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Unorthodox C,O Binding Mode of Me_2BINOL in Pt(II) Complexes

Nicole M. Brunkan, Peter S. White, and Michel R. Gagné*

Department of Chemistry, CB#3290
University of North Carolina
Chapel Hill, North Carolina 27599-3290

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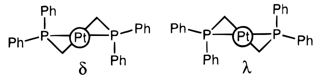
The enantiomeric forms of 1,1′-bi-2-naphthol (BINOL) have often been incorporated into early transition metal catalyst systems as chiral auxiliaries for asymmetric induction.[1] When bound to a metal through both oxygen atoms, the ligand adopts a C_2-symmetric conformation that effectively controls the orientation of bound substrate, providing excellent stereoselectivity in a variety of reactions. Including the ligand in late transition metal catalysts could extend the usefulness of BINOL, an idea recently explored through the synthesis of BINOL-containing Os, Pt, and Pd complexes.[2] All of the crystal structures of binaphtholate complexes (Ti, Mo, W, Pt, and lanthanides) published to date show BINOL (or 3,3′-disubstituted BINOL derivatives) coordinated to the active metal center(s) in the expected O,O′ fashion.[2−4] Herein we report the observation of a novel C,O binding mode for the modified BINOL ligand 3,3′-dimethyl-1,1′-bi-2-naphthol (Me_2BINOL) in a late metal system.

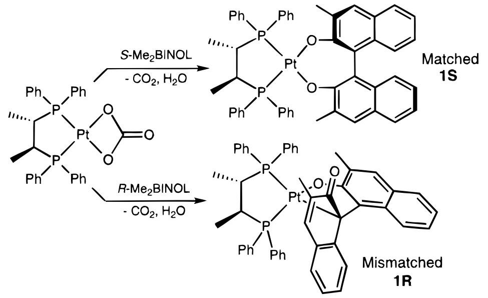
Recently, we compared the interactions of (*R*)- and (*S*)-BINOL with the chiral diphosphine (2*S*,3*S*)-bis(diphenylphosphino)butane ((*S*,*S*)-chiraphos) in square planar Pt(II) complexes to contrast the flexibilities of these chiral ligands.[4] (*S*)-BINOL and (*S*,*S*)-chiraphos were designated "matched" ligands because they favor the same conformation (δ-skew; Scheme 1) of the five-membered diphosphine chelate ring. X-ray analysis of ((*S*,*S*)-chiraphos)Pt((*S*)-BINOL) confirmed adoption of the δ conformation in the complex. In the "mismatched" case, (*R*)-BINOL, which induces the λ conformation in the diphosphine,[5] competes with (*S*,*S*)-chiraphos for structural dominance. Despite the fact that *eight* conformationally distinct molecules of ((*S*,*S*)-chiraphos)Pt((*R*)-BINOL) are present in the crystallographic asymmetric unit, all diphosphine chelates adopt the δ conformation; thus (*S*,*S*)-chiraphos has a stronger conformational preference than (*R*)-BINOL.

The main source of steric contention between BINOL and a diphosphine is the interaction of BINOL's 3- and 3′-hydrogens with the phosphine's phenyl groups. To increase the magnitude of this interaction, BINOL was modified by methylation at these positions.[6] The matched and mismatched complexes, ((*S*,*S*)-chiraphos)Pt((*S*)-Me_2BINOL) (**1S**) and ((*S*,*S*)-chiraphos)Pt((*R*)-Me_2BINOL) (**1R**), were synthesized as shown in Scheme 2.[7]

Scheme 1



Scheme 2



As expected, the C_2-symmetric, O,O′-bound binaphtholate **1S** closely resembles ((*S*,*S*)-chiraphos)Pt((*S*)-BINOL)[4] by X-ray crystallography[8] and ^{31}P NMR, giving a single resonance at 28.0 ppm ($^1J_{\text{Pt−P}} = 3560$ Hz). However, the ^{31}P spectrum of the mismatched complex **1R** consists of two doublets ($J_{\text{P−P}} = 23$ Hz), one at 30.1 ppm with $^1J_{\text{Pt−P}}$ similar to that of **1S** (3540 Hz) and one at 48.7 ppm with a substantially reduced Pt−P coupling constant (2440 Hz). The smaller Pt−P coupling constant indicates binding of a ligand that exerts a stronger trans influence than oxygen-bound BINOL.

