*trans-Coordinating Diphosphane*

# SPANphos: A $C_2$-Symmetric *trans*-Coordinating Diphosphane Ligand[**]

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In the last few decades much effort has been devoted to the development of sophisticated ligands for specific applications. Among these, chelating diphosphanes could be considered to be the most popular class of ligands for catalysis. Surprisingly, an overview on the vast number of known diphosphanes revealed that only a limited number of *trans*-chelating diphosphanes has been reported, and even fewer asymmetric variants thereof.[1] Diphosphanes that coordinate only in a *trans* fashion that is not achieved through coordination of an additional heteroatom (i.e., in fact tridentate ligands), are very rare. The TRANSphos ligand, developed by Venanzi et al.,[2] is a flexible ligand that can achieve chelation angles of 175.7°, but *cis* structures have also been reported. In 1991, Ito et al. introduced a new family of *trans*-diphosphanes, namely, the TRAP ligands,[3] which already proved to be active in several asymmetric catalytic reactions in which *cis*-coordinating ligands failed to give enantioselectivity.

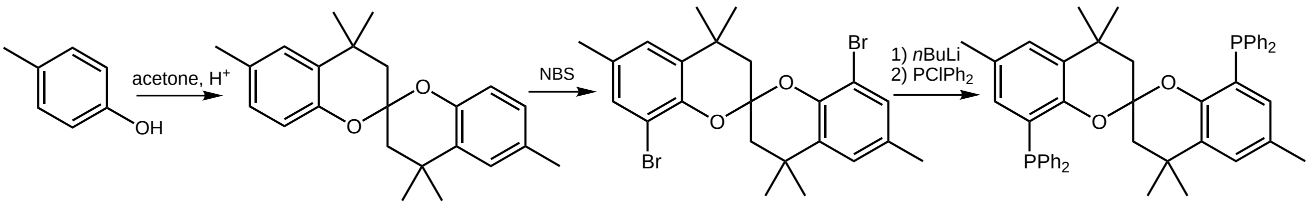
The synthesis of new, purely *trans*-diphosphanes is still a worthwhile challenge, because they will provide access to scarcely explored catalysts with unusual dispositions of ligands around the active metal center. By using *trans*-chelating ligands, some coordination positions that are traditionally available when *cis*-diphosphanes are used can be inhibited, and new families of catalysts with new properties could thus be discovered.[1]

We report here the synthesis of a new *trans*-coordinating diphosphane, which is readily available in three steps from cheap reagents, characterization of Rh, Pd, and Pt complexes thereof, and some preliminary catalytic experiments.

Scheme 1 shows the synthetic path to SPANphos (**3**). Racemic 4,4,4′,4′,6,6′-hexamethylspiro-2,2′-bichroman (**1**) was obtained on a 10 g scale by acid-catalyzed reaction of *p*-cresol with acetone.[4] Spirane **1** was brominated with *N*-bromosuccinimide (NBS) to obtain 8,8′-dibromo-4,4,4′,4′,6,6′-hexamethylspiro-2,2′-bichroman (**2**), which was treated with *n*BuLi and chlorodiphenylphosphane to give SPANphos in about 80% overall yield. Optically pure samples of **3** were obtained by racemic resolution by chiral HPLC.[5]

The molecular structure of **3** was determined by X-ray crystallographic analysis (Figure 1).[6] It has an intramolecular P···P distance of 4.991 Å. All atoms in each chroman fragment are nearly in a single plane, except for the spiro carbon atom on the idealized $C_2$ axis, which lies about 0.7 Å above either plane. The dihedral angle between the two mean planes of 43.9(1)° results in an "*anti*" disposition of the lone pairs of the P atoms, which seems incompatible with a chelating coordination mode of the ligand.

Reaction of **3** with stoichiometric amounts of $[PtCl_2(CH_3CN)_2]$ and $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene) gave *trans*-$[PtCl_2(\mathbf{3})]$ (**4**) and *trans*-$[PdCl_2(\mathbf{3})]$ (**5**).



