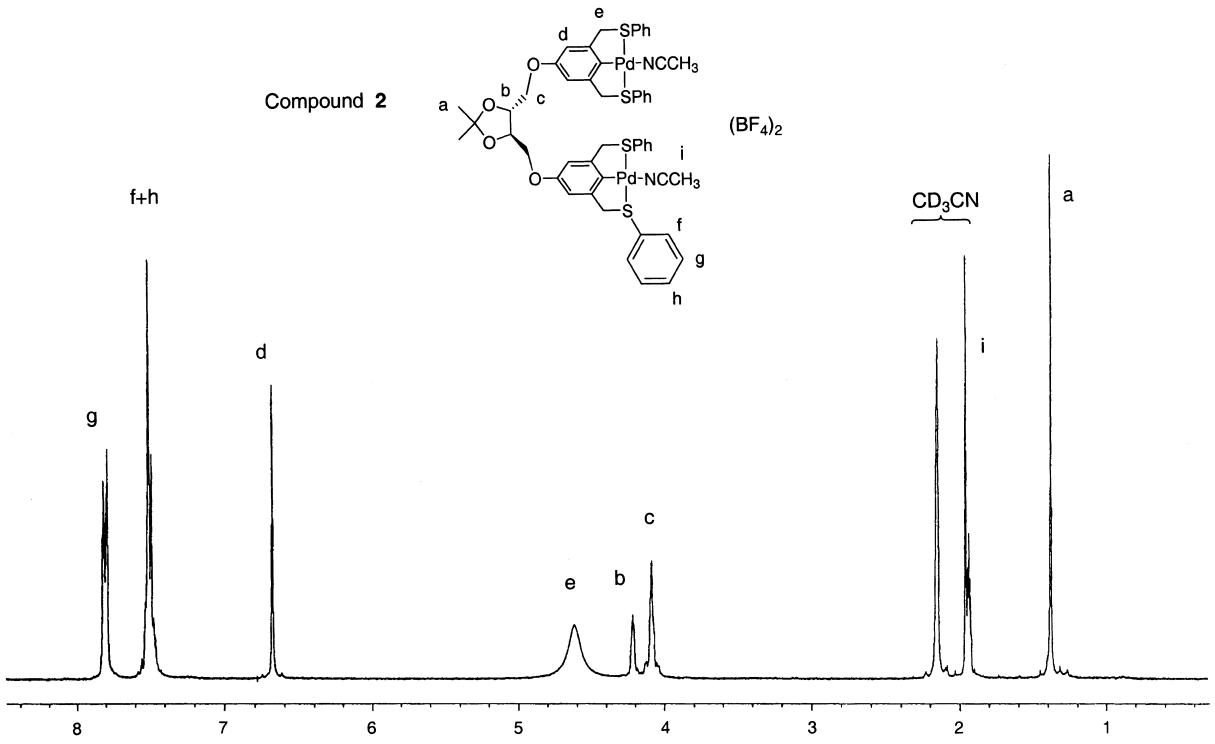
We have been interested in SCS-type palladium complexes due to their established versatility. In particular they have been shown to be useful in supramolecular chemistry and can be used to form self-assembled polymers and macrocycles [6,7], molecular recognition elements [8–12], and multimetallic dendrimers [13–17]. Their chemical versatility is further illustrated in a recent report wherein a SCS-type palladium complex was shown to be an efficient catalyst for the Heck reaction [18]. Due to the divalency of sulfur, the cavity about the metal center should be bigger in SCS-type compounds than in PCP- or NCN-type pincer complexes. As a result while these complexes may display broad substrate tolerances, it is a challenge to produce a complex of this class that exhibits stereoselective synthesis. In our quest to produce a effective asymmetric SCS-type catalyst we have taken the unconventional approach of placing the chiral centers remote to the catalytic site of a bimetallic complex. Hence, we have new bimetallic palladium(II) compounds **1**, **2** (Fig. 2) in which each palladium atom is coordinated to a SCS-type ligand, and the two pincer units are linked by a chiral spacer derived form *O*-isopropylidene-L-threitol. Our rational for pursuing this path is based upon the idea that once coordinated to the bimetallic system the carbonyl of the isocyanide intermediate may interact with the second palladium to produce a geometrically constrained metal–substrate complex. If this two center catalysis were to take place [19] the reaction would occur in a highly chiral pocket and should be enantioselective. We also report herein the mononuclear complex **3**, which was prepared for comparative experiments.





