Stereoselective formation of a single-stranded helicate: Structure of a bis(palladium-allyl)quaterpyridine complex and its use in catalytic enantioselective allylic substitution

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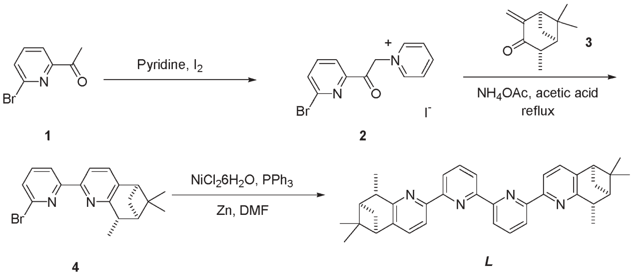
Chiral C_2-symmetric quaterpyridine L reacts with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ to form a chiral single-stranded helical binuclear palladium complex of formula $[Pd_2(\eta^3\text{-}C_3H_5)_2(L)]^{2+}$; the complex can efficiently catalyze allylic substitution of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate with enantioselectivity up to 85%.

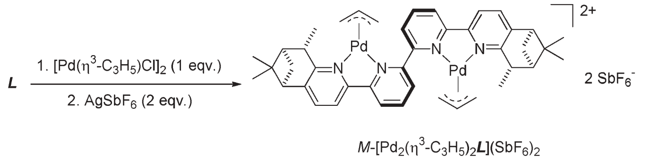
Helicates are polymetallic helical complexes that contain one or more ligand strands.[1] Much effort has been devoted to understanding the interplay between the metal ions and the ligands in helicates and to their application in the selective preparation of complicated organized chemical architectures.[1a,b] Most studies have focused on double- or triple-stranded helicates.[2] Single-stranded helicates,[3] like their double or triple stranded counterparts, are inherently chiral, though all reported single-stranded helicates are racemic in nature.[4] Although one of the potential application of chiral helicates is in asymmetric catalysis, to the best of our knowledge, there has been no report on the use of helicates as chiral or achiral catalysts for organic tranformation. Herein, we report the novel stereoselective formation of a chiral single-stranded binuclear palladium 2,2′:6′,2″:6″,2‴-quaterpyridine helicate and its application in asymmetric allylic substitution.

The chiral quaterpyridine ligand **L** was synthesized by a three-step procedure starting from 2-acetyl-6-bromopyridine **1** (Scheme 1). The key intermediate, bipyridine **4** was obtained in good yield *via* Kröhnke condensation of pyridinium iodide **2** and α,β-unsaturated ketone **3**, which was prepared from (*R*)-(−)-isopinocampheol.[5] **L** was readily prepared by Ni(0)-mediated homocoupling of **4** and the structure was assigned unambiguously by conventional spectroscopic methods.†



Scheme 1

The self-assembly of the Pd helicate was achieved by stirring a solution of **L** in CH_2Cl_2 with $[Pd(\eta^3\text{-}C_3H_5)_2Cl]_2$ dimer in 1 : 1 ratio (Scheme 2). An air-stable yellow solid was isolated as SbF_6 salts in good yield (62%). The stoichiometry of the complex, 2 : 1 metal to ligand, was confirmed as satisfactory by elemental analysis (also confirmed by ESI-MS). Single crystals suitable for X-ray analysis were obtained from the slow evaporation of CH_2Cl_2 and $CHCl_3$ mixture.‡ As shown in Fig. 1, the complex $[Pd_2(\eta^3\text{-}C_3H_5)_2\mathbf{L}](SbF_6)_2$ adopts a bimetallic monohelical structure with each Pd atom in a distorted square-planar geometry. The Pd atom is 0.68 Å above the bipyridyl plane and the bite angle ∠N(1)–Pd(1)–N(2) is 79.9(2)°. The dihedral angle of the interpyridyl bonds between the two bipyridine moieties is 43.4(1)°. The small helical twist of the bridging ligand results in a short Pd......Pd distance (3.934(2) Å). The complex cation lies on a twofold axis which bisects the C(1)–C(1*) bond. The solid state structure revealed the stereoselective formation of M-helix with



