NMR Structure of an Unusual $Pt_2(\mu$-BINOL) Dimer: More Surprises from a Seemingly Simple Chiral Ligand

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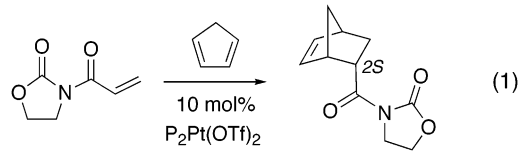
A novel $[(dppe)_2Pt_2(\mu\text{-BINOL})]^{2+}[OTf]^-_2$ dimer (**A**) was cleanly produced by addition of 1 equiv of HOTf to (dppe)Pt(*S*-BINOL) (**1**) or via "comproportionation" of **1** with (dppe)Pt-$(OTf)_2$ (**2**). The structure of **A** was investigated by ^1H, ^{31}P, and ^{13}C NMR spectroscopy, as well as 2D $^1H/^1H$ (COSY) and $^{13}C/^1H$ (HMQC, HMBC) correlation experiments, revealing that both halves of the bridging BINOL ligand have undergone "enol−keto" tautomerization in this complex. Two symmetry-equivalent (dppe)Pt fragments coordinate in an *anti* fashion via Pt−C σ bonds to the adjacent atoms C_1 and $C_{1'}$ of the resulting "diketo" BINOL ligand. η^1-Coordination of the carbonyl groups of "diketo" BINOL to Pt was proposed to fill the fourth coordination site of each Pt square plane in dimer **A**, generating favorable five-membered Pt-chelate rings; the P−Pt coupling constants observed for **A** are consistent with C═O→Pt coordination. The driving force for dimer formation is likely electrostatic, as dimerization distributes the dicationic charge of Pt Lewis acid **2** over two Pt centers, facilitated by the "diketo" BINOL bridge.

Introduction

Square planar, dicationic $P_2Pd(II)$ and $P_2Pt(II)$ complexes have been used as Lewis acid catalysts for a variety of organic transformations, including enantioselective reactions.[1] For example, the Lewis acids $P_2Pt(OTf)_2$ (P_2 = dppe (**2**), *R*-BINAP) catalyze the Diels−Alder reaction of *N*-acryloyloxazolidinone with cyclopentadiene (eq 1) in good yield, and the chiral *R*-BINAP



(1)

catalyst affords the *2S*-enantiomer of the Diels−Alder product in 96−98% ee.[1a,2] Because little mechanistic information about $[P_2M]^{2+}$ (M = Pd, Pt) catalysts had previously been reported, we recently undertook a comprehensive study of the Pt-catalyzed Diels−Alder reactions in eq 1.[2] Our experiments revealed that the late-metal $P_2Pt(OTf)_2$ Lewis acids do exhibit unique reactivity, compared to their early-metal, p-block, or first-row (Cu(II) or Zn(II)) counterparts. In fact, the reactivity observed highlighted the importance of several fundamental characteristics inherent in these Pt(II) complexes.

For example, ligand substitution of substrate for Pt-coordinated product (rather than cycloaddition of diene to the activated, Pt-coordinated substrate) was found to be the turnover-limiting step of the Diels−Alder catalytic cycle, consistent with the fact that complexes of the third-row metal Pt are not very labile.[2a] Also, diene reacted with the Pt-coordinated dienophile extremely rapidly, even at 195 K, showing that these $P_2Pt(OTf)_2$ Lewis acids are remarkably electrophilic. Displacement of OTf^- from the catalyst by coordination of dienophile (through the carbonyl oxygens) was observed to be thermodynamically favorable, corroborating this assessment of the catalyst's electrophilicity. Finally, an unexpected catalyst decomposition pathway involving reaction of $P_2Pt(OTf)_2$ with cyclopentadiene to produce $[P_2Pt(\eta^5\text{-Cp})]^+[OTf]^-$ demonstrated that the "soft", late-metal Pt center prefers to bind to "softer" carbon rather than "harder" oxygen atoms, making it more carbophilic than oxophilic.[2b,3]

This last feature of Pd and Pt metal centers has previously been documented in several reports. Pd-catalyzed imine and aldehyde alkylation reactions, for instance, were found to proceed via C-coordination of Mukaiyama-type nucleophiles to the catalyst, rather than by activation of the imines or aldehydes through N- or O-coordination.[4] In the area of coordination chemistry, the bidentate ligands *R*-3,3′-Me_2BINOL,[5]

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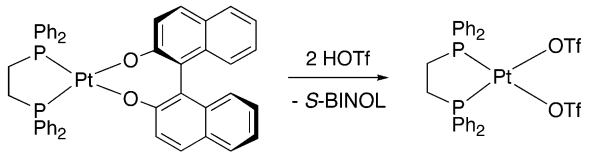
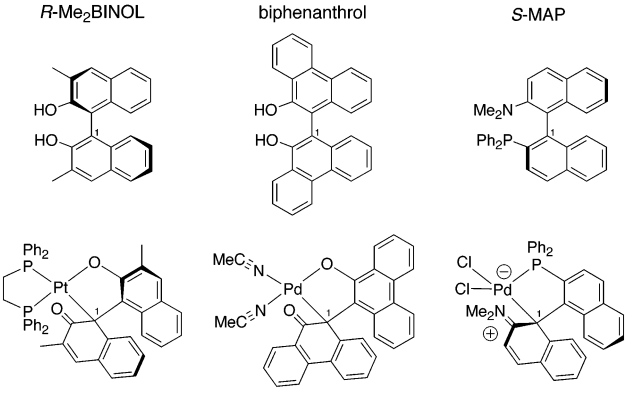
Scheme 1