2. Experimental

2.1. Materials and methods

Anhydrous *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane, acetonitrile and diethyl ether were purchased from Aldrich in sure seal bottles. Other solvents were spectral grade (EM sciences or Mallinckrodt). Reagents were purchased from Aldrich and used without further purification. Air- and moisture-sensitive reactions were carried out in oven-dried glassware under an atmosphere of dry argon employing standard Schlenk techniques. The silica-supported catalysts were prepared using silica gel (40 μm, 60 Å, irregular, surface area 550 $m^2\,g^{-1}$) from Mallinckrodt Baker, dried in a oven at 120°C for 3 days. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Unity 300 or Varian VXR 500 spectrometers. All of the chemical shifts are reported in ppm relative to TMS (0 ppm) in proton spectra and to residual $CHCl_3$ (77 ppm), DMSO (39.5 ppm) or CH_3CN (118.7 ppm) in carbon spectra. Infrared spectra were recorded on a Nicolet Impact 410 FT-IR using polystyrene as a standard. High-resolution FAB mass spectrometry was performed on a VG analytical ZAB-E instrument using $CHCl_3$ as a solvent with 3-nitrobenzyl alcohol as the matrix. GC analyses were performed on a HP 6890 series equipped with a flame ionization detector and a chiral capillary column (20% permethylated, β-cyclodextrine capped).

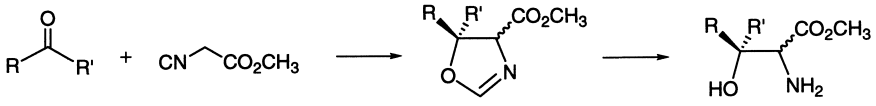


Fig. 1. Aldol reaction of methyl isocyanoacetate with Ketones to give amino acids.

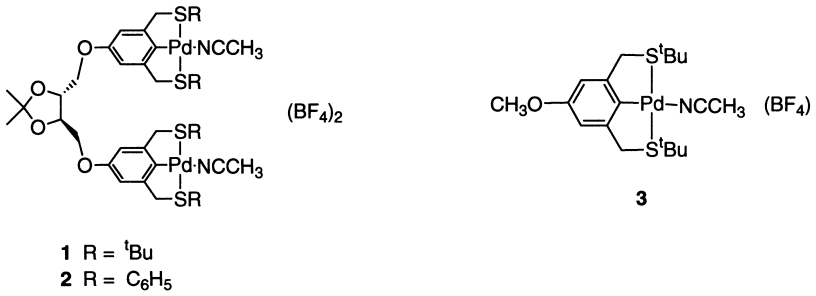


Fig. 2. Pincer complexes investigated for homogenous catalysis.

