

Metal ion effects on the asymmetric dimerization of 1-phenyl-3,4-dimethylphosphole

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Received (in Cambridge, UK) 29th September 1999, Accepted 10th December 1999

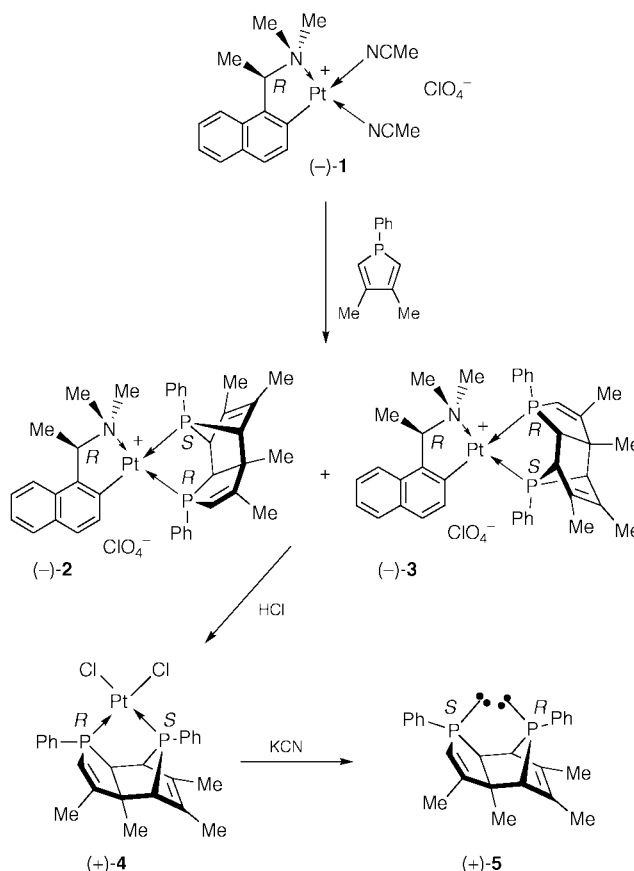
An optically pure P-chiral diphosphine has been prepared efficiently from the asymmetric dimerization of 3,4-dimethyl-1-phenylphosphole in the presence of an organoplatinum(II) complex derived from (*R*)-*N,N*-dimethyl-1-(1-naphthyl)ethylamine.

Recently we have reported a series of asymmetric Diels–Alder reactions between the cyclic diene 3,4-dimethyl-1-phenylphosphole (DMPP) and various dienophiles in the presence of an organopalladium complex containing the enantiomerically pure forms of *N,N*-dimethyl-1-(1-naphthyl)ethylamine.¹ This organopalladium complex has been employed frequently because it is perhaps the most efficient reaction promoter and stereochemical controller for the activation of DMPP in these asymmetric syntheses. In cases where vinylphosphines were used as dienophiles, optically pure P-chiral diphosphines were obtained in high yields.² In theory, the [4 + 2] *exo*-cycloaddition reaction between two DMPP molecules will produce a rigid chiral diphosphine containing two phosphorus and four carbon stereogenic centres. Interestingly, this asymmetric dimerization process could not be achieved with the chiral organopalladium complex despite the fact that it has activated DMPP effectively as a cyclic diene in many cycloaddition reactions. Apparently, the organopalladium complex is not an efficient promoter for the activation of the dienophilicity of DMPP. Here we report the application of an analogous organoplatinum complex for the high yield synthesis of the desired optically active DMPP dimer.

