results from our experiment in so far as the dissociation to H and NO is lower in energy than a cyclic transition state for the direct reaction of **1** to **2** on the singlet as well as the triplet potential-energy surface.

What can we say about the geometry of **2**? The calculations[8] reveal a typical O–H bond length for isonitroso hydrogen (**2**) ($d = 0.984$ Å; *trans*-HONO: $d(\mathrm{OH}) = 0.98$ Å). The N–O bond length (1.323 Å) is very long and lies between a double (*trans*-HONO: $d(\mathrm{N{=}O}) = 1.20$ Å) and a single bond (*trans*-HONO: $d(\mathrm{N{-}O}) = 1.46$ Å). These structural data of isonitroso hydrogen (**2**) express the character of a nitrene. In other words: This molecule should be regarded as "hydroxy nitrene".

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Palladium-Mediated Dynamic Kinetic Resolution: Stereoselective Synthesis of Vicinal Diamines**

Gregory R. Cook,* P. Sathya Shanker, and Ketheeswaran Pararajasingham

The palladium-catalyzed allylic substitution reaction has emerged as a powerful methodology in organic synthesis.[1] The stereoselective variants have focussed primarily on enantioselective processes which utilize chiral ligands and achiral substrates.[2] When chiral substrates are used, the configuration of the allylic leaving group controls the configuration of the product through a double inversion mechanism. In contrast, little attention has been paid to diastereoselectivity in the nucleophilic addition to π-allyl palladium complexes with an adjacent stereocenter,[2–4] and a study of the asymmetric induction by acyclic substrates in intermolecular reactions has not been previously reported.[5] For stereocenters outside of the allyl framework to control the addition of a nucleophile, the palladium complex must be able to undergo rapid allyl inversion (Figure 1). Our interest in dynamic transition metal complexes[6] has led us to probe the diastereoselectivity in such a system, and our results are reported herein. This process constitutes an example of palladium-mediated dynamic kinetic resolution.[3b, 7]

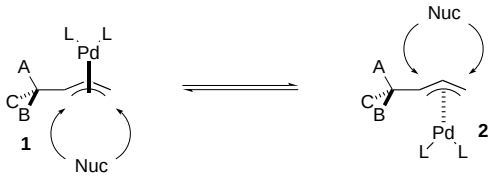

Figure 1. Selectivity issues in dynamic diastereomeric complexes (see text for details).

Several issues of regio- and stereoselectivity need to be addressed when considering the allylic substitution reaction. The palladium-catalyzed reaction usually favors addition at the less substituted terminus. For complexes **1** and **2** (Figure 1), this mode of reactivity must be reversed in order to generate a new stereocenter. While many allyl complexes are configurationally stable, rapid equilibration is common, and this usually results in loss of allyl stereochemistry. For selectivity in a diastereoselective process, such as described here, the rate of π-allyl inversion relative to the rate of nucleophilic addition is important (Figure 1).

We have shown[6] that chiral 5-vinyloxazolidinones **3** derived from α-amino acids react with palladium(0) catalysts to afford 5-vinyloxazolines **6** by oxidative insertion, loss of CO_2, and subsequent cyclization at the amide oxygen atom (Scheme 1). The oxazoline products were obtained with

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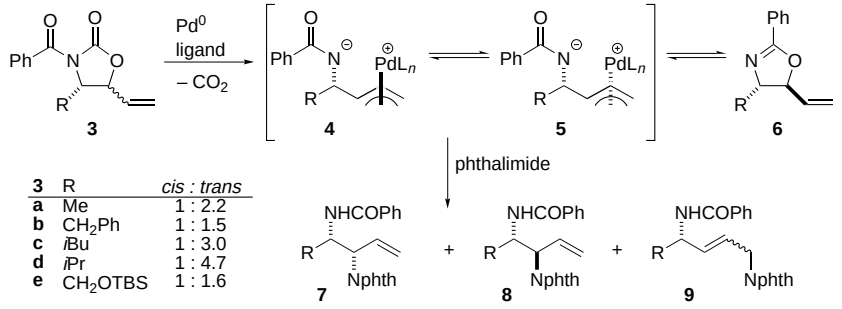