**1** **2** SPANphos(**3**)

***Scheme 1.*** Synthetic route to SPANphos **3**.

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[**] The NRSCC is kindly acknowledged for financial support.

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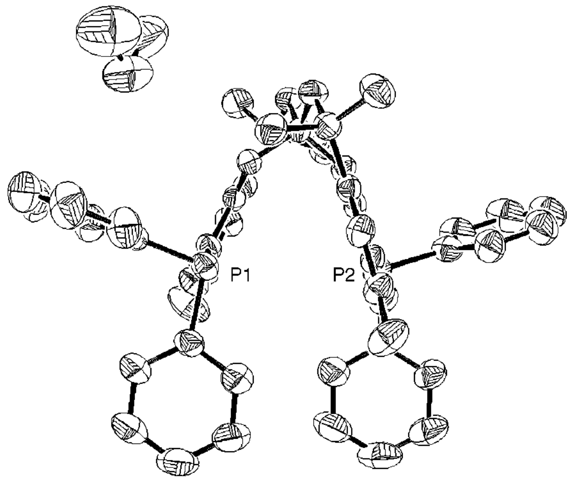


***Figure 1.*** Molecular structure of **3** (ORTEP plot).

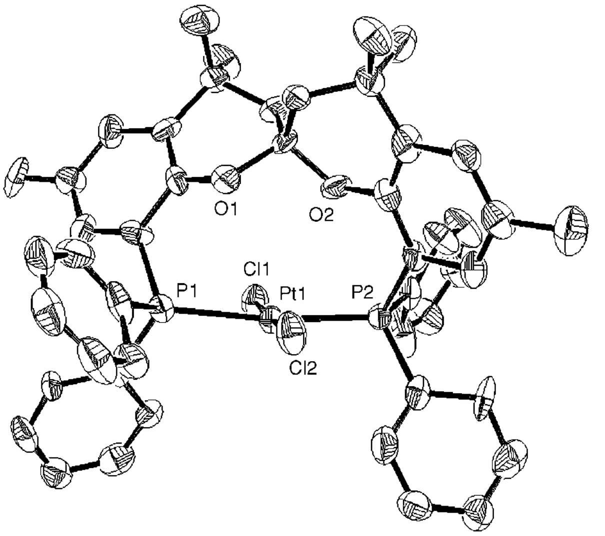


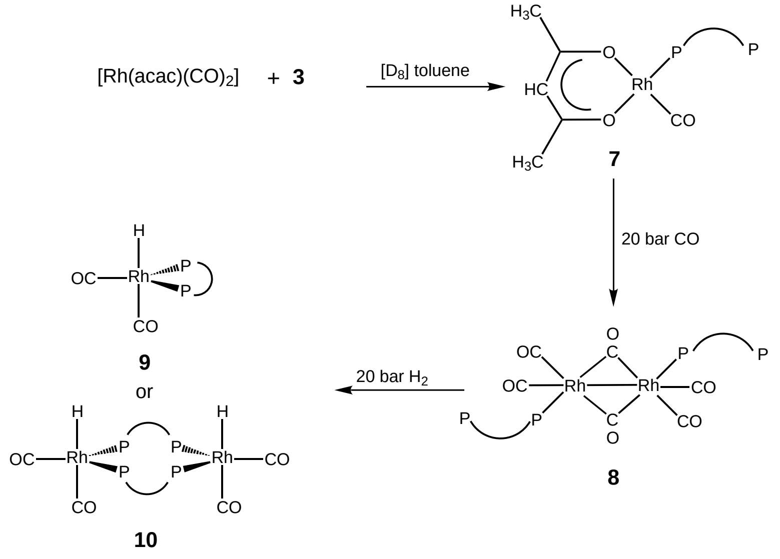
***Figure 2.*** Molecular structure of **4** (ORTEP plot). Selected bond lengths [Å] and angles [°] for **4**. Pt1–Cl1 2.294(8), Pt1–Cl2 2.338(9), Pt1–P1 2.315(5), Pt1–P2 2.293(4), Cl1-Pt1-Cl2 176.4(3); Cl1-Pt1-P1 89.3(2), Cl1-Pt1-P2 92.9(2), Cl2-Pt1-P1 91.1(3), Cl2-Pt1-P2 86.2(2), P1-Pt1-P2 171.9(4).