2.2. Synthesis of the ligands and complexes

2.2.1. Synthesis of (S,S)-(−)-1,4-di-O-[3,5-bis (methylcarboxyl)phenyl]-2,3-O-isopropylidene-L-threitol (4)

A total of 6.5 mmol (3.06 g) of commercially available (*S,S*)-(−)-1,4-di-*O*-tosyl-2,3-*O*-isopropylidene-L-threitol, 13 mmol (2.73 g) of methyl 5-hydroxyisophthalate and 15 mmol (2.07 g) of potassium carbonate and 60 ml of DMF were heated for 4 h at 120°C. After this time, 100 ml of water were added and extracted with 2 × 100 ml of hexane/ethyl acetate 2/1. The organic layers were combined and washed with 2 × 100 ml of water, dried over $MgSO_4$ and rotary-evaporated under vacuum to yield a yellow oil which was purified by column chromatography (silica gel hexane/ethyl acetate, 2/1) to yield **4** as a white solid in 66%. IR (NaCl, nujol, ν cm^{-1}): 1712 (C=O), 1593 (C–C), 1244 (C–O). ^{1}H NMR ($CDCl_3$, δ ppm): 1.52 (s, 6H), 3.94 (s, 12H), 4.30 (m, 4H), 4.43 (t, 2H), 7.79 (d, J = 1.5 Hz, 4H), 8.31 (t, J = 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, δ ppm): 27.22, 52.67, 69.05, 76.67, 110.93, 120.06, 123.78, 132.08, 158.68, 166.14.

2.2.2. Synthesis of (S,S)-(−)-1,4-di-O-[3,5-bis(hydroxymethyl)phenyl]-2,3-O-isopropylidene-L-threitol (5)

To a suspension of 18.5 mmol (703 mg) of $LiAlH_4$ in 50 ml of THF at 0°C is added dropwise a solution of **4** (5.3 mmol, 2.3 g) in 20 ml of THF. The reaction mixture is allowed to reach room temperature and stirred for 14 h. Water was added dropwise after cooling the reaction mixture at 0°C and the mixture was filtered to remove salts. The clear solution was extracted several times with ethyl acetate. After drying the organic layer was rotary-evaporated under vacuum to give **5** as a pure cloudy tacky oil. Yield: 80%. IR (NaCl, nujol, ν cm^{-1}): 3350 (O–H), 1594 (C-Car), 1287 (C–O), 1169, 1044 (br). ^{1}H NMR (d_6-DMSO, δ ppm): 1.40 (s, 6H), 4.11–4.29 (m, 6H), 4.44 (d, J = 5.8 Hz, 8H), 5.17 (t, J = 5.8 Hz), 6.77 (s, 4H), 6.86 (s, 2H). ^{13}C NMR (d_6-DMSO, δ ppm): 26.95, 62.81, 68.10, 76.04, 109.43, 110.62, 116.87, 143.98, 158.21.

2.2.3. Synthesis of (S,S)-(−)-1,4-di-O-[3,5-bis(bromomethyl)phenyl]-2,3-O-isopropylidene-L-threitol (6)

A solution of imidazole (15 mmol, 1.02 g) and **5** (2.35 mmol, 1.02 g) in 25 ml of acetonitrile and 70 ml of diethylether is cooled at 0°C. Then dibromotriphenylphosphorane (13 mmol, 5.56 g) is added slowly. After stirring for 4 h at 0°C, the white solids are removed by filtration through a short pad of silica gel. The solids are further washed with ether, the solution is evaporated to dryness and the residue is purified by column chromatography using dichloromethane as eluent. A total of 1.04 g of **6** is obtained as a white solid. Yield: 64%. ^{1}H NMR ($CDCl_3$, δ ppm): 1.53 (s, 6H), 4.22 (m 4H), 4.36 (t, 2H), 4.43 (s, 8H), 6.91 (d, J = 1.2 Hz, 4H), 7.04 (t, J = 1.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, δ ppm): 27.41, 33.10, 68.99, 77.00, 110.95, 115.65, 122.80, 140.13, 159.13.

2.2.4. Synthesis of (S,S)-(−)-1,4-di-O-[3,5-bis(tert-butylthiomethyl)phenyl]-2,3-O-isopropylidene-L-threitol (7)

To a solution of 3.83 mmol (153 mg) of NaOH in 50 ml of water is added a solution of **6** (0.697 mmol, 478 mg) in 40 ml of toluene and a catalytic amount (50 μl) of ADOGEN 464 (methyltrialkyl (C_8–C_{10})

ammonium chloride). Next, 2-methylpropanethiol (3.06 mmol, 0.34 ml) is added and the mixture is stirred vigorously with a stirbar and refluxed for 2 h under an argon atmosphere. After cooling to room temperature, the organic layer is extracted with H_2O and the toluene is removed by distillation. The resulting residue was purified by column chromatography (silica gel hexane/ethyl acetate, 25/1) to produce **7** as a colourless oil in 87% yield (440 mg). ^{1}H NMR ($CDCl_3$, δ ppm): 1.34 (s, 36H), 1.50 (s, 6H), 3.70 (s, 8H), 4.16 (m, 4H), 4.34 (m, 2H), 6.80 (s, 4H), 6.95 (s, 2H). ^{13}C NMR ($CDCl_3$, δ ppm): 27.01, 30.87, 33.29, 42.81, 68.45, 76.78, 110.31, 113.62, 122.44, 140.21, 158.62.

