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A P-O Chelation with Palladium: Toward Understanding of the Stereochemistry of An Optically Active Sulfinyl-substituted Phosphine with Five Stereogenic Centres

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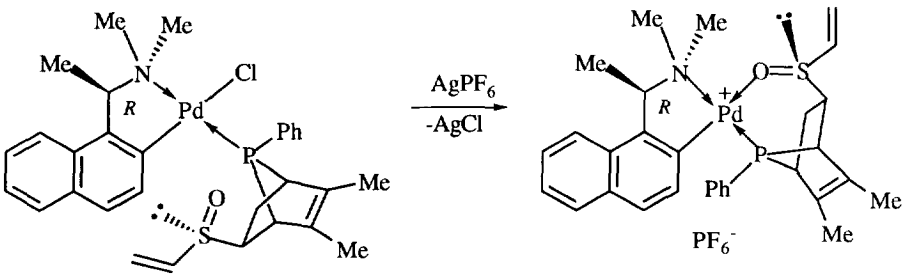
Abstract: The enantiomerically pure Diels-Alder product (-)-**1** was subjected to chloride abstraction to give the title complex (-)-**2**. The absolute stereochemistry of the optically active ligand, 2,3-dimethyl-7-phenyl-5-vinylsulfinyl-7-phosphabicyclo[2.2.1]hept-2-ene **3**, in (-)-**2** was confirmed by crystallographic analysis. **3** formed a six-membered P-O chelate with the [(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]palladium(II) unit.

Stereochemical and conformational rigidity has always been regarded as one of the main criteria in chiral ligand design for an asymmetric metal-based system.[1,2] The asymmetric induction or discriminating ability of a chiral auxiliary depends strongly on its conformational stability on a metal, which is, in turn, controlled stereoelectronically by metal-ligand interactions[3,4] and rigidity of the ligand skeletal framework.[5,6] At present, research endeavours in developing chiral ligands by introducing chirality on rigid building blocks are receiving considerable attention.[7-9] Since P-chiral ligands are by far the more accessible asymmetric auxiliaries,[10,11] our research group has undertaken the preparation of rigid and enantiomerically pure phosphabicyclo[2.2.1]heptenes incorporating different functionalities.[12,13]

Recently, we reported (-)-**1** as a cycloaddition product from a palladium-promoted asymmetric Diels-Alder synthesis.[13] (*R*)-*N,N*-dimethyl-1-(1-naphthyl)ethylamine was used as a chiral auxiliary in the palladium promoter. The metal-activated 1-phenyl-2,3-dimethylphosphole (DMPP) reacted with divinyl sulfoxide to give the enantiomerically pure ligand **3** (Figure 2), 2,3-dimethyl-7-phenyl-5-vinylsulfinyl-7-phosphabicyclo[2.2.1]hept-2-ene, in the complex (-)-**1**. As proposed in our brief communication,[13] solvent-activation was involved to give the chloro-product, (-)-**1**. In order to investigate the stereochemistry implicated in the product formation, and to examine the coordination chemistry displayed by **3**, it is necessary to remove the chloro ligating group.

(-)-**1** was subjected to chloride abstraction by treatment with $AgPF_6$ in acetone (Scheme 1). The crude product was obtained after the removal of AgCl. The pure (-)-**2** [m.p. 192-194 °C; $[\alpha]_D^{27}$ = -214 (c 0.50, CH_2Cl_2)][14] was crystallized as clear yellow prisms from a benzene/acetone mixture with the slow introduction of hexane. The solid-state structural characterization of (-)-**2** was carried out by X-ray crystallographic analysis: $C_{30}H_{35}F_6NOP_2PdS$, M_w = 739.99, orthorhombic, space group $P2_12_12_1$, a = 11.508(7) Å, b = 14.910(7) Å, c = 18.566(7) Å, V = 3186(3) Å^3, Z = 4, D_c = 1.543 g cm^{-3}, μ = 8.09 cm^{-1}, $F(000)$ = 1504. The reflections



(-)-**1** (-)-**2**

Scheme 1

were collected using MoKα radiation on a Marresearch Image Plate system. The crystal was positioned 75 mm from the image plate and 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program[15a] to obtain independent reflections. The structure was solved by direct methods using SHELXS-86[15b] and refined (all non-hydrogen atoms anisotropically, hydrogen atoms isotropically in fixed positions) with all data on F^2 to wR2 of 0.1002 using SHELXL-93.[15c] The final conventional R for the 4816 data with $F_o > 2\sigma(F_o)$ was 0.0363. The absolute stereochemistry of (-)-**2** (Figure 1)[16] was determined by the use of the (*R*)-*N*,*N*-dimethyl-1-(1-naphthyl)ethylamine unit as an internal reference for configuration assignment.