Scheme 2

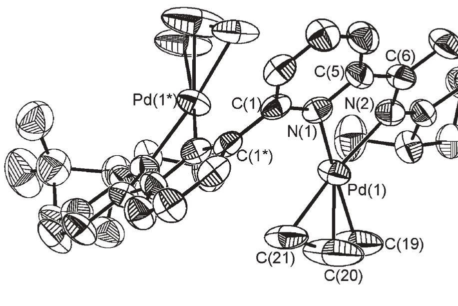


Fig. 1 ORTEP[7] drawing of $[Pd_2(\eta^3\text{-}C_3H_5)_2(\mathbf{L})][SbF_6]_2$ showing a partial atom labeling scheme. The thermal ellipsoids are drawn at the 30% probability level. The H atoms, SbF_6^- counterions and $CHCl_3$ molecules are omitted for clarity. Symmetry operation used to generate equivalent atoms is (1 − *x*, 1 − *y*, *z*).

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(R)-isopinocampheol auxiliary. Bond length and bond angles of the complex are not significantly different from the mononuclear N,N-bidentate palladium π-allyl complexes.[6]

The solution stability and integrity of the helicate are of main concern for the homogenous catalyst. The solution behaviour of the helicate was studied by its NMR spectra. The major diastereomer of the Pd(II) helicate exhibits C_2-symmetry in ^{1}H and ^{13}C NMR spectra (THF-d_8), which reveal distinctive patterns for the 2,2′-bipyridyl moieties, with a total of 5 proton signals (4 doublets and 1 triplet) from δ 7.8–8.8 ppm and 10 carbon signals from δ 115–170 ppm of aromatic resonances. The π-allyl resonances are positioned at δ 2.6, 3.6 and 5.7 ppm and δ 65, 68 and 129 ppm of the ^{1}H and ^{13}C NMR spectra respectively.

The helical structure of the Pd helicate is retained in solution as examined by CD experiments (Fig. 2). It shows two strong absorptions (Cotton effect) at 330–360 nm in both THF and CH_2Cl_2 solutions which are more intense than the free ligand. In contrast, in CH_3CN, disordered random conformations seem to dominate.

The potential of the chiral single-stranded Pd helicate in asymmetric catalysis was first tested in the enantioselective allylic substitution of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate. Preliminary results were promising (Table 1, entry 1). Under the standard procedure,[8] significant rate enhancements and better ee were achieved by changing KOAc to LiOAc as base. The best result was obtained in THF; the allylic substitution was completed within 5 h, affording (R)-product with 85% ee in quantitative yield (Table 1, entry 5). Interestingly, the solvent again plays a crucial role in the reaction. The ee dropped to 75 and 5% when the reactions were run in CH_2Cl_2 and CH_3CN respectively (Table 1, entries 3 and 9). Though the mechanism of the reaction in our system is still not clear, the change of ee observed in different solvents seems to show some correlation with the helical chirality of the single-stranded Pd complex.

In summary, we have demonstrated a novel chiral single-stranded bis(allyl) dipalladium complex with new chiral quaterpyridine **L**, which is an effective catalyst for asymmetric allylic substitution with excellent yield and ee up to 85%. This represents the first application of a single-stranded helicate in asymmetric catalysis. The X-ray crystal structure and the CD analyses of the complexes confirmed the stability and integrity of the helicate both in solid and solution state. Further experiment is underway to examine the importance of helical chirality in this reaction and the use of helical chirality in other asymmetric catalytic reaction.