1 **2**

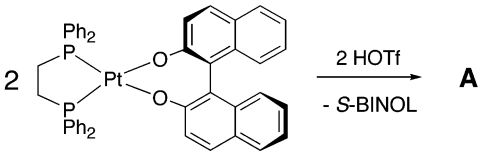
biphenanthrol,[6] and *S*-MAP[7] have all been observed to



tautomerize in order to coordinate to Pd or Pt via M−C rather than M−O or M−N bonds. The unique characteristics of both the ligands and the metals involved in these complexes contribute to observation of the M−C binding mode. For the ligands, the thermodynamic and kinetic accessibility of "keto" or "imino", in addition to "enol" or "enamine", tautomers makes C_1-based reactivity feasible. This reactivity has been demonstrated in organic reactions that take advantage of the anionic character of C_1 in binaphthyl-type substrates as well.[8] The key features of Pd and Pt that promote M−C complexation include their carbophilic natures and their propensities to form five-membered rather than larger metallochelate rings. The driving force for observation of C,O- instead of O,O-chelates has been ascribed to the relief of steric strain that would be present in the expected O,O-bound complexes.[5,6]

In the Diels−Alder experiments discussed above, the nonisolable $P_2Pt(OTf)_2$ Lewis acid catalysts used were routinely generated in situ by adding 2 equiv of triflic acid (HOTf) to the stable precursors P_2Pt(*S*-BINOL) (Scheme 1, P_2 = dppe (**1**)). In the dppe case, a small amount of a nonsymmetric (dppe)Pt species (**A**) was often observed by ^{31}P NMR spectroscopy during the catalyst activation step. To identify this impurity, the complex was synthesized independently, and its structure was investigated by ^{31}P, ^{1}H, $^{13}C\{^{1}H,^{31}P\}$, and 2D $^{13}C/^{1}H$ NMR techniques. These experiments revealed

Scheme 2



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that **A** is an unusual $Pt_2(\mu$-BINOL) dimer containing symmetry-equivalent (dppe)Pt fragments bound via Pt−C σ bonds to adjacent C_1 and $C_{1'}$ carbons of a "diketo" BINOL ligand, in which *both* halves of BINOL have undergone "enol−keto" tautomerization. The "diketo" ligand was identified by comparison of its NMR spectroscopic features with those observed for the "keto" half of Me_2BINOL in the complex (*S*,*S*-chiraphos)Pt(*R*-Me_2BINOL) (**8**).[5]

Results and Discussion

(1) Formation of A from 1 and HOTf. Nonsymmetric species **A**, whose ^{31}P NMR spectrum consists of a pair of sharp doublets (J_{P-P} = 9.0 Hz) with Pt satellites at δ 49.6 ($^{1}J_{P-Pt}$ = 3090 Hz) and 31.8 ($^{1}J_{P-Pt}$ = 3690 Hz) ppm, was initially observed as a minor product of the reaction of (dppe)Pt(*S*-BINOL) (**1**) with HOTf to generate the active Diels−Alder catalyst (dppe)-$Pt(OTf)_2$ (**2**; Scheme 1). Complex **A** formed only when *less than 2* equiv of HOTf was added to **1**, and the **2**:**A** ratio observed varied with the amount of HOTf used in the experiment; for example, 1.95 equiv of HOTf produced about 95% **2** accompanied by 5% **A**, while 1.90 equiv of HOTf gave 90% **2** and 10% **A**. The observed correlation between the reactant and product ratios suggested that **A** might be quantitatively produced by addition of *1* equiv of HOTf to **1**. Indeed, adding 1 equiv of freshly distilled HOTf to a solution of **1** in dry CD_2Cl_2 resulted in 93% conversion to **A** (Scheme 2); an unidentified symmetric species **B** (7%) was also observed as a sharp singlet with Pt satellites at δ 32.8 ppm ($^{1}J_{P-Pt}$ = 3606 Hz) by ^{31}P NMR.

Upon standing in an NMR tube capped with a rubber septum, the yellow **A**/**B** mixture gradually became colorless, starting *from the top* of the reaction solution. Periodic ^{31}P NMR spectra of the mixture revealed that **A** was slowly being converted to **B**, most likely by reaction with oxygen or water that diffused into the NMR tube through the septum. After several days, ^{31}P NMR spectra showed complete transformation of **A** to **B**, and a ^{1}H NMR spectrum of the colorless reaction mixture contained a broad resonance with Pt satellites ($^{2}J_{H-Pt}$ = 7.5 Hz) at δ 2.9 ppm, which integrated for 1 H compared to the Pt-coordinated dppe ligand of **B**. Resonances for free *S*-BINOL were also observed. Symmetric species **B** was identified as the μ-OH dimer $[(dppe)Pt(\mu\text{-}OH)]_2^{2+}[OTf]^-_2$ by comparison with NMR data reported in the literature for $[(dppe)Pt(\mu\text{-}OH)]_2^{2+}$-$[BF_4]^-_2$.[9,10] The BF_4^- analogue of **B** was isolated from the reaction of $(dppe)PtCl_2$ with $AgBF_4$ in MeOH and

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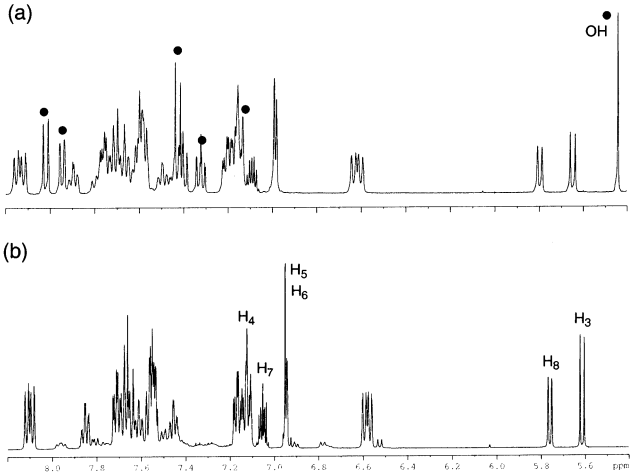