*2.2.5. Synthesis of (S,S)-(−)-1,4-di-O-[3,5-bis(phenylthiomethyl)phenyl]-2,3-O-isopropylidene-*L*-threitol (**8**)*

To a solution of 3.73 mmol of NaOH (149 mg) in 25 ml of water is added a solution of **6** (0.58 mmol, 400 mg) in 20 ml of toluene and a catalytic amount of ADOGEN 464. To this mixture 2.33 mmol (0.24 ml) of thiophenol is added followed by stirring and refluxed for 2 h under argon. The organic layer is then separated, extracted with water, dried, and rotary-evaporated in vacuum. The residue was chromatographed on silica gel using a hexane/ethyl acetate (10/1) eluent to give yield 91% (428 mg) of **8** as a colorless oil. ^{1}H NMR ($CDCl_3$, δ ppm): 1.47 (s, 6H), 3.99 (s, 8H), 4.04 (m, 4H), 4.24 (m, 2H), 6.73 (s, 2H), 6.83 (s, 1H), 7.14–7.27 (m, 20H). ^{13}C NMR ($CDCl_3$, δ ppm): 27.00, 38.91, 68.44, 76.67, 110.10, 113.80, 122.23, 126.38, 128.80, 129.90, 136.09, 139.23, 158.55.

2.2.6. Synthesis of the palladium complexes: general procedure

A solution of the ligands, **7** or **8** (0.28 mmol) and triethylamine (68 mg, 0.67 mmol) in 2 ml of acetonitrile was added dropwise to an acetonitrile solution of commercially available palladiumtetrakis(acetonitrile) bis(tetrafluoroborate) (297 mg, 0.67 mmol). The solution was then refluxed for 3 h, filtered through Celite, and evaporated to dryness. The tacky residue was then treated with water to give a yellow–orange solid precipitate. This solid was purified by dissolution in dichloromethane, filtration, and re-precipitated by the addition of diethyl ether. (**1**) Yield: 80%. ^{1}H NMR (CD_3CN, δ ppm): 1.39 (s, 6H), 1.51 (s, 36H), 1.96 (s, 6H), 4.01 (m, 4H), 4.22 (m, 10H), 6.61 (s, 4H). ^{13}C NMR (CD_3CN, δ ppm): 27.60, 31.01, 42.06, 54.04, 69.63, 77.61, 110.01, 111.26, 158.03 (C–Pd not detected). MS (FAB^+, 3-NBA matrix): 1103 $[M–BF_4]^+$. (**2**) Yield: 68%. ^{1}H NMR (CD_3CN, δ ppm): 1.38 (s, 6H), 1.96 (s, 6H), 4.09 (m, 4H), 4.22 (m, 2H), 4.62 (broad s, 8H), 6.68 (s, 4H), 7.46–7.53 (m, 12H), 7.79–7.82 (m, 8H). ^{13}C NMR (CD_3CN, δ ppm)): 27.64, 51.11, 69.80, 77.63, 111.13, 111.32, 118.68, 131.49, 132.15, 132.29, 132.89, 152.71, 158.43. MS (FAB^+, 3-NBA matrix): 1180 $[M–BF_4]^+$.

Compound **3** was prepared similarly by starting from 5-hydroxyisophthalic acid dimethyl ester. Firstly, it was protected with *tert*-butyldimethylsilyl chloride and the esters were reduced to the alcohols. Then, the hydroxyl groups were converted into bromo groups and coupled to 2-methylpropanethiol. Removal of the silyl part, alkylation with methyl iodide and complex formation gave **3**.