As illustrated in Scheme 1, the reaction between the chiral platinum (–)-**1** and 2 mol of DMPP in CHCl₃ at 30 °C for 60 d gave a 3:1 mixture of the regioisomers (–)-**2** and (–)-**3** in quantitative yield. The cationic complexes, which could not be separated by fractional crystallization, were separated efficiently by silica gel chromatography. The 202 MHz ³¹P NMR spectrum of each regioisomer in CDCl₃ exhibited a pair of doublets. For the major isomer (–)-**2**, the doublet resonances occurred at δ 37.7 (*J*_{PtP} 3285 Hz, *J*_{PP} 7 Hz) and 133.7 (*J*_{PtP} 1548 Hz, *J*_{PP} 7 Hz). For the minor regioisomer (–)-**3**, the doublets were observed at δ 52.3 (*J*_{PtP} 1476 Hz, *J*_{PP} 7 Hz) and 104.8 (*J*_{PtP} 3216 Hz, *J*_{PP} 7 Hz). The low field doublets in these isomeric complexes are typical for bridgehead phosphorus adopting the *exo-syn* stereochemistry.⁴ It is noteworthy that the Pt–P(bridgehead) coupling of (–)-**2** is significantly smaller than that of (–)-**3** as the former P(bridgehead) donor is located *trans* to a strong π-accepting aromatic carbon atom.⁵ Treatment of both isomeric complex mixtures with conc. HCl removed the naphthylamine auxiliary chemoselectively to give the same dichloro complexes (+)-**4** as pale yellow prisms (70%, mp 200–202 °C (decomp.), [α]_D +58.4 (c 0.7, CH₂Cl₂)). The ³¹P NMR spectrum of (+)-**4** in CDCl₃ exhibited a pair of doublets at δ 39.6 (*J*_{PtP} 3193 Hz, *J*_{PP} 16.8 Hz) and 107.0 (*J*_{PtP} 3265 Hz, *J*_{PP} 16.8 Hz). The molecular structure and the absolute stereochemistry of (+)-**4** were determined by X-ray structural analyses (Fig. 1).[†] The studies reveal that the absolute configurations at P(1), P(2), C(1), C(4), C(5) and C(6) in the complex are *S*, *R*, *R*, *S*, *R*, and *R*, respectively. It should be noted that the dimerization process could be completed in 8 d by heating the reaction mixture at 100 °C in a sealed tube. Under

these more vigorous conditions, however, product formation becomes less regioselective and a 1.5:1 mixture of (–)-**2** and (–)-**3** was obtained in somewhat lower yields.

Treatment of a CH₂Cl₂ solution of (+)-**4** with aqueous cyanide liberated the optically pure diphosphine (+)-**5** quantitatively as an air-sensitive oil with [α]_D +145 (c 0.5, CH₂Cl₂). The ³¹P NMR spectrum of the free diphosphine in CDCl₃ exhibited a pair of doublets at δ 4.9 and 104.2 (*J*_{PP} 43.9 Hz). The low field ³¹P resonance indicates that the *exo-syn* stereochemistry is retained. It is noteworthy that the apparent inversion of configuration that takes place at both phosphorus stereogenic centres during the liberation reaction is merely a consequence of the Cahn–Ingold–Prelog (CIP) rules.⁶ The optical purity of (+)-**5** was confirmed by the quantitative reparation of (–)-**2** and (–)-**3** from the liberated ligand and (–)-**1**; the 202 MHz ³¹P NMR spectrum of the crude product exhibited signals due to the two regioisomers only. Unlike those obtained directly from the coupling reaction, the simple complexation process between (+)-**5** and (–)-**1** regenerated (–)-**2** and (–)-**3** as a 1:3 diastereomeric mixture. In a further test of optical purity, (+)-**5** was coordinated to the equally accessible (*S*_c)-(+)-**1**. The ³¹P NMR spectrum of the crude product in CDCl₃ exhibited two new doublet resonances at δ 56.7 (*J*_{PtP} 1506 Hz, *J*_{PP} 10 Hz) and