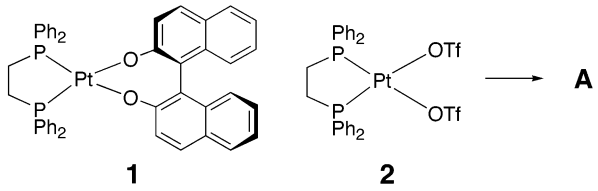
Figure 1. (a) Aromatic region of the 400 MHz ^{1}H NMR spectrum obtained from reaction of **1** with 1 equiv of HOTf in CD_2Cl_2 (Scheme 1), including resonances for **A** and free *S*-BINOL (●). (b) Aromatic region of the 500 MHz ^{1}H NMR spectrum of **A** (93%; 7% **1**, small peaks) produced by "comproportionation" of **1** and **2** (Scheme 2). The BINOL protons of **A** are numbered as shown in Figure 4 (vide infra).

presumably formed via reaction of the unstable Lewis acid "(dppe)Pt$(BF_4)_2$" with adventitious water in the solvent, consistent with the hypothesis that **B** is produced by reaction of water with **A**. The decomposition of **A** to **B** was effectively suppressed by using airtight J. Young NMR tubes for subsequent reactions.

(2) Identification of A as a $Pt_2(\mu$-BINOL) Dimer. A priori, reaction of **1** with a single equivalent of HOTf was expected to produce a nonsymmetric Pt complex containing a monodentate, monoprotonated BINOL ligand (structure **3**). However, the ^{1}H NMR spectrum of **A** was not consistent with **3**, since it lacked the 12 resonances predicted for the nonequivalent protons of the nonsymmetric, monoprotonated BINOL ligand. Instead, the spectrum clearly showed that half of the *S*-BINOL in the reaction mixture was no longer coordinated to Pt at all, while the other half remained bound to Pt in a C_2-symmetric fashion (only six resonances observed for Pt-bound BINOL; Figure 1a)! Furthermore, two doublets assigned to the Pt-coordinated ligand appeared unusually far upfield at δ 5.61 and 5.76 ppm (by contrast, all BINOL resonances appear downfield of 6.55 ppm in the spectrum of **1**). Integration of the resonances for Pt-coordinated BINOL with respect to those assigned to Pt-bound dppe revealed that **A** contains only *one* BINOL per *two* symmetry-equivalent dppe ligands. Thus **A** must be a dimer whose single BINOL ligand symmetrically bridges two chemically equivalent (dppe)Pt centers (e.g., structure **4**). The identity of the fourth ligand (**L**) in the coordination sphere of each square planar Pt(II) center was not obvious from ^{1}H and ^{31}P NMR data (vide infra).

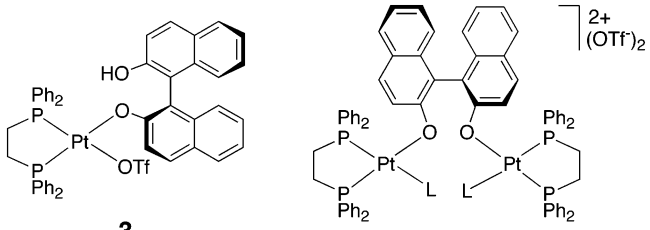
(3) Formation of A from 1 and 2. The stoichiometry of **A** suggested that it might be cleanly prepared (without concomitantly generating an equivalent of free BINOL) by "comproportionation" of **1** and **2** (Scheme 3).

Scheme 3



1 **2**

Indeed, adding 1 equiv of **1** to a CD_2Cl_2 solution of **2** prepared in situ from (dppe)$PtCl_2$ and 2 equiv of AgOTf yielded 93% pure **A**, uncontaminated by free BINOL (7% **1** by ^{31}P NMR; ^{1}H NMR spectrum in Figure 1b).[11] Analogues of **A** with counterions BF_4^-, PF_6^-, and SbF_6^- were also prepared by adding **1** to solutions of (dppe)-$PtCl_2$ and the appropriate silver salts.[12] ^{31}P and ^{1}H NMR spectra of all these complexes were identical, suggesting that the counterions are not closely associated with Pt in **A** and that triflate is therefore not the fourth ligand **L** in the coordination sphere of Pt in structure **4**. Note that crystals of **A** suitable for X-ray diffraction could not be obtained; numerous attempts always yielded **A** as a yellow oil.



3 **4**

The conclusion that **L** ≠ OTf^- was supported by our initial interpretation of the ^{31}P NMR data for **A** as follows. In the ^{31}P NMR spectrum of **A**, the resonance at 31.8 ppm with $^1J_{P-Pt} = 3690$ Hz was initially assigned to phosphorus *trans* to a BINOL oxygen (structure **4**) because its chemical shift and P−Pt coupling constant were similar to those of **1** (δ 27.2, $^1J_{P-Pt} = 3640$ Hz). The magnitude of the P−Pt coupling constant for the other ^{31}P resonance (δ 49.6, $^1J_{P-Pt} = 3090$ Hz) was then considered too small to be consistent with coordination of a ligand that exerts only a weak *trans* influence on phosphorus,[13] such as triflate, water, or even chloride (compare to $^1J_{P-Pt} = 4160$ for (dppe)$Pt(OTf)_2$,[2a] 3950 for $[(dppe)Pt(OH_2)_2]^{2+}[OTf]^-_2$,[2a] 3620 for (dppe)$PtCl_2$[14]). Yet, the coupling constant was too large to account for coordination of a strong *trans* director, such as a

(10) Independent synthesis of **B** from (dppe)$PtCO_3$ and 1 equiv of HOTf yielded pure material, uncontaminated by free BINOL (the byproduct when **B** forms from **A**), which was isolated as a white, air- and moisture-stable solid for characterization purposes.