Single-crystal X-ray analysis revealed that the asymmetry of **1R** is due to a novel C,O Me_2BINOL coordination mode, which allows the ligand to avoid unfavorable steric interactions with the phenyl groups of (*S*,*S*)-chiraphos (Figure 1).[9] The O → C migration of Pt initiates an enol−keto tautomerization of BINOL that destroys the aromaticity of ring **A** and positions the **A**/**B** binaphthyl rings perpendicular to the **C**/**D** binaphthyl plane. Consistent with this picture is the short $C_{31}-O_2$ bond distance (1.245(9) Å, compared to $C_{11}-O_1$ 1.342(9) Å). In accordance with the observed $^1J_{\text{Pt−P}}$ values, the Pt−P_1 bond distance is 2.229(2) Å (trans to O), while the Pt−P_2 bond distance is 2.268(2) Å (trans to C). The distance of the centroid of BINOL aromatic ring **B** from the plane containing phosphine phenyl ring **E** is 3.23 Å, indicating a short slipped π-stack in the solid state.[10]

Me_2BINOL undoubtedly adopts the C,O binding mode in **1R** in response to unfavorable steric interactions in a hypothetical O,O′-bound complex. These unfavorable interactions occur on combination of the *mismatched* (*R*)-Me_2BINOL and (*S*,*S*)-chiraphos pair of ligands and are less significant in the matched case. **1R** is able to accommodate the peculiar C,O binding mode for several reasons. (1) Formation of the fully aromatic **B** ring helps offset the loss of partial aromaticity in the **A** ring. This effect is known to shift the reactivity of BINOL from the 2 to the 1 position (e.g., Scheme 3).[11] (2) Tautomerization (O → C) produces a five- rather than seven-membered metal chelate. (3) The soft acid Pt(II) center coordinates the softer benzyl enolate

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[1] Seyden-Penne, J. *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*; Wiley: New York, 1995.

[2] Griffith, W. P.; Nogueira, H. I. S.; White, A. J. P.; Williams, D. J. *Polyhedron* **1997**, *16*, 1323−1329.

[3] (a) Boyle, T. J.; Eilerts, N. W.; Heppert, J. A.; Takusagawa, F. *Organometallics* **1994**, *13*, 2218−2229 and references therein. (b) Erickson, M. S.; Fronczek, F. R.; McLaughlin, M. L. *J. Organomet. Chem.* **1991**, *415*, 75−85. (c) Kuntz, B. A.; Ramachadran, R.; Taylor, N. J.; Guan, J.; Collins, S. *J. Organomet. Chem.* **1995**, *497*, 133−142. (d) Totland, K. M.; Boyd, T. J.; Lavoie, G. G.; Davis, W. M.; Schrock, R. R. *Macromolecules* **1996**, *29*, 6114−6125. (e) Heppert, J. A.; Dietz, S. D.; Eilerts, N. W.; Henning, R. W.; Morton, M. D.; Takusagawa, F. *Organometallics* **1993**, *12*, 2565−2572. (f) Shibasaki, M.; Sasai, H.; Takayoshi, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1236−1256.

[4] Brunkan, N. M.; White, P. S.; Gagné, M. R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1579−1582.

[5] Deduced from the crystal structure of (dppe)Pt((*R*)-BINOL), in which dppe adopts exclusively the λ conformation [dppe = 1,2-bis(diphenylphosphino)ethane]. (*S*,*S*)-chiraphos inherently prefers the δ conformation, which places the backbone *trans*-methyl substituents in pseudoequatorial positions on the chelate ring.

[6] Peacock, S. S.; Walba, D. M.; Gaefa, F. C. A.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 2043−2052.

[7] Synthesis based on Andrews, M. A.; Voss, E. J.; Gould, G. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 5730−5740.

[8] Crystal data for **1S**: orthorhombic, space group *I*222, yellow crystal 0.30 × 0.20 × 0.05 mm, $a = 18.2701(8)$ Å, $b = 18.6389(8)$ Å, $c = 26.7318(12)$ Å, $Z = 8$, $R_f = 0.047$, GOF = 2.53.

[9] Crystal data for **1R**: orthorhombic, space group $P2_12_12_1$, yellow crystal 0.25 × 0.25 × 0.40 mm, $a = 11.8022(5)$ Å, $b = 14.2088(6)$ Å, $c = 28.8782(13)$, $Z = 4$, $R_f = 0.058$, GOF = 2.28.

[10] Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768−4774.

[11] (a) Kyba, E. P.; Gokel, G. W.; de Jonge, F.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Kaplan, L.; Sogah, G. D. Y.; Cram, D. J. *J. Org. Chem.* **1977**, *42*, 4173−4184. (b) Georghiou, P. E.; Ashram, M.; Clase, H. J.; Bridson, J. N. *J. Org. Chem.* **1998**, *63*, 1819−1826.