Figure 2 shows the molecular structure of **4**.[7] The structure confirms the *trans* coordination of the diphosphane ligand, with a P-Pt-P angle of 171.9°. This angle is about 10° wider than those reported for square-planar Pd and Rh complexes of TRAP derivatives.[8] This wider bite angle is likely related to the larger P···P distance enforced by the bichroman backbone, as opposed to the highly congested biferrocenyl backbone of TRAP ligands. In contrast to the free ligand, in complex **4**, the oxygen atom and the carbon atom adjacent to the spiro center lie above and below the plane defined by the aromatic ring of the chroman fragment. This brings the phosphorous atoms 0.40 Å closer to one another than in the free ligand (P···P in **4**: 4.591 versus 4.991 Å in the free ligand) and appropriately orientates the lone pairs of these atoms for *trans* chelation.

The $^{31}$P NMR spectrum of **4** shows a single signal with Pt satellites ($\delta = 17.6$ ppm, $^1J(\text{Pt,P}) = 2723$ Hz), which strongly suggests that the mononuclear *trans* complex is the only species in solution. The $^{31}$P NMR spectrum of **5** also shows a single signal with the same chemical shift as the Pt complex, which indicates the same molecular structure for both complexes. Furthermore, the related [PdClMe(**3**)] (**6**) shows a singlet at $\delta = 24.7$ ppm in the $^{31}$P NMR spectrum and a triplet ($\delta = -0.27$ ppm, $^2J(\text{P,H}) = 6.1$ Hz) in the $^1$H NMR spectrum, indicative of the *trans* disposition of the bidentate ligand.[9]

The reaction of $[\text{Rh(acac)(CO)}_2]$ with a stoichiometric quantity of **3** produced the mononuclear complex [Rh(acac)(CO)($\eta^1$-**3**)] (**7**; Scheme 2); this indicates that the ligand cannot achieve a 90° chelation angle. This was also confirmed when complex **7** was treated with 20 bar of CO in a high-pressure (HP) NMR tube. Formation of the new binuclear complex $[\text{Rh}_2(\mu\text{-CO})_2(\text{CO})_4(\eta^1\text{-}\mathbf{3})_2]$ (**8**) was observed, as demonstrated by the $^{31}$P NMR signals ($\delta =$ 21.1, m, 1P; −15.6 ppm, brs, 1P) as well as by HP-IR experiments. Complex **8** slowly evolves under 20 bar of $H_2$ into a new species characterized by a doublet ($\delta =$ 33.3 ppm, $^1J(\text{Rh,P}) = 143.7$ Hz) in the $^{31}$P NMR spectrum and a triplet of doublets in the $^1$H NMR spectrum ($\delta =$ −9.5 ppm, $^1J(\text{Rh,P}) = 6.2$, $^1J(\text{Rh,H}) = 3.7$ Hz). These signals are consistent both with a mononuclear complex $[\text{RhH(CO)}_2(\mathbf{3})]$ (**9**) and a binuclear species **10** with two bridging diphosphane ligands. Both spectra are consistent with bisequatorial coordination of the P-donor ligand, as was corroborated by HP-IR spectroscopy under CO/$H_2$ and CO/$D_2$. Further investigations to distinguish between these two species by using DOSY techniques are planned.