(11) AgCl, the byproduct when **2** is formed from (dppe)$PtCl_2$ and AgOTf, was always removed from the reaction mixture by filtration before **1** was added to **2** to avoid decomposition of solutions of **A** generated by this route (solutions turned brown and precipitate formed if AgCl was present).

(12) Decomposition of BF_4^-, PF_6^-, and SbF_6^- versions of **A** was often unavoidable, perhaps because $AgBF_4$, $AgPF_6$, and $AgSbF_6$ are somewhat soluble in CD_2Cl_2, precluding complete removal of excess AgX from solution by filtration. Also, unidentified symmetric and asymmetric species other than **A** and **B** were often observed in ^{31}P NMR spectra of these reactions, even before decomposition was evidenced by color changes and precipitate formation.

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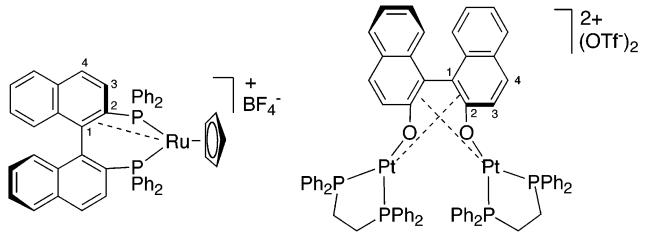
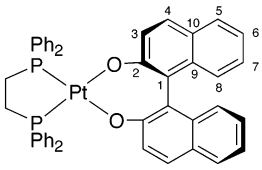
σ-bound alkyl group or phosphine ($^1J_{P-Pt}$ = 1790 for (dppe)$PtMe_2$,[13b] 2270 for $[(S,S\text{-chiraphos})_2Pt]^{2+}[Cl]^-_2$[15]).



5 **6**

Because similar structures had previously been reported by Pregosin[16] and others[17] (for example **5**), we then hypothesized that two of the double bonds of BINOL might coordinate to the Pt centers of dimer **A** in an η^2-fashion, filling the fourth binding site in each Pt square plane (structure **6**).[18] Although few square planar Pt(II) complexes containing an η^2-olefin ligand *trans* to a phosphine (PBu_3) have been observed, the P−Pt coupling constants reported for them (3200−3400 Hz) are similar to those of **A**.[19] Coordination of BINOL double bonds to Pt might also account for the doublets observed at δ 5.61 and 5.76 ppm in the ^{1}H NMR spectrum of **A** (Figure 1), since C═C binding is expected to disrupt the aromaticity of the oxygen-substituted BINOL rings, potentially shifting the ^{1}H NMR resonances for protons on the C_3═C_4 bond (structure **6**) upfield from the aromatic to the alkene region of the spectrum. Although no upfield shift was reported for analogous protons in Pregosin's complex **5**, η^2-coordination of the C_1═C_2 bond of BINAP to Ru was clearly evidenced by characteristic upfield shifts of the ^{13}C NMR resonances for C_1 and C_2 to 88.2 and 56.9 ppm, respectively.[16b] Therefore, ^{13}C NMR data for **A** (obtained via 2D ^{13}C/^{1}H correlation experiments) were examined for evidence of BINOL double-bond coordination to Pt.



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	δ ^{13}C	δ ^{1}H		δ ^{13}C	δ ^{1}H
1	124.9		6	121.2	7.14
2	162.5		7	124.6	7.02
3	125.9	6.56	8	125.2	6.86
4	127.3	7.54	9	135.7	
5	127.7	7.75	10	128.7	

Figure 2. ^{13}C and ^{1}H NMR chemical shifts for the BINOL ligand in (dppe)Pt(*S*-BINOL) (**1**).

(4) Investigation of the Structure of A by 2D NMR. A concentrated solution of **A** (93%; 7% **1**) in CD_2Cl_2 was prepared by the "comproportionation" method (Scheme 3), and one-dimensional $^{13}C\{^1H\}$ and $^{13}C\{^{31}P,^1H\}$ NMR spectra, as well as 2D gradient COSY ($^1H-^1H$ through-bond coupling), HMQC (one-bond $^{13}C-^1H$ coupling), and HMBC (long-range $^{13}C-^1H$ coupling) spectra were acquired. Analogous spectra of a CD_2Cl_2 solution of pure **1** were also acquired and compared with those of the **A**/**1** mixture to identify resonances due to the impurity. All proton resonances in the 1D ^{1}H NMR spectra of **A** and **1** were assigned using the COSY data. Carbon resonances in the $^{13}C\{^{31}P,^1H\}$ spectra were assigned with the aid of HMBC and HMQC data.[16,20] HMBC spectra proved particularly helpful for identifying resonances due to carbons without protons bonded to them, as cross-peaks indicated the coupling of ^{13}C and ^{1}H nuclei separated by three bonds. For example, BINOL C_1 was readily identified via its coupling to H_3 and H_8, while C_2 was distinguished by its coupling to H_4 (see Figure 3 and Supporting Information). Reconciliation of the known structure of **1**[21] with ^{1}H and ^{13}C NMR data was straightforward, producing the ^{1}H and ^{13}C chemical shift assignments listed in Figure 2.[22]