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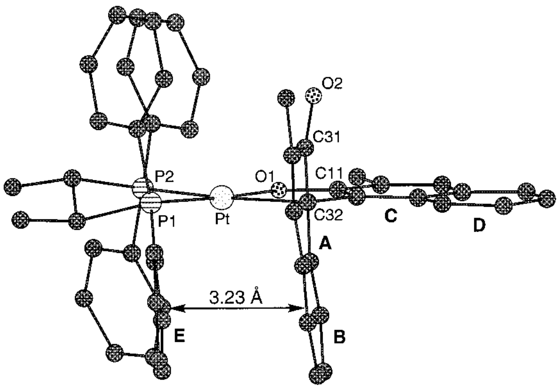
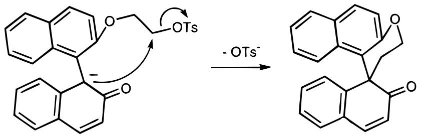


Figure 1. X-ray structure of **1R**. Selected bond distances (Å) and angles (deg): Pt−P$_1$ 2.229(2), Pt−P$_2$ 2.268(2), Pt−O$_1$ 2.050(5), Pt−C$_{32}$ 2.199(7), C$_{11}$−O$_1$ 1.342(9), C$_{31}$−O$_2$ 1.245(9), P$_1$−Pt−P$_2$ 85.70(7), O$_1$−Pt−C$_{32}$ 82.7(2), P$_1$−Pt−C$_{32}$ 103.9(2), P2-Pt-O1 87.7(1).

Scheme 3



carbon.[12] The latter argument is often invoked to explain why late transition metal enolates are generally C-bound, while early transition metal enolates are O-bound.[13]

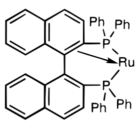
The relative ground-state energies of **1S** and **1R** were determined through a binaphtholate exchange reaction (eq 1). Integration of the ^{31}P NMR resonances of the Pt complexes afforded a K_{eq} of 1.4(3) at 25 °C in CD_2Cl_2 ($\Delta G° = -0.2(1)$ kcal·mol^{-1}).[14] Although the O,O′-bound form of **1S** and the C,O-bound form of **1R** have nearly the same ground-state energy, attempts to observe a C,O-bound form of **1S** were unsuccessful.[15] We hypothesize that the C,O form of **1R** is stabilized by the short slipped π-stack seen in the X-ray structure, which is unavailable in **1S** for conformational reasons.[10]

$$\mathbf{1R} + (S)\text{-Me}_2\text{BINOL} \rightleftharpoons \mathbf{1S} + (R)\text{-Me}_2\text{BINOL} \tag{1}$$

Unlike **1S** and **1R**, the complex (dppe)Pt((*R*)-Me$_2$BINOL) exists as an equilibrium mixture of C,O-($\mathbf{2_{C,O}}$) and O,O′-bound ($\mathbf{2_{O,O}}$) isomers ($\mathbf{2_{O,O}} \rightleftharpoons \mathbf{2_{C,O}}$).[16] The equilibrium constant is solvent dependent: $K_{eq} = 3.3(2)$ in CH_2Cl_2 and 1.38(5) in chlorobenzene (25 °C).[14,17] A crystal grown from a chlorobenzene solution of **2** and analyzed by X-ray diffraction revealed that only $\mathbf{2_{C,O}}$ crystallizes from the equilibrium mixture.[18] As predicted by analogy to the (*S*,*S*)-chiraphos complexes, dppe adopts the δ conformation in $\mathbf{2_{C,O}}$ as in **1R** (the structures are almost identical). Presumably dppe adopts the λ conformation in $\mathbf{2_{O,O}}$. Dissolution of crystalline $\mathbf{2_{C,O}}$ results in rapid equilibration with $\mathbf{2_{O,O}}$ (minutes).

The relationship of $\mathbf{2_{C,O}}$ to $\mathbf{2_{O,O}}$ was further investigated through variable temperature ^{31}P NMR experiments. Heating in chlorobenzene causes the equilibrium to shift toward $\mathbf{2_{C,O}}$ ($K_{eq} = 1.1$ at −5 °C, 2.1 at 75 °C). A van't Hoff analysis yielded values for $\Delta H°$ of +1.9(4) kcal·mol^{-1} and $\Delta S°$ of +7(1) eu.[19] $\Delta S°$ is unexpectedly large and positive for this unimolecular reaction. This is partially due to the loss of symmetry on conversion of $\mathbf{2_{O,O}}$ to $\mathbf{2_{C,O}}$ (∼+1.4 eu),[20] while the rest of the gain can probably be ascribed to solvation effects. Consistent with this hypothesis, different values for $\Delta S°$ (+3(2) eu) and $\Delta H°$ (0.2(4) kcal·mol^{-1}) were obtained upon carrying out the van't Hoff analysis in CD_2Cl_2.