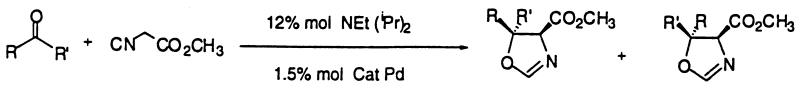
2.3. Procedure for the preparation of the silica-supported catalysts

The vicinal diols of **1** are prepared by the hydrolysis of the ketals. To a solution of 75 mg of **1** in 20 ml of acetone, is added 50 mg of NaCl in 5 ml of HCl 1 N dropwise. The mixture is stirred at room temperature for 3 h, the solid was filtered off, washed with water and then dried under vacuum to yield 55 mg (90%) of **9**. IR (NaCl, nujol, ν cm^{-1}): 3356 (OH). ^{1}H NMR (CD_3CN, δ ppm): 1.52 (s, 36H), 3.99 (m, 6H), 4.05 (m, 8H), 6.48 (s, 4H).

Si1: 50 mg of silica gel and 2 ml of thionyl chloride were refluxed under argon for 1 h. After this time the unreacted thionyl chloride is distilled off, 5 ml of dry toluene is added to the flask and subsequently 50 mg of complex **9** dissolved in 2 ml of toluene is added. The suspension is stirred overnight at room temperature and filtered through a 4–8 μm glass-frit and the yellow silica gel is washed sequentially with hexanes, water (until the washes were pH = 5) and then acetone to dissolve unreacted palladium complex. The functionalized silica gel was dried under high vacuum.

Si2: a flame dried flask is charged with 20 mg of silica gel **Si1** and kept under vacuum. In a glove box, 5 ml of dry hexanes and 0.5 ml of dodecyltrichlorosilane

Table 1



Entry	R	R′	Catalyst	Time (h)	Conversion (%)	*Trans*/*cis*	ee (*trans*) (%)
1	^{i}Pr	H	**1** + **base**	4	>95	95/5	<1
2	^{i}Pr	H	**2** + **base**	2	>95	95/5	<1
3	^{i}Pr	H	**3** + **base**	4	>95	95/5	–
4	^{i}Pr	H	**Base**	64	66	95/5	–
5	C_6H_5	H	**1** + **base**	4	>95	55/45	<1
6	C_6H_5	H	**2** + **base**	2	>95	55/45	<1
7	C_6H_5	H	**3** + **base**	16	>95	57/43	–
8	C_2H_5	CH_3	**1** + **base**	60	0	–	–
9	C_2H_5	CH_3	**2** + **base**	60	0	–	–
10	^{i}Pr	H	**Si1** + **base**	20	80	95/5	2
11	^{i}Pr	H	**Si2** + **base**	18	73	95/5	3

are added. The mixture is stirred overnight at room temperature, filtered off and washed several times with hexanes and methanol. The silica was dried under high vacuum. IR (KBr pellet, ν cm^{-1}): 2969–2850 (CH).