The ^{13}C NMR data for **A**, however, were not consistent with structure **6**. Although a resonance was observed at 89.0 ppm in the ^{13}C NMR spectrum of **A**, in the region expected for a carbon σ-bound to Pt, the second low-field resonance predicted for **6** was missing. Instead, a resonance was unexpectedly observed at 201.5 ppm, in the C═O region of the spectrum! These resonances were assigned via HMBC to BINOL carbons C_1 and C_2, respectively (Figures 3 and 4; structure **7**).[23] Moreover, comparison of the ^{13}C NMR spectrum of **A** with that of (*S*,*S*-chiraphos)Pt(*R*-Me_2BINOL) (**8**), whose Me_2BINOL

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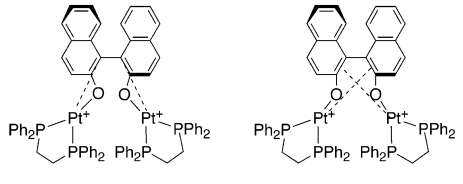
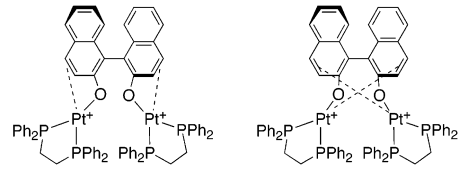
(18) Actually, four different C_2-symmetric structures can be drawn, in which each Pt of dimer **A** coordinates to one double bond of BINOL (**6a**−**d**). The structures differ as to *which* BINOL double bond coordinates to Pt (C_1═C_2 for **6a** and **6b** vs C_3═C_4 for **6c** and **6d**) and whether the double bond binds to the same Pt center as the oxygen nearest it (**6a** and **6c**) or to the other Pt of the dimer (**6b** and **6d**). The gross features of the ^{31}P and ^{1}H NMR data for these structures are expected to be similar.



6a **6b**



6c **6d**

(19) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1987**, 139−143.

(20) Due to extensive coupling of ^{13}C to ^{31}P in $^{13}C\{^1H\}$ spectra, ^{31}P-decoupled ^{13}C spectra proved more tractable.

(21) Brunkan, N. M.; White, P. S.; Gagné, M. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1579−1582.

(22) Only BINOL data are given in Figure 2. See Supporting Information for dppe data.

(23) Pt satellites were not observed for any ^{13}C resonances of **A**, even in ^{31}P-decoupled spectra.

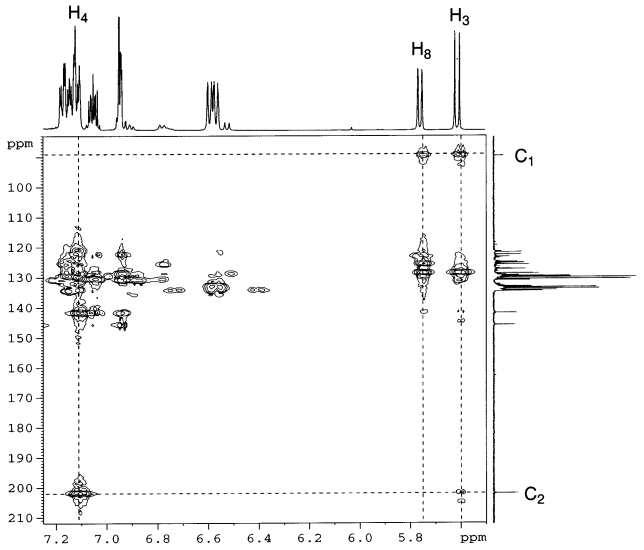
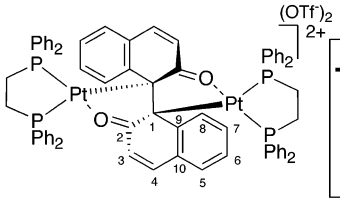


Figure 3. Part of the 500 MHz gradient HMBC spectrum of **A**, showing the coupling of protons three bonds away to C_1 (H_3, H_8) and C_2 (H_4). C_2 also shows weak coupling to H_3, two bonds away. The BINOL protons of **A** are numbered as shown in Figure 4 (vide infra). See Supporting Information for complete ^{13}C and ^1H chemical shift assignments for **A**.

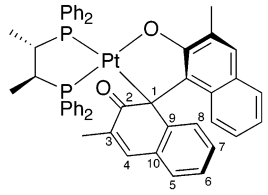


7

	δ ^{13}C	δ ^1H
1	89.0	
2	201.5	
3	122.7	5.61
4	145.2	7.15
5	130.0	6.95

	δ ^{13}C	δ ^1H
6	125.3	6.95
7	130.5	7.05
8	122.0	5.76
9	141.3	
10	128.2	

Figure 4. ^{13}C and ^1H NMR chemical shifts for the "diketo" BINOL ligand in **A**. Structure **7** is consistent with the NMR data for **A**.



8

	δ ^{13}C
1	82.4
2	195.5
4	147.4
9	140.6

Figure 5. ^{13}C NMR chemical shifts for selected carbons of the "keto" half of the Me_2BINOL ligand in (*S*,*S*-chiraphos)Pt(*R*-Me_2BINOL) (**8**).

ligand has undergone "enol−keto" tautomerization, enabling it to bind to Pt in an unusual C,O fashion, revealed that the ^{13}C NMR chemical shifts of *all* the BINOL resonances of **A** (C_1, C_2, C_4, and C_9 are diagnostic) are similar to those of the "keto" half of Me_2BINOL in **8** (Figure 5).[5] Note that the structures of both **8** and the related C,O-bound complex (dppe)-Pt(*R*-Me_2BINOL) (pictured in the Introduction section, vide supra) have been determined by X-ray crystallography, unequivocally documenting the tautomerization of 3,3′-Me_2BINOL and its C,O-coordination to the P_2Pt center.[5]