The catalytic activity of metal complexes containing *rac*-**3** was tested in several reactions. It was shown to be an efficient ligand for rhodium-catalyzed hydroformylation of 1-octene and styrene, palladium-catalyzed allylic alkylation of 1,3-



***Scheme 2.*** Rhodium complexes of **3**, which were confirmed by NMR and IR experiments.

diphenylprop-2-ene-1-yl acetate and Michael reaction of ethyl α-cyanopropionate with methyl vinyl ketone.

No activity was observed for palladium-catalyzed CO/ethene oligomerization under different conditions, and not even the formation of methyl propanoate was detected. Recent results suggest that a *cis* arrangement of the diphosphane ligand is necessary to enable solvolysis of the acyl group, which is the main chain-transfer mechanism in CO/ethene oligomerization cycles starting with a palladium hydride species.[10] Hence, these results reinforce the idea that **3** neither forms *cis* compounds, nor undergoes dissociation of one of the phosphorus atoms during the catalytic cycle.

In conclusion, we have synthesized a new $C_2$-symmetric *trans*-diphosphane ligand that is readily accessible from cheap reagents. Neither *cis–trans* isomerization nor decoordination of one of the P atoms appears to occur under CO/ethene oligomerization conditions. In Pd or Pt complexes SPANphos acts as a purely *trans*-coordinating diphosphane ligand. This is corroborated by NMR studies on rhodium complexes, which showed that chelation angles close to 90° cannot be achieved by this ligand.

As we mentioned before, the introduction by Ito et al. of the TRAP type ligands showed that these chiral *trans*-coordinating diphosphanes provide excellent enantiomeric excesses in some reactions in which *cis*-diphosphanes are inefficient.[3] From the viewpoint of enantioselective discrimination, the main difference between *cis*-and *trans*-diphosphanes is the role of their chiral backbone. For instance, in a square-planar complex, when a *trans*-chelating diphosphane is used, both the backbone and the substituents on the P atoms directly contribute to the formation of a chiral cavity around the metal center. This represents an advantage over the classical *cis*-chelating ligands, in which the backbone is not directly exposed to the active sites of the metal, and the chiral environment is mainly produced by the substituents on the phosphorus atoms by chirality-transfer mechanisms. The potential of the chiral cavity generated by TRAP ligands is evidenced by the remote stereoselective formation of C–C bonds on atoms not directly attached to the metal center.[11]

Investigations on SPANphos derivatives containing the same or related backbones will lead us to a family of potentially chiral, easily accessible *trans* ligands. Catalytic experiments on asymmetric reactions with enantiopure samples of the **3** are currently under development.

## Experimental Section

Bichroman **1** was prepared according to a modified literature procedure.[4]

**2:** A solution of NBS (3.23 g) in DMF (40 mL) was added dropwise to a solution of **1** (2.56 g, $7.25\times10^{-3}$ mol) in DMF (125 mL). The reaction mixture was monitored by GC-MS. After five days, it was quenched with water and extracted with $Et_2O$. The combined organic layers were dried over magnesium sulfate, and the solvent was evaporated. The product was crystallized from methanol to give a white solid (yield 84 %). $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 7.11$, 7.09 (s, s, 2H, 2H; H5, H5′, H7, H7′), 2.29 (s, 6H; $CH_3$6, $CH_3$6′), 2.21 (d, $^2J$(H,H) = 14.0 Hz, 2H; H3a, H3a′), 2.10 (d, $^2J$(H,H) = 14.0 Hz, 2H; H3b, H3b′), 1.78 (s, 6H; $CH_3$4a, $CH_3$4a′), 1.38 ppm (s, 6H; $CH_3$4b, $CH_3$4b′); $^{13}$C NMR (125.7 MHz, $CDCl_3$): $\delta = 144.94$, 133.53, 131.86, (CH arom.), 131.09, 126.15, (CH arom.), 111.22 (CH arom.), 98.60 (C2), 46.86 ($CH_2$3, $CH_2$3′), 33.07 ($CH_3$), 32.21 ($CH_3$), 31.18 (C4, C4′), 20.54 ppm ($CH_3$).