2.4. General procedure for the catalytic aldol reaction

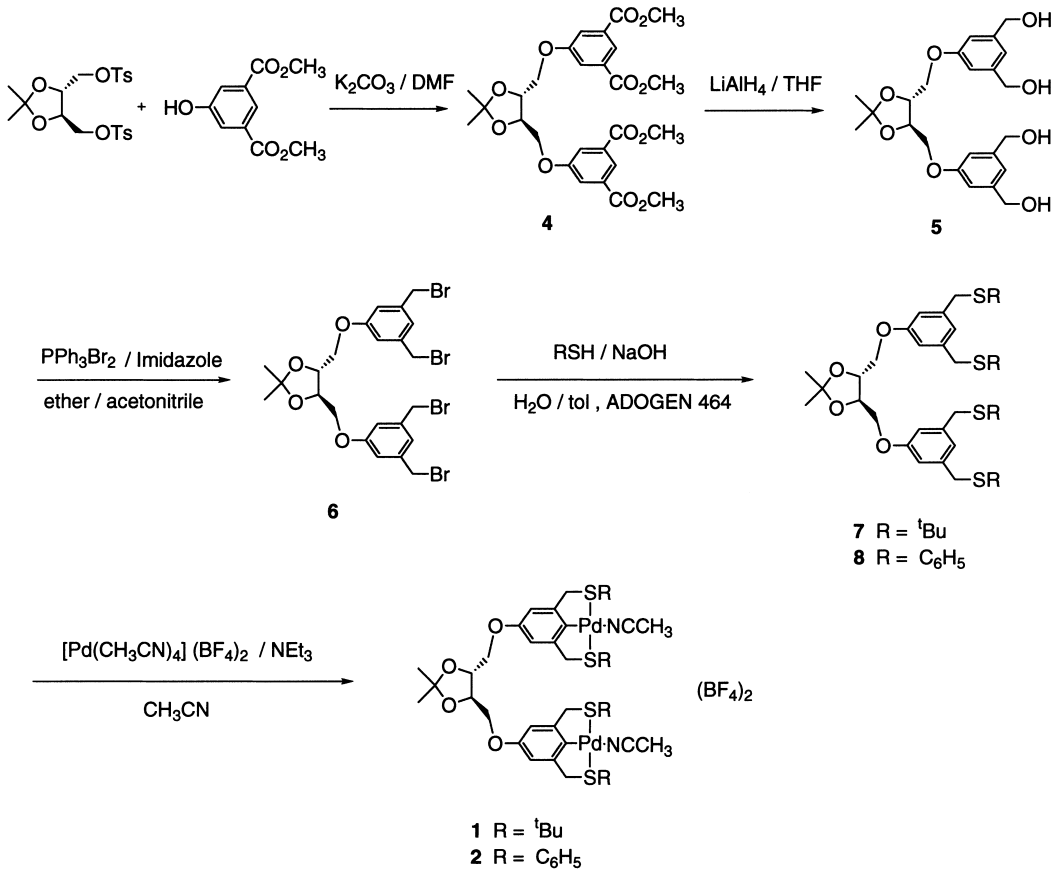
To a suspension of the palladium complex **1**, **2** or **3** (1.5 mol%) (or 10 mg of the silica-supported catalysts **Si1** and **Si2**) in 5 ml of dry dichloromethane was added 0.5 mmol (46 μl) of methyl isocyanoacetate. Then, 0.5 mmol of the appropriate aldehyde and 65 μmol (12 mol%) of *N*,*N*-diisopropylethylamine are added sequentially. The mixture was stirred at room temperature and monitored by GC and/or ^{1}H NMR until completion (see Table 1). For the solution catalysis the solvent is evaporated using a vacuum line, dry diethyl ether is added and the soluble material was filtered through celite. For the silica-supported catalysis the reaction mixture is filtered through a glass-frit. An aliquot of filtrate is used for the GC analysis. The *cis*/*trans* ratio is determined by integrating the methyl singlet of the ester in the ^{1}H NMR spectrum.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of the dinuclear complexes is shown in Scheme 1.

A particular challenge in this synthesis is to maintain an intact ketal moiety throughout the various reactions. The initial step is a Williamson-type alkylation that proceeds best in *N*,*N*-dimethylformamide, which provides shorter reaction times and better yields than ketone solvents. The reduction of the ester to alcohol using lithium aluminum hydride was highly effective since the tetrareduction proceeds in high overall isolated yield (80%, ca. 95% per ester). To convert the hydroxyl groups to bromides we investigated several reaction conditions in an effort to avoid the deprotection/decomposition of the ketal group. It proved difficult to obtain a good yield of the tetrahalogenated compound. Eventually, using dibromotriphenylphosphorane and imidazole as reagents we were able to produce **6** in 64% isolated yield. The tetrathioether was obtained almost quantitatively by reaction with the corresponding sulfide under phase transfer catalysis conditions. Finally, the palladium complexes were made by reaction of the ligand with tetrakis(acetonitrile)palladium(II) bis(tetrafluoroborate) and triethylamine to prevent ketal deprotection. The palladium complexes are stable to air and our characterization suggests that the structure about the metal center similar to that described by Shaw [20] and Bergbreiter [18] in which the *tert*-butyl or phenyl groups attached to sulfur are disposed with a C_2 symmetry with respect to the palladium coordination plane. The benzylic protons appear as a broad singlet in the NMR spectra because of dynamic conformation in solution due to palladocycle puckering or/and sulfur inversion [21].