Remarkably, both C_2-symmetric halves of BINOL have apparently undergone "enol−keto tautomerization" in **A**, destroying the aromaticity of both oxygen-substituted BINOL rings. Thus the $C_3{=}C_4$ bond of the modified ligand is olefinic rather than aromatic; however, only one of the protons on this double bond is shifted upfield from the aromatic to the alkene region in the ^1H NMR spectrum of **A** (H_3, 5.61 ppm; Figure 1b). The other upfield resonance (5.76 ppm) in the proton spectrum is assigned (via COSY data) to H_8, one of the protons on the back, still-aromatic ring of the modified BINOL ligand (Figure 4). Although highly unusual, this chemical shift for H_8 is consistent with ^1H NMR data observed for the analogous proton on the "keto" half of Me_2BINOL in the C,O-bound complexes **8** and (dppe)Pt(*R*-Me_2BINOL) (H_8 resonances are doublets at 5.75 and 5.80 ppm, respectively).[24] The upfield shift of H_8 in these Pt-"keto-BINOL" complexes could arise from shielding by a well-organized π-stack between one of the P−Ph groups of dppe and the back BINOL ring (see X-ray structure of **8**)[5] or may reflect the electronic consequences of Pt σ-coordination to C_1, only three bonds away from it. In any case, observation of the characteristic upfield shift of H_8 in the ^1H NMR spectrum of **A** strongly supports the "diketo" structure assigned to the bridging BINOL ligand in structure **7**.

The 89.0 ppm ^{13}C NMR chemical shift observed for C_1 clearly indicates coordination to Pt via a Pt−C σ bond. Additionally, the symmetry of dimer **A** requires that *both* the adjacent, equivalent carbons C_1 and $C_{1'}$ of "diketo" BINOL are coordinated to chemically equivalent (dppe)Pt fragments.[25] Steric as well as symmetry considerations dictate that these (dppe)Pt moieties bind in an *anti* fashion to opposite faces of the "diketo" ligand (structure **7**). The fact that no other carbon resonances (besides C_1) of BINOL or dppe exhibit upfield shifts in the ^{13}C NMR spectrum precludes π-coordination of ligand C=C bonds to Pt in **A**. Instead, η^1-coordination of the carbonyl groups of "diketo" BINOL to Pt through the oxygen atoms is proposed to fill the fourth coordination site of each Pt(II) center, forming favorable five-membered metallochelate rings (structure **7**). Coordination of the C=O moiety to Pt is expected to be more sterically viable, as well as more thermodynamically favorable,[26] than OTf^- binding. η^2-Binding of $C_2{=}O$ to Pt in **A** is deemed unlikely because C_2 in **A** resonates *downfield* of C_2 in the "keto" half of the BINOL ligand in **8**, rather than exhibiting the significant upfield ^{13}C NMR shift characteristic of a metal-bound carbon atom.

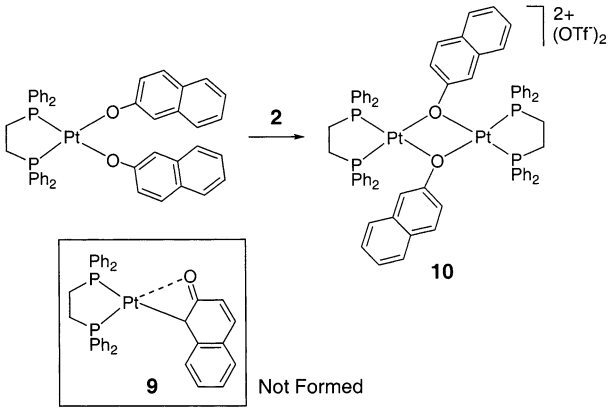
By comparison with the ^{31}P NMR spectra of **8** and the related C,O-bound complex (dppe)Pt(*R*-Me_2BINOL), in which the phosphorus *trans* to the σ-bound carbon of the "keto" half of Me_2BINOL resonates at δ 48.7 ($^1J_{P-Pt}$ = 2440 Hz) or δ 46.4 ppm ($^1J_{P-Pt}$ = 2510 Hz), respectively,[5] the resonance at δ 49.6 ppm ($^1J_{P-Pt}$ = 3090 Hz) in the ^{31}P NMR spectrum of **A** was assigned to the phosphorus *trans* to σ-bound C_1 of "diketo" BINOL. The fact that the Pt coupling of P *trans* to C_1

(24) See the Supporting Information from ref 5.

(25) We also considered a monomeric (dppe)Pt("keto-2-naphthol") structure (**9**), which could be formed by cleavage of the $C_1{-}C_{1'}$ bond of BINOL, for **A**; however, this structure was incompatible with the ^1H NMR data for **A** (no H_1 resonance was observed) and with the fact that exposing **A** to water generates free BINOL. Subsequent attempts to prepare **9** from (dppe)Pt$(ONp)_2$ and **2** were unsuccessful (vide infra).