**3:** *n*BuLi (2.5 mL, 2.5 M in hexane, $1.2\times10^{-2}$ mol) was added dropwise to a refluxing solution of **2** (2.99 g, $5.8\times10^{-3}$ mol) in THF (150 mL). Upon completion of the reaction, monitored by GC-MS, $ClPPh_2$ (2.3 mL, $1.2\times10^{-2}$ mol) was added, and the reaction mixture stirred at room temperature for 16 h. The reaction was quenched with degassed water and extracted with $Et_2O$. The combined organic layers were dried over magnesium sulfate, and the solvent was evaporated. The product was crystallized from methanol (yield 89 %). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.42$–7.00 (m, 22H; CH arom), 6.64 (m, 2H; CH arom.), 2.00 (s, 6H; $CH_3$6, $CH_3$6′), 1.82 (d, $^2J$(H,H) = 14.1 Hz, 2H; H3a, H3a′), 1.82 (s, 6H; $CH_3$4a, $CH_3$4a′),1.62 (d, $^2J$(H,H) = 14.1 Hz, 2H; H3b, H3b′), 1.22 ppm (s, 6H; $CH_3$4b, $CH_3$4b′): $^{13}$C NMR (75.4 MHz, $CDCl_3$): $\delta = 151.80$ (d, $J$(P,C) = 10.8 Hz; C arom.), 139.26 (d, $J$(P,C) = 8.4 Hz; C arom.), 138.56 (d, $J$(P,C) = 8.1 Hz; C arom.), 134.92 (d, $J$(P,C) = 12.4 Hz; CH arom.), 134.44 (d, $J$(P,C) = 11.6 Hz; CH arom.), 133.24 (s; CH arom.), 131.79 (s; C arom.), 131.25 (s; C arom.), 129.14–128.20 (m, C; CH arom.), 125.55 (d, $J$(P,C) = 8.8 Hz; C arom.), 98.80 (s; C2), 47.65 (s; $CH_2$3, $CH_2$3′), 34.29 ($CH_3$), 33.08 ($CH_3$), 30.94 (C4, C4′), 21.35 ppm ($CH_3$). $^{31}$P NMR (121.5 MHz; $CDCl_3$): $\delta = -14.6$ ppm (s).

CCDC-196129 and CCDC-196130 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: October 25, 2002 [Z50435]

**Keywords:** homogeneous catalysis · ligand design · platinum · P ligands

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[6] $C_{47}H_{46}O_2P_2\cdot CH_2Cl_2$, $M_r = 704.8$, triclinic, $P\bar{1}$, $a = 11.9743(5)$, $b = 13.240(1)$, $c = 14.808(1$ Å, $\alpha = 73.807(7)$, $\beta = 79.854(8)$, $\gamma = 71\,369(7)°$, $V = 2126.6(3)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.23$ g cm$^{-3}$, $\lambda(Cu_{K\alpha}) = 1.5418$ Å, $\mu(Cu_{K\alpha}) = 2.37$ mm$^{-1}$, $F(000) = 832$, room temperature, final $R = 0.061$ for 6974 observed reflections.

[7] $C_{47}H_{46}Cl_2O_2P_2Pt$, $M_r = 487.2$, orthorhombic, $Pbn2_1$, $a = 13.167(1)$, $b = 17.369(1)$, $c = 17.735(2)$ Å, $V = 4056.0(6)$ Å$^3$, $Z =$

4, $\rho_{\text{calcd}} = 1.59\ \text{g}\,\text{cm}^{-3}$, $\lambda(\text{Cu}_{\text{K}\alpha}) = 1.5418$ Å, $\mu(\text{Cu}_{\text{K}\alpha}) = 8.73\ \text{mm}^{-1}$, $F(000) = 1944$, room temperature, final $R = 0.059$ for 3641 observed reflections.

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