Scheme 1. Palladium(0)-mediated synthesis of chiral vicinal diamines from chiral oxazolidinones. phth = phthalimidyl, TBS = *tert*-butyldimethylsilyl.

enhanced diastereomeric ratios, which suggested that the intermediate π-allyl palladium complexes **4** and **5** were undergoing rapid equilibration. Oxazolines **6** were also ionized by the palladium catalyst and were in equilibrium with **4** and **5**, thus giving rise to thermodynamically controlled product ratios. We reasoned that these dynamic intermediates could be trapped with external nitrogen-containing nucleophiles under kinetic control to afford chiral diamines **7** and/or **8**.

The oxazolidinones **3a**–**e** were prepared as mixtures of diastereomers from α-amino acids as previously described.[6] The allylic substitution with phthalimide as the nucleophile was investigated, and the results are described in Table 1.

Table 1. Dynamic kinetic resolution of chiral 5-vinyloxazolidinones **3**.[a]

Entry	Substrate	Ligand	Reaction time [h]	1,2:1,4 (**7**+**8**:**9**)	*syn*:*anti* (**7**:**8**)	Yield [%] (combined)
1	**3a**	dppe	20	5.5:1	97:3	97
2	**3a**	dppp	2	6.0:1	95:5	92
3	**3a**	dppb	1	6.0:1	94:6	98
4	**3a**	dppf	0.5	7.0:1	93:7	97
5	**3b**	dppp	1.5	1.6:1	97:3	98
6	**3c**	dppp	2	3.2:1	> 99:1	91
7	**3d**	dppp	2	7.9:1	> 99:1	99
8	**3e**	dppb	5	3.6:1	> 99:1	98

[a] All reactions were run at 25 °C with 1 mol % of the Pd dimer catalyst and 4 mol % of the ligand in THF. Isomer ratios were determined by NMR spectroscopy.

Treatment of **3a** with 1 mol % of [{(π-C_3H_5)-PdCl}$_2$], 4 mol % of bis(diphenylphosphanyl)ethane (dppe), and phthalimide with catalytic amounts of potassium phthalimide in THF at room temperature afforded, after 20 hours, a mixture of *syn*- and *anti*-1,2-diamine isomers (**7a**:**8a** = 97:3) and the 1,4-diamine regioisomer **9a**. We were delighted to find the ratio of regioisomers was 5.5:1 favoring the 1,2-isomer. The use of 1,1′-bis(diphenylphosphanyl)propane (dppp) or 1,1′-bis(diphenylphosphanyl)butane (dppb) as ligand led to decreased diastereoselectivity with the same level of regioselectivity (Table 1, entries 2 and 3). The rate of these reactions was notably faster, affording complete conversion in two hours or less as compared to dppe. The ligand 1,1′-bis(diphenylphosphanyl)ferrocene (dppf) gave the best regioselectivity and the lowest diastereoselectivity for substrate **3a** (entry 4).

As the size of the substituent at the stereogenic center was increased, selectivities also increased. Under the standard conditions with dppp as ligand, the phenylalanine-derived substrate **3b** led to diamine products with good diastereoselectivity (97:3); however, the regioselectivity dropped significantly (entry 5). Changing from a benzyl group to an isobutyl group (**3c**) to an isopropyl group (**3d**) resulted in higher regio- and diastereoselectivity (entries 5–7). In the latter two cases, the *syn* product was the only diastereomer detectable by ^{1}H NMR spectroscopy. The serine-derived substrate also afforded excellent diastereoselectivity. The yield of purified product in all cases was greater than 90 %.