(26) Complexes of the dicarbonyl chelates *N*-acryloyloxazolidinone and Diels−Alder adduct (eq 1) with $[P_2Pt]^{2+}$ are more thermodynamically stable than $P_2Pt(OTf)_2$, suggesting that C=O binds more strongly to Pt than OTf^-.[2a]

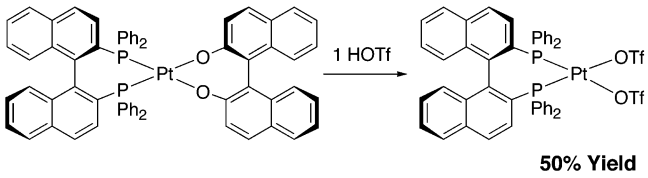
Scheme 4



in **A** is 580−650 Hz larger than that of the analogous phosphorus in the previously observed complexes indicates that the Pt−C bond is weaker in **A** than in C,O-bound species such as **8**.[13] This disparity can be attributed to coordination of the C_1-bound enolate carbonyl group in **A** to a Lewis acidic Pt center, which inductively withdraws electron density from the carbonyl group and C_1, leaving less electron density in the Pt−C_1 bond. The resonance at δ 31.8 ppm ($^1J_{P-Pt}$ = 3690 Hz) in the ^{31}P NMR spectrum of **A** was then assigned to the phosphorus *trans* to the Pt-coordinated carbonyl group. The fact that the Pt coupling for P *trans* to O=C is 300−420 Hz smaller than the coupling constants previously measured for $[(dppe)Pt(L)]^{2+}[OTf]^-_2$ complexes containing bidentate, η^1-bound dicarbonyl ligands (L = *N*-acryoyloxazolidinone, Diels−Alder adduct (see eq 1))[2a] suggests that the carbonyl groups of **A** bind more strongly to Pt than those in other complexes.[13] This behavior reflects the enolate nature of the carbonyl group in **A**, as the partial anionic charge (δ^-) on its neighbor C_1 inductively increases electron density on the carbonyl oxygen, enabling greater O→Pt σ-donation.

In complex **8**, minimization of steric conflict between the methyl groups of 3,3′-Me_2BINOL and the phenyl groups of the conformationally unyielding *S*,*S*-chiraphos ligand was postulated to trigger the enol−keto tautomerization of BINOL and formation of Pt−C bonds.[5] However, the reasons for "double BINOL tautomerization" and formation of dimeric structure **A** are less obvious. To explore the generality of structures such as **A**, we tried to prepare analogues of the complex; however, no other species like **A** were observed. For example, attempts to make a monomeric version of **A** containing the ligand 2-naphthol (ONp) rather than binaphthol (structure **9**), by reaction of $(dppe)Pt(ONp)_2$ with **2**, did not lead to ONp tautomerization (Scheme 4). Instead, a new yellow species (**10**) with a symmetric ^{31}P NMR spectrum (s, δ 36.1, $^1J_{P-Pt}$ = 3830 Hz) was obtained. The ^{1}H NMR spectrum of **10** contained resonances for Pt-coordinated NpO and dppe ligands in a 1:1 ratio, but was devoid of resonances upfield of 6.0 ppm. A $^{13}C\{^{31}P,^1H\}$ spectrum of **10** also displayed resonances for only the usual "enol" form of a Pt-naphtholate. On the basis of these NMR data, **10** was tentatively identified as the dimer $[(dppe)Pt(\mu\text{-ONp})]_2^{2+}[OTf]^-_2$.[27,28] Also, efforts to generate an *R*-BINAP analogue of **A** by addition of 1 equiv of HOTf to (*R*-BINAP)Pt(*S*-BINOL) instead merely produced

Scheme 5



50% (*R*-BINAP)$Pt(OTf)_2$ and 50% starting material (Scheme 5).

Summary and Conclusions

A novel $[(dppe)_2Pt_2(\mu\text{-BINOL})]^{2+}[OTf]^-_2$ dimer (**A**) can be cleanly produced by addition of 1 equiv of HOTf to (dppe)Pt(*S*-BINOL) (**1**) or via "comproportionation" of **1** with $(dppe)Pt(OTf)_2$ (**2**). ^{1}H, ^{31}P, and ^{13}C NMR data for **A**, as well as 2D ^{1}H/^{1}H and ^{13}C/^{1}H correlation experiments, revealed that both halves of the bridging BINOL ligand have undergone "enol−keto" tautomerization in this complex. Two symmetry-equivalent (dppe)Pt fragments coordinate in an *anti* fashion via Pt−C σ bonds to the adjacent atoms C_1 and $C_{1'}$ of the resulting "diketo" BINOL ligand. η^1-Coordination of the carbonyl groups of "diketo" BINOL to Pt is proposed to fill the fourth coordination site of each Pt square plane in dimer **A**, generating favorable five-membered Pt-chelate rings.

The reasons for enol−keto tautomerization and formation of Pt−C bonds in **A** are not as straightforward as in the case of **8** (minimization of steric strain). However, we postulate that the driving force behind the formation of dimer **A** is primarily electrostatic in nature. In other words, formation of a dinuclear, BINOL-bridged structure from **1** and **2** occurs largely because this structure allows the +2 charge localized on the electron-deficient Pt center of **2** to be distributed throughout the entire dimer (two Pt centers plus the bridge) in **A**. The energetic advantages of this arrangement clearly outweigh the unfavorable entropic costs of dimerization (in the dppe case; steric constraints must prove prohibitive in the *R*-BINAP case, since an *R*-BINAP analogue of **A** was not observed). Furthermore, enol−keto tautomerization of BINOL substantially lowers the enthalpic costs of the dimerization reaction, as two weak Pt−O bonds and an unfavorable seven-membered metallochelate in **1** are replaced by two strong Pt−C σ bonds and two five-membered chelate rings in **A**, while two stronger C=O→Pt interactions replace the very weak Pt−OTf bonds of **2**. Finally, reaction of **2** with the relatively stable species **1** to produce **A** again demonstrates that **2** acts as a strong Lewis acid whose Pt^{2+} center is highly electrophilic and extremely reactive.