Scheme 1.

3.2. Catalytic aldol reaction

The catalytic activity of our palladium complexes were tested for the reaction of methyl isocyanoacetate with aldehydes (isobutyraldehyde and benzaldehyde) and ethyl methyl ketone. The results are gathered in Table 1.

The reactions with aldehydes proceed efficiently in dichloromethane at room temperature with all complexes. The conversion is complete after 4 h in all cases. From the results of Table 1, wherein lower conversions and longer times are obtained for the uncatalyzed reaction (entry 4), it is clear that both the dinuclear compounds (**1**, **2**) and the mononuclear (**3**) provide considerable acceleration in the reaction (entries 1–3). The *cis*/*trans* ratio is not affected by the structure of the catalyst and only depends on the structure of the aldehyde (entries 1–3 and 5–7). Qualitative comparisons reveal that the activity of the mononuclear complex is similar to the dinuclear complexes in terms of rate and selectivity. The later feature suggests that bimetallic catalysts **1** and **2** function in a similar fashion to the mononuclear **3**. Consistent with this finding, all of the solution phase reactions provide no enantioselectivity in the aldol products. As expected, when the catalytic centers are behaving independently the remote chiral centers are ineffective at inducing a predominance of one chiral conformation about the active site.

3.3. Study of the catalysis with palladium complexes immobilized on silica gel

Our solution studies suggested that a more rigid catalyst system wherein the palladium centers were constrained to be proximate to each other might be

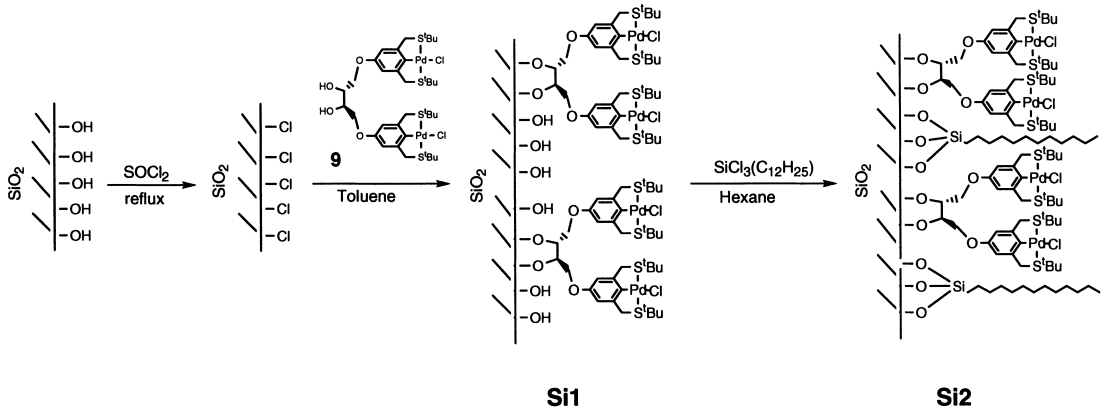


Fig. 3. Formation of silica-supported catalysts.