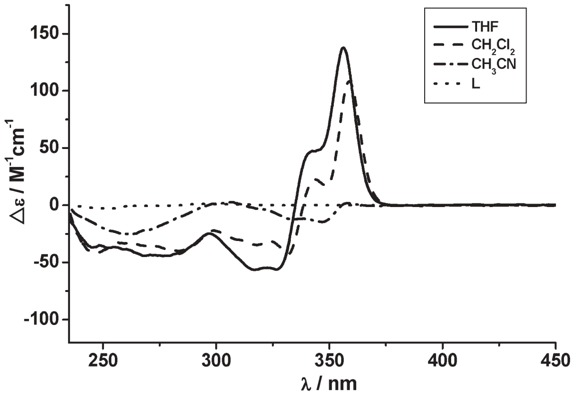
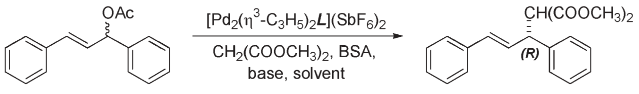


Fig. 2 Circular dichroism spectra of **L** in CH_2Cl_2 and the complex $[Pd_2(\eta^3\text{-}C_3H_5)_2(\mathbf{L})][SbF_6]_2$ in various solvents were recorded at rt.

Table 1 Allylic substitution of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate using the complex, $[Pd_2(\eta^3\text{-}C_3H_5)_2(\mathbf{L})](SbF_6)_2$[a]



Entry	Solvent	Base	Time/h[b]	Yield (%)[c]	ee (%)[d,e]
1	CH_2Cl_2	KOAc	30	>99	55
2	CH_2Cl_2	NaOAc	15	>99	57
3	CH_2Cl_2	LiOAc	9	>99	75
4	THF	KOAc	30	>99	57
5	THF	LiOAc	5	>99	85
6	Toluene	KOAc	30	52	54
7	Toluene	LiOAc	12	>99	81
8	CH_3CN	KOAc	30	48	4
9	CH_3CN	LiOAc	15	>99	5

[a] Reactions conditions: $[Pd_2(\eta^3\text{-}C_3H_5)_2(\mathbf{L})](SbF_6)_2$ (0.037 equiv.), 1,3-diphenylprop-2-enyl acetate (1.0 equiv.), $CH_2(COOCH_3)_2$ (3.0 equiv.), BSA (3.0 equiv.) and a catalytic amount of base at 50 °C. [b] Reactions were monitored by TLC analysis. [c] Isolated yield. [d] Determined by HPLC with Chiralcel OD column. [e] Absolute configuration was determined by comparison with literature data.[9]

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Notes and references

† ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.70 (s, 6H), 1.37 (d, 2H, J = 9.9 Hz), 1.45 (s, 6H), 1.51 (d, 6H, J = 7.2 Hz), 2.18–2.23 (m, 2H), 2.57–2.64 (m, 2H), 2.85 (t, 2H, J = 5.7 Hz), 3.26–3.33 (m, 2H), 7.38 (d, 2H, J = 7.8 Hz), 7.97 (t, 2H, J = 7.8 Hz), 8.34 (d, 2H, J = 7.5 Hz), 8.51 (d, 2H, J = 8.1 Hz), 8.64 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$): δ 18.31, 20.99, 26.42, 28.71, 39.01, 41.55, 46.98, 47.34, 117.94, 120.39, 120.68, 133.50, 137.57, 142.15, 153.61, 155.52, 156.13, 160.22; anal. calcd. for $C_{36}H_{38}N_4$: C, 82.01; H, 7.21; N, 10.63. Found: C, 80.76; H, 7.11; N, 10.20%; IR (KBr, ν_{max}/cm^{-1}): 2929.88s, 1557.60vs, 1432.25vs, 816.58s, 790.78s; ESI-MS m/z: 527 (M$^+$ + 1).

‡ Selected crystal data for $[Pd_2(\eta^3\text{-}C_3H_5)_2(\mathbf{L})][SbF_6]_2$: $Pd_2Sb_2N_4C_{44}H_{50}Cl_6F_{12}$, M = 1531.90, orthorhombic, primitive, space group $P2_12_12$, a = 16.179(13), b = 15.653(12), c = 10.866(8) Å, V = 2751.7(37) Å^3, D_{calc} = 1.849 g cm^{-3}, Z = 2, λ(Mo-Kα) = 0.7107 Å, μ(Mo-Kα) = 19.80 cm^{-1}. 32129 reflections measured, 6341 unique, R = 0.074 (all data) and R_w = 0.047 (all data). Flack parameter = 0.00(4). CCDC 610954. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608481h

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