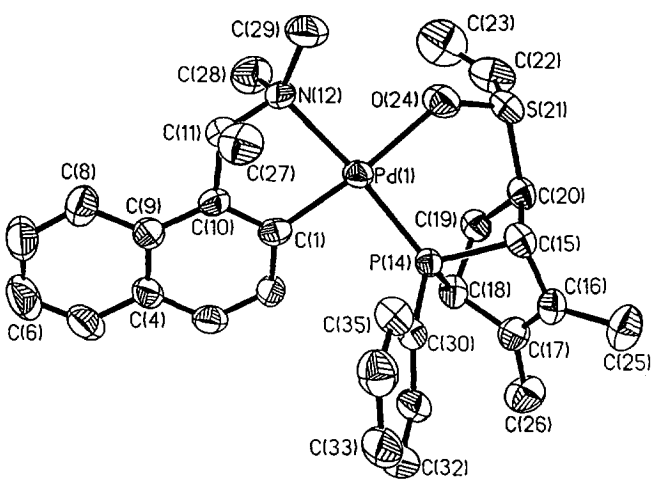


Figure 1. ORTEP drawing of (-)-**2**

Absolute configurations of the five stereogenic centres in (-)-**2** were found to be the same as in (-)-**1**. In agreement with the stereoelectronic effects postulated in a previous paper,[17] the phenylphosphino group and the sulfinyl-oxygen are coordinated *trans* to the nitrogen and the aryl carbon of the optically active amine respectively. Thus, a P-O six-membered ring was formed by **3** on chelation. The observed Pd-P an P-N bond distances are very close to the values reported for (-)-**1**. It is noteworthy that the Pd-C bond distance of 1.969 Å is shorter than that observed in (*S*) , (*S*) - [1 - [1 - (dimethylamino) ethyl] - 2 - naphthalenyl - *C* , *N*] [[2-(methylsulfinyl)ethyl]diphenylphosphine-*O*,*P*]palladium(II) **4** (Figure 3; Pd-C for **4a**: 2.009 Å and **4b**: 1.981 Å). Conversely, the Pd-O distance at 2.160 Å was found to be significantly longer when compared with that in **4** (Pd-O, av. 2.125 Å). These can be rationalised in terms of the weaker Pd-O interaction in (-)-**2** due to the electronic effects and appreciable conformational strains experienced by the rigid phosphabicyclo[2.2.1]heptene

ring of **3** in forming the six-membered ring. The rationale is also evinced by the elongation of P(14)-C(15) following the O-coordination of the sulfinyl moiety. Another feature that is worth mentioning is the evident change in S-O bond distance. In agreement with literature findings,[18a] the O-coordination brings about a reduction in π character in S=O. However, the observed value of 1.495 Å in **2** falls closer to the range for S-bonded sulfoxides (1.46-1.49 Å) than that reported for the O-bonded moieties (1.52-1.56 Å).[18]

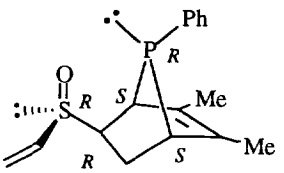


Figure 2. Ligand **3**

As expected, the orthometallated (*R*) amine in (-)-**2** was found to adopt the δ conformation[19] (Figure 1). A close examination on the structure revealed a twisted 'boat' conformation for the six-membered P-O ring formed by **3**. Crystallographic analysis also confirmed that the complex only presents as one single conformer in the solid state, unlike **4** wherein two conformers **4a** and **4b** coexist in a unit cell. The slight twist displayed by the P-O ring in (-)-**2** is due to the rigidity of the ligand framework and apparently the inflexibilty does, *inter alia*, confine (-)-**2** to adopt only one conformation.

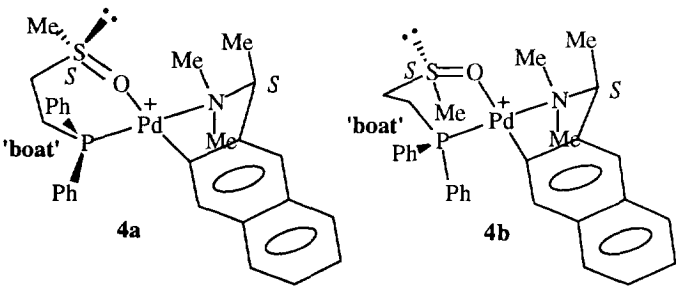


Figure 3. The two conformers in **4**: **4a** and **4b**.

Currently, in order to define the stereochemistry of our palladium systems, we are investigating the participation of the non-bonded lone pairs in the S=O group. The P-O chelation in (-)-**2** is in accord with the intermediacy of a transition state assembly with both of the diene and dienophile coordinated to the palladium centre during the course of the Diels-Alder reaction. Similar to its analogous complex, **4**, the sulfoxide group binds to the metal through its oxygen and coordinates *trans* to the electron withdrawing aryl carbon. However, it is noteworthy that six-membered chelate rings usually adopt the sterically favourable 'chair' conformation. The unexpected boat conformation observed for the P-O rings in both (-)-**2** and **4** is probably due to the stereoelectronic consequence arising from the interactions of the S=O lone pairs. Further investigation on the coordination chemistry of chelating sulfoxide ligand is currently in progress.

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16. Selected bond length (Å), bond angles (°) and torsional angles (°) of (-)-**2**: Pd-C(1), 1.969(5); Pd-N(12), 2.141(4); Pd-O(24), 2.160(4); Pd-P(14), 2.217(2); P(14)-C(18), 1.841(5); P(14)-C(15), 1.849(5); S(21)-O(24), 1.495(4); S(21)-C(22), 1.758(7); S(21)-C(20), 1.808(5); C(16)-C(17), 1.317(8); C(19)-C(20), 1.545(7); C(22)-C(23), 1.290(13); C(18)-P(14)-C(15), 81.1(2); C(17)-C(18)-C(19), 108.7(4); C(16)-C(15)-C(20), 105.7(4); C(17)-C(16)-C(15), 110.6(5), C(19)-C(20)-C(15), 105.1(4); C(15)-C(20)-S(21), 108.8(3); O(24)-S(21)-C(20), 109.9(2); S(21)-O(24)-Pd, 129.9(2); Pd-O(28)-S(21)-C(20), 17.1(4); O(24)-Pd-P(14)-C(15), -4.6(2); P(14)-C(15)-C(20)-S(21), -90.1(3).
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