The influence of chiral ligands in the allylic amination was explored with binaphthyl-based ligands. The results of this study are summarized in Table 2. Although the selectivities for reactions of the methyl substrate **3a** were lower with chiral ligands than with achiral ligands, an interesting trend for positive (matched) and negative influences (mismatched) was observed (entries 1 and 2). While the (*R*)-BINAP ligand was matched for regioselectivity (3:1 versus 1.5:1), the (*S*)-BINAP ligand was matched for diastereoselectivity (96:4 versus 88:12). The diastereoselectivity was controlled by the substrate, not the ligand, as the *syn* product was obtained in both

Table 2. Influence of chiral ligands on regio- and diastereoselectivity.[a]

Entry	Substrate	Ligand	Reaction time [min]	1,2:1,4 (**7**+**8**:**9**)	*syn*:*anti* (**7**:**8**)	Yield [%] 1,2[b]	1,4[b]	combined[c]
1	**3a**	(*R*)-BINAP	30	3:1	88:12	71	25	99
2	**3a**	(*S*)-BINAP	30	1.5:1	96:4	–[d]	–[d]	99
3	**3b**	(*R*)-BINAP	20	20:1	> 99:1	90	5	98
4	**3b**	(*S*)-BINAP	30	3:1	98:2	–[d]	–[d]	99
5	**3b**	(*R*)-Tol-BINAP	10	19:1	> 99:1	91	5	98
6	**3b**	(*S*)-Tol-BINAP	30	3.5:1	98:2	–[d]	–[d]	99
7	**3c**	(*R*)-BINAP	20	3.4:1	> 99:1	77	22	99
8	**3c**	(*S*)-BINAP	20	2.2:1	> 99:1	–[d]	–[d]	99
9	**3d**	(*R*)-BINAP	20	10:1	> 99:1	81	9	89
10	**3d**	(*S*)-BINAP	20	10:1	> 99:1	–[d]	–[d]	89
11	**3e**	(*R*)-Tol-BINAP	20	6.5:1	> 99:1	81	12	94
12	**3e**	(*S*)-Tol-BINAP	20	1:1	> 99:1	–[d]	–[d]	92

[a] All reactions were run at 25 °C with 1 mol % of the Pd dimer catalyst and 4 mol % of the ligand in THF. Isomer ratios were determined by NMR spectroscopy. [b] Determined after chromatographic separation. [c] Determined before chromatographic separation. [d] Not determined. BINAP = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl; Tol-BINAP = 2,2′-bis(di-*p*-tolylphosphanyl)-1,1′-binaphthyl.

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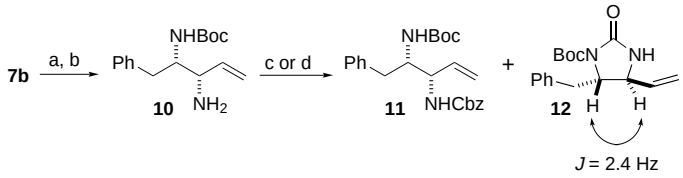
cases. With all other substrates, the regioselectivity was also matched with the *R* ligand, and selectivities in general were better than with achiral ligands. The benzyl substrate **3b** afforded the best result, with (*R*)-BINAP giving rise to excellent regioselectivity (20:1): **7b** was formed as a single diastereomer detectable by ^{1}H NMR spectroscopy (entry 3). (*R*)-Tol-BINAP performed equally well in the amination reaction (entry 5). Interestingly, the *S* ligand gave lower regio- and diastereoselectivity for substrate **3b**.

While a steric effect on the selectivities was also observed when the chiral ligands were utilized (compare entries 7 and 9), the benzyl derivative **3b** did not follow the same trend as in the previous experiments with achiral ligands. The role of the benzyl group in obtaining high regioselectivity is not clear. Electronic effects in the interaction of the aromatic system with the BINAP ligand may be attenuating the steric effects that are present; however, the nature of this interaction is not obvious. With oxazolidinones **3b**–**e**, the substrate control of diastereoselectivity was essentially complete, affording *syn*-diamine derivatives as the only detectable 1,2-products.