more effective. We considered the potential methods for restricting the conformation of the catalyst such as macrocycle formation and greater rigidity. However, our initial attempts at producing macrocycles wherein the two different α,α′-dibromo-*meta*-xylyl groups are bridged proved synthetically inaccessible. This led us to pursue an alternative approach wherein the monolayers were organized and constrained in thin films or at an interface. In this regard we were encouraged by the dramatic enhancements in selectivity reported by Milstein for catalysts immobilized in Langmuir–Blodgett films [22]. We reasoned that it we could restrict the conformational freedom similarly by covalent attachment to a substrate, then we could produce a more selective catalyst. We envisioned three specific features of this immobilization, which could be advantageous. First by anchoring the catalyst to a surface we are effectively constraining the molecule to only adopt conformations that place all of the substituents on one side of a plane. Secondly, we considered that if a dense packing of catalytic complexes or isolated complexes in an array of inert filler molecules could further constrain the catalysts' conformational space. Thirdly, the heterogeneous nature of the reaction should facilitate the separation of the catalyst from the reaction medium by filtration.

We chose to produce functionalized silica gel as shown in Fig. 3. To activate the surface we subjected the gel to an excess of thionyl chloride. This procedure produces electrophilic Si–Cl groups at the surface that have been shown to react with alcohol groups to form functionalized surfaces [23,24]. This method was particularly conducive to our objective since our catalysts contain a protected vicinal diol that could be easily unveiled by the hydrolysis of the ketal functionality. We expect that this diol functionality can chelate to the surface of the silica and thereby produce a robust supported catalyst. We further considered that this approach involving reaction with an electrophilic and likely positively charged surface, would give the most selective reaction with the nucleophilic diol. This is particularly important to minimize the possibility of catalyst attachment through the cationic palladium centers.

We prepared two surface immobilized catalysts. The first material (**Si1**), is formed by treatment of the activated silica gel with the binuclear pincer complex containing a vicinal diol. As indicated in Fig. 2 a portion of the surface hydroxyl groups are replaced with a dinuclear palladium compound. In a second step of the procedure for producing **Si1** the silica gel is hydrolyzed to transform all of the Si–Cl groups back to Si–OH groups. This procedure produces a material, (**Si1**), that is light yellow thereby indicating that the intact catalyst has been attached to the support. The heterogeneous nature and low surface coverage of the catalyst precluded a detailed characterization of this material to prove the structures shown in Fig. 2. However, the catalytic activity vide infra confirms that an intact and active catalyst is present. A second heterogeneous catalyst was produced by subsequently reacting the free surface hydroxyl groups of **Si1** with

trichlorododecylsilane. This procedure was performed in an attempt to fill in the voids between isolated catalytic species. It is well know in self-assembled monolayers [25] that at low coverages the species tend to bend over and interact with the surface. At high coverages the surface species "stand up straight" and can even produce a two-dimensional crystalline phase on a planar surface. In the case at hand, silica gel presents a very rough surface, which will preclude the formation of a highly organized monolayer. Nevertheless, we considered that surrounding the catalytic sites with a dense packed layer of dodecyl groups should force them to organize normal to the surface as illustrated in Fig. 2 and thereby further restrict the conformational options available to the catalyst in **Si2**.

The results of the catalysis with functionalized silica gels **Si1** and **Si2** are gathered in Table 1 (entries 10 and 11). The selectivity *cis*/*trans* observed is the same as those obtained in solution. As expected the reaction is slower due to the smaller amount of metal present. The catalyst appears to remain intact throughout the reaction and can be easily separated from the mixture by filtration. We are cautiously optimistic that surface immobilization produces a more enantioselective catalyst. The measured values for the enantiomeric excesses are very small (<2–3%), but reproducible. The effectiveness of **Si1** and **Si2** are similar.

In summary we have reported the synthesis of two new bimetallic palladium complexes with a SCS-type pincer ligand. The systems were designed to contain remote chirality in an effort to produce a stereo induction to be realized when both metal centers interact with the substrate. While our attempts to introduce significant enantioselective catalysis were unsuccessful, we were able to produce the first examples of heterogeneous pincer complexes. The supported catalysts function similar to the solution species and our results indicate that supported catalysts may offer greater selectivity. Aside from the results presented herein these chiral bimetallic complexes are attractive groups for the formation of new supramolecular metallo-polymers.

Acknowledgements

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