Scheme 1

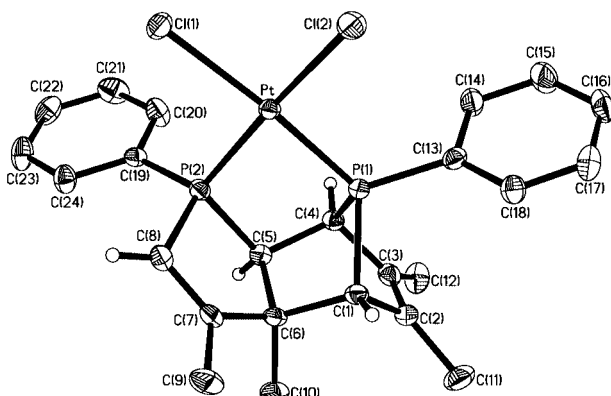


Fig. 1 Molecular structure and absolute stereochemistry of (+)-**4**. Selected bond lengths (Å) and angles (°): Pt–P(1) 2.214(1), Pt–P(2) 2.222(1), Pt–Cl(1) 2.381(1), Pt–Cl(2) 2.369(1), P(1)–C(1) 1.887(4), P(1)–C(4) 1.850(4), P(1)–C(13) 1.799(4), P(2)–C(5) 1.854(4), P(2)–C(8) 1.791(4), P(2)–C(19) 1.802(4), C(5)–C(6) 1.578(5), C(6)–C(7) 1.526(5), C(7)–C(8) 1.332(5), P(1)–Pt–P(2) 82.4(1), P(1)–Pt–Cl(1) 172.0(1), P(1)–Pt–Cl(2) 96.2(1), P(2)–Pt–Cl(1) 90.4(1), P(2)–Pt–Cl(2) 172.9(1), Cl(1)–Pt–Cl(2) 91.4(1), C(1)–P(1)–C(4) 80.2(2).

107.7 (J_{PtP} 3131 Hz, J_{PP} 10 Hz). According to the Pt–P coupling constants, these new signals are due to the S_c diastereomer of complex **3**. Interestingly, the S_c diastereomer of complex **2** was not formed *via* this coordination pathway, presumably due to steric reasons. More importantly, no resonance signals were detected at δ 37.7, 52.3, 104.8 and 133.7. It is noteworthy that the enantiomeric diphosphine (–)-**5** can be prepared similarly from the dimerization of DMPP using (+)-**1** as the chiral reaction promoter. However, diphosphine **5** was not obtained when the palladium analogue of **1** was used as the reaction promoter.

Finally, it is interesting to note that under different reaction conditions, complex **1** is able to activate DMPP both as a cyclic diene and as a dienophile toward the chemically reactive cyclopentadiene. Thus, when a CHCl_3 solution of (–)-**1**, DMPP, excess cyclopentadiene and a small quantity of NH_4Cl was heated at 60 °C for 24 h,¹ the ^{31}P NMR spectrum of the crude reaction mixture in CDCl_3 exhibited only two low field singlets of similar intensities at δ 98.3 and 98.1. The two

singlets are of the same Pt–P coupling (3781 Hz). These low field NMR signals confirmed that two diastereomeric cycloadducts were formed and DMPP reacted as the cyclic diene under these conditions. On the other hand, when the reaction was carried out at room temperature for 24 h in the absence of the chloride anion,¹ only one isomer was produced. The ^{31}P NMR spectrum of the crude product exhibited a sole singlet at δ 14.5 (J_{PtP} 3703 Hz). This relatively high field ^{31}P NMR signal indicated that DMPP had reacted as the dienophile rather than the cyclic diene in this cycloaddition reaction. Investigations on the absolute stereochemistry of these cyclic adducts and the dienophilicity of DMPP toward other dienes are currently in progress.

We are grateful to the National University of Singapore for support of this research (Grant No. RP960675) and research scholarships to GSH.

Notes and references

† *Crystal data* for (+)-**4**: $[\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{P}_2\text{Pt}]$, $M = 642.38$, orthorhombic, space group $P2_12_12_1$, $a = 11.288(1)$, $b = 13.478(1)$, $c = 15.818(1)$ Å, $V = 2406.6(1)$ Å³, $Z = 4$, $D_c = 1.773$ g cm^{–3}, $\mu(\text{Mo-K}\alpha) = 17.73$ cm^{–1}, $F(000) = 1248$. A pale yellow prism with dimensions 0.20 × 0.14 × 0.10 mm was used for diffraction studies. A total of 5275 independent reflections were measured on a Siemens SMART CCD diffractometer with Mo-K α radiation (graphite monochromator) using ω -scans. All the non-hydrogen atoms were refined anisotropically. In the full-matrix least-squares based on F^2 with absorption corrected data to give $R_1 = 0.0199$, $wR_2 = 0.0434$. The absolute stereochemistry was determined unambiguously by refining the Flack parameter [$x = 0.01(1)$]. CCDC 182/1507. See <http://www.rsc.org/suppdata/cc/a9/a907846k/> for crystallographic data in .cif format.

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Communication a907846k