Elaboration of the diamine derivative **7b** was readily accomplished (Scheme 2). Protection with the *tert*-butoxycarbonyl (Boc) group followed by selective hydrazinolysis to remove the phthalimide and benzoyl groups afforded the



Scheme 2. a) Boc_2O, DMAP; b) H_2NNH_2/H_2O, MeOH, 89% (over two steps); c) CbzCl, Et_3N, 14% (**11**) and 38% (**12**); d) CbzCl, NaOH (aq.), 85% (only **11**). Cbz = benzyloxycarbonyl, DMAP = 4-dimethylaminopyridine.

monoprotected diamine **10** in high yield. Initial attempts to protect the free amine with a carbobenzoxy group by reaction with CBzCl and triethylamine resulted in a low yield of **11** accompanied by the cyclic urea **12**. The yield of **11** could be increased to 85% with no formation of **12** by utilizing aqueous NaOH as the base. The relative configuration of **7b** was established by comparison of the proton coupling constants of **12** with known cyclic ureas.[8] The stereochemical assignment was further confirmed by independent preparation of the minor diastereomer **8b**.[9]

We have established a new palladium-mediated process for dynamic kinetic resolution which affords a facile method for the preparation of enantio- and diastereomerically pure *syn*-1,2-diamines. Vicinal diamines have well-documented utility as chiral auxiliaries and chiral ligands.[10] In addition, unusual diamino acids are emerging as important components of new protease inhibitors.[11]

Experimental Section

7b (representative procedure): Oxazolidinone **3b** (345 mg, 1.123 mmol), (*R*)-BINAP (28 mg, 0.094 mmol), phthalimide (182 mg, 1.236 mmol), potassium phthalimide (21 mg, 0.112 mmol), and $[\{\pi\text{-}C_3H_5)PdCl\}_2]$ (4.1 mg, 0.011 mmol) were placed in a test tube that was sealed with a rubber septum. The tube was evacuated and flushed with nitrogen three times. THF (4 mL) was added, and the reaction was stirred at ambient temperature for 20 min (until thin-layer chromatography (TLC) indicated consumption of the starting material). The solution was filtered through a small plug of silica gel, washed with ethyl acetate/dichloromethane (1/1, 10 mL), and concentrated to afford **7b** (single diastereomer) and **9b** (*cis*:*trans* = 1:1) as a 20:1 mixture (452 mg, 1.101 mmol, 98% combined yield). The regioisomers were readily separated on silica gel (200–400 mesh, 20 → 40% (v/v) ethyl acetate in hexanes) to afford pure **7b** (414 mg, 1.008 mmol) in 90% yield and **9b** (24 mg, 0.058 mmol, *cis*:*trans* = 1:1) in 5% yield.

7b: White solid, m.p. 126–128 °C; $[\alpha]_D^{25} = -55.8^\circ$ ($c = 2.18$, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.16$ (d, $J = 8.6$ Hz, 1H), 7.74–7.91 (m, 6H), 7.41–7.52 (m, 3H), 7.12–7.24 (m, 5H), 6.08 (ddd, $J = 16.4$, 10.5, 5.6 Hz, 1H), 5.0–5.22 (m, 4H), 2.96 (dd, $J = 14.2$, 6.1 Hz, 1H), 2.79 (dd, $J = 14.2$, 7.5 Hz, 1H); ^{13}C NMR (100.5 MHz, CD Cl_3): $\delta = 169.0$, 166.9, 137.0, 134.6, 134.4, 132.6, 131.6, 131.5, 129.3, 128.7, 128.6, 127.1, 126.8, 123.8, 118.0, 55.7, 52.6, 38.7; IR (neat): $\tilde{\nu} = 3352$, 1771, 1709, 1647, 1532, 1356 cm^{-1}; elemental analysis calcd: C 76.08, H 5.40, N 6.82; found: C 76.05, H 5.42, N 7.00.

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Novel Infinite Three-Dimensional Networks with Highly Conjugated Polynitrile Ligands: Syntheses, Crystal Structures, and Magnetic Properties of $[Cu\{C[C(CN)_2]_3\}(H_2O)_2]_n$ and $[Cu\{C[C(CN)_2]_3\}(en)]_n$ ($en = NH_2CH_2CH_2NH_2$)

Smaïl Triki, Jean Sala Pala,* Marc Decoster, Philippe Molinié, and Loïc Toupet

Many cyanocarbon and cyanocarbanion derivatives are distinguished by unusual physical properties that are attractive for potential applications, for example as organic metals and molecular ferromagnets.[1] As recently noted[2] solids that contain transition metal cations and polycyano units can be grossly divided into two categories: one in which the ligand is σ bonded to the cation, and one which contains stacked anionic organic systems, which are usually obtained from electron acceptors such as tetracyanoethylene (TCNE) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ). As part of our investigations into the first class we described recently the intriguing three-dimensional polymeric structure of the silver complex with the cyanocarbon ligand $\{[C(CN)_2C(CN)]_2N\}^-$.[3] We were thus interested in novel polymeric solids based on transition metal cations and such highly conjugated polynitrile anions that present a plurality of cyano groups juxtaposed in such a way that they cannot all coordinate to the same metal cation.