Broadening and partial coalescence of the ^{31}P resonances for the isomers was also observed as temperature increased in the chlorobenzene experiments. Rate constants for the interconversion of $\mathbf{2_{O,O}}$ and $\mathbf{2_{C,O}}$ were obtained by simulation of the broadened spectra.[21] The barrier for the $\mathbf{2_{O,O}} \rightarrow \mathbf{2_{C,O}}$ conversion ($\Delta G^{\ddagger}$) is 16.07(6) kcal·mol^{-1} at 25.7 °C. A weighted nonlinear least squares Eyring analysis produced values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 14.6(3) kcal·mol^{-1} and −4.7(9) eu, respectively.[22] The recent discovery of η^2-coordinated biaryl diphosphines such as **3**[23] suggests that **4** is a reasonable intermediate or transition state structure for the $\mathbf{2_{O,O}}/\mathbf{2_{C,O}}$ interconversion.



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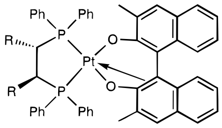

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In summary, we have observed that Pt(II) binaphtholates can access a novel C,O binding mode that is, in some cases, competitive with the traditional O,O′ coordination mode. Steric interactions between the diphosphine and Me$_2$BINOL ligands determine whether the C,O or O,O′ binding mode is preferable in a given complex. Since dynamic exchange between these forms is possible, the C,O-bound isomer could be important to the reactivity of late metal BINOL systems.

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data for **1S**, **1R**, and **2**, VT ^{31}P NMR data, van't Hoff and Eyring plots, and tables of crystallographic data collection parameters and metrical parameters for **1S**, **1R**, and $\mathbf{2_{C,O}}$ (43 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[12] Pearson, R. G. *Hard and Soft Acids and Bases*; Dowden, Hutchinson, and Ross: Stroudsburg, PA, 1973.

[13] (a) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4899−4907. Recent examples of late metal C-bound enolates: (b) Bergman, R. G.; Kaplan, A. W. *Organometallics* **1997**, *16*, 1106−1108. (c) Hsu, R. H.; Chen, J. T.; Lee, G. H.; Wang, Y. *Organometallics* **1997**, *16*, 1159−1166. (d) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 12382−12383. A late-metal O-bound enolate: (e) Slough, G. A.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 938−949.

[14] For all K_{eq} values, digits in parentheses represent the standard deviation (σ) of the value's last significant digit.

[15] No C,O-bound **1S** was observed by ^{31}P NMR at 90 °C in chlorobenzene; no O,O′-bound **1R** was observed at −80 °C in CH_2Cl_2. Experiments were designed based on the $\mathbf{2_{O,O}}/\mathbf{2_{C,O}}$ equilibrium (*vide infra*).

[16] $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2) $\delta = 46.4$ (d, $^2J_{P-P} = 8.9$ Hz, $^1J_{P-Pt} = 2510$ Hz; *trans* to C, $\mathbf{2_{C,O}}$), 28.6 (d, $^2J_{P-P} = 8.9$ Hz, $^1J_{P-Pt} = 3560$ Hz; *trans* to O,$\mathbf{2_{C,O}}$), 23.8 ($^1J_{P-Pt} = 3660$ Hz; $\mathbf{2_{O,O}}$).

[17] In CH_2Cl_2: 76% $\mathbf{2_{C,O}}$: 24% $\mathbf{2_{O,O}}$; $\Delta G° = 0.67$ kcal·mol^{-1} (25 °C). In chlorobenzene: 58% $\mathbf{2_{C,O}}$: 42% $\mathbf{2_{O,O}}$; $\Delta G° = 0.18$ kcal·mol^{-1} (25 °C).

[18] Crystal data for $\mathbf{2_{C,O}}$: monoclinic, space group *P*21, yellow crystal 0.35 × 0.15 × 0.05 mm, $a = 11.6797(7)$ Å, $b = 18.7909(11)$ Å, $c = 18.3581(10)$ Å, $\beta = 107.941(1)°$, $Z = 4$, $R_f = 0.036$, GOF = 1.15.

[19] Errors represent the standard error of the mean (SEM) at the 95% confidence level. Each integral was assumed to have a 10% error, and the experiment was carried out over an 80 °C temperature range.

[20] Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; p 601. By virtue of its C_2 symmetry, $\mathbf{2_{O,O}}$ has an entropy of symmetry ($-R(\ln 2)$) associated with it, while $\mathbf{2_{C,O}}$ has none.

[21] Software used was Xsim-DNMR3. Xsim is copyright 1994−1997 by Kirk Marat, University of Manitoba, Winnipeg, Manitoba, Canada, R3T 2N2. The original authors of DNMR3 were G. Binsch and D. Kleier, University of Notre Dame, Notre Dame, IN 46556.

[22] The analysis, carried out with a computer program kindly provided by Professor Barry Carpenter (Cornell University), allows a different relative error to be ascribed to each simulated rate constant and reports the SEM at the 95% confidence level. An unweighted Eyring analysis is provided in the Supporting Information.

[23] Feiken, N.; Pregosin, P. S.; Trabesinger, G.; Albinati, A.; Evoli, G. L. *Organometallics* **1997**, *16*, 5756−5762 and references therein.