Our objective is to examine the ability of these organic ligands to create a range of two- or three-dimensional polymeric metallacycle networks. This study will therefore contribute to the understanding of properties of molecular systems, such as binary metal/TCNX (X = E, Q) compounds, which present fascinating properties,[1, 2] but for which the detailed structures are as yet unknown. We focus here on the use of the symmetrical 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide anion $[C\{C(CN)_2\}_3]^{2-}$ (**1**) with copper(II) ions; several studies of the chemical and physical properties of this anion have been reported,[4] but as far as we know no crystal structure of solids containing a transition metal cation σ bonded to this ligand has been reported. We report here the syntheses, crystal structures, and preliminary magnetic properties of compounds **2** and **3**, which have unprecedented three-dimensional polymeric networks.

$[\{Cu\{C[C(CN)_2]_3\}(H_2O)_2\}_n]$ **2**

$[\{Cu\{C[C(CN)_2]_3\}(en)\}_n]$ **3**
(en = ethylenediamine = $NH_2CH_2CH_2NH_2$)

X-ray analyses[5] of **2** and **3** show they have polymeric structures based on networks of octahedrally coordinated Cu^{II} centers linked by $[C\{C(CN)_2\}_3]^{2-}$ ligands (Figures 1a and 2a). In both structures, each $[C\{C(CN)_2\}_3]^{2-}$ ligand acts in a polybridging mode with four of its six nitrogen atoms bound to four different copper cations. Each metal cation in complex **2** has a pseudo-octahedral *trans*-CuO_2N_4 environment with four nitrogen atoms from four different organic ligands and two oxygen atoms from the water molecules (Figure 1a). While the bond angles around the Cu atom only deviate moderately from 90°, the Cu–N bond lengths of the perfectly planar CuN1N2N1N2 unit are significantly different (1.978(5) and 2.051(5) Å). The most important distortion of the octahedron corresponds to an elongation along the pseudo fourfold axis with a Cu–O bond length of 2.191(5) Å.

The molecular unit from which the molecular arrangement can be easily described is the 12-membered metallacycle **A** (Cu ··· Cu 7.026 Å) (Figure 1a). These metallacycles are connected to each other through Cu atoms to give the first monodimensional chain **Ch1** (**A-A-A-A**), which runs along the [−110] direction (Figure 1b). Such infinite units form eclipsed stacks parallel to the [100] direction and separated by 8.108 Å. Furthermore, each metallacycle **A** is laterally connected to two metallacycles **A′** by two organic ligands; this affords a second monodimensional chain **Ch2** (**A′-A′-A′-A′**) that is crystallographically equivalent to **Ch1** chain but runs orthogonally (along the [110] direction). This generates the three-dimensional structure represented in Figure 1b.

In complex **3** each Cu atom presents a CuN_4N_2 distorted octahedral coordination with four nitrogen atoms from four organic ligand and two nitrogen atoms from a classical bidentate en ligand. The Cu^{II} coordination octahedron is much more severely distorted here than in complex **2**. Whilst the CuN2N5N7N8 fragment is planar within ±0.03 Å and presents almost equivalent Cu–N bond lengths (1.977(4) and 1.980(4) Å from the polynitrile ligand; 2.008(4) and 2.013(5) Å from the en ligand), the two *trans*-CuN1 and CuN6 bonds are much longer (2.437(5) and 2.449(5) Å, respectively). The extended molecular structure of complex **3** represented in Figure 2b is very similar to that of complex **2** described above; the main difference lies in the absence of the monodimensional chain observed in **2**; the fictive chain is destroyed by the coordination of the bidentate en ligand. This leads to linear successions along the [101] direction of metallacycles fairly similar to those described in complex **2**;

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