The fact that **A** forms only when *less than 2* equiv of HOTf are added to **1** during generation of the Pt Lewis acid catalyst **2** (Scheme 1) also proved useful during Diels−Alder experiments (eq 1).[2] Because HOTf itself is a highly reactive (albeit nonselective) Brønsted acid that catalyzes the Diels−Alder reaction far more efficiently than $[P_2Pt]^{2+}$,[29] even very small amounts of

(27) A similar $Pd_2(\mu\text{-OAr})_2$ dimer has been reported: Ruiz, J.; Marti, J. M.; Florenciano, F.; López, G. *Polyhedron* **1999**, *18*, 2281−2285.

(28) Formation of **9** is less favorable than formation of **A** both because the "keto" tautomer of NpOH is less accessible than the "keto" tautomer of BINOL[8b] and because η^1-coordination of the C=O group to Pt in **9** would yield a sterically strained four-membered chelate ring, rather than the five-membered chelate of **A**.

HOTf present in a catalytic reaction mixture may significantly enhance Diels–Alder reaction rates. Observation (by ^{31}P NMR) of small amounts of **A** (<3%) in solutions of **2** ensured that no excess HOTf was added to **1** during catalyst activation, making it certain that acceleration of Diels–Alder reactions involving **2** stemmed entirely from catalysis by **2** and decomposition products thereof.[2b]

Finally, the observation of M–C bonds in **A** demonstrates once again that the potential for C- rather than O-based coordination to Pt or Pd must be kept in mind when considering the reactivity of organometallic P_2Pt/Pd complexes, particularly when ligand tautomerization is possible.[2,4,7]

Experimental Section

General Methods. All chemicals except *R*-BINAP, dppe, and silver salts AgOTf, $AgBF_4$, $AgPF_6$, and $AgSbF_6$ (Strem) were purchased from Aldrich. *S*-BINOL (>98% ee) was obtained by resolution of *rac*-BINOL with *N*-benzylcinchonidinium chloride.[30] The silver salts AgX were dried in vacuo at room temperature for at least 24 h prior to use and stored under N_2 (AgOTf at −35 °C). HOTf was distilled under static vacuum (35 °C/30 mTorr), giving a colorless liquid that was stored in a glass-capped Schlenk flask under N_2 and redistilled at the first hint of color. CD_2Cl_2 was vacuum transferred from CaH_2 and stored under N_2. Pt complexes (dppe)$PtCl_2$,[14] (dppe)$PtCO_3$,[31] (dppe)Pt(*S*-BINOL) (**1**),[21] and (*R*-BINAP)Pt(*S*-BINOL)[32] were prepared according to literature protocols and were dried in vacuo at 55 °C overnight before use to remove traces of water.

All reactions were performed under N_2 in an MBraun LabMaster 100 glovebox. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer; $^{13}C\{^{31}P,^1H\}$ NMR spectra were recorded on a Bruker AMX 300 MHz instrument; 2D gradient COSY, NOESY, HMQC, and HMBC spectra were recorded on a Bruker Avance 500 MHz spectrometer. Chemical shifts are given in ppm and referenced to residual solvent peaks (^1H and ^{13}C NMR) or to an external standard (85% H_3PO_4, ^{31}P NMR).

Formation of A from 1 and HOTf. A solution of **1** (12.7 mg, 13.2 mmol) in CD_2Cl_2 was prepared in the glovebox in an NMR tube capped with a rubber septum. Outside the glovebox, HOTf (1.2 μL, 13.6 μmol) was added through the septum using a 10 μL syringe. A $^{31}P\{^1H\}$ NMR spectrum of the yellow reaction mixture showed 93% **A** (d δ 49.6, $^2J_{P-P}$ = 9.0 Hz, $^1J_{P-Pt}$ = 3090 Hz, *trans* to C_1; d δ 31.8, $^2J_{P-P}$ = 9.0 Hz, $^1J_{P-Pt}$ = 3690 Hz, *trans* to C_2=O) and 7% $[(dppe)Pt(\mu\text{-}OH)]_2^{2+}[OTf]^-_2$ (**B**; s, δ 32.8, $^1J_{P-Pt}$ = 3606 Hz). One equivalent of free *S*-BINOL was observed by ^1H NMR (Figure 1a).

Formation of $[(dppe)Pt(\mu\text{-}OH)]_2^{2+}[OTf]^-_2$ from (dppe)$Pt(CO_3)$ and 1 Equiv of HOTf. Using the same procedure for generation of **A** from **1**, $[(dppe)Pt(\mu\text{-}OH)]_2^{2+}[OTf]^-_2$ (**B**) was generated from 12.5 mg of (dppe)$PtCO_3$ (19.1 μmol) and 1.7 μL of HOTf (19.2 mmol) in quantitative yield by ^{31}P NMR.

Formation of A by "Comproportionation" of 1 and 2. In the glovebox, (dppe)$PtCl_2$ (34.3 mg, 51.6 μmol) and AgOTf (27.3 mg, 106.3 μmol) were combined in CD_2Cl_2 to generate **2**. The reaction mixture (a suspension of white solid in colorless solution) was stirred for 30 min, and the insoluble byproduct AgCl was removed by filtration. The filtrate was added to yellow solid **1** (49.9 mg, 51.8 μmol) in a J. Young NMR tube, which was sealed with a Teflon stopcock and shaken until all the solid dissolved, producing a dark yellow solution. A ^{31}P NMR spectrum of the reaction mixture showed 93% **A** and 7% residual **1**. The sample was used for 1D $^{13}C\{^1H\}$ and $^{13}C\{^{31}P,^1H\}$ and 2D NMR experiments; no decomposition was observed over 7 days.

Reaction of (dppe)$Pt(ONp)_2$ with 2. As described for preparation of **A** from **1** and **2**, a CD_2Cl_2 solution of **2** prepared from (dppe)$PtCl_2$ (7.9 mg, 11.9 μmol) and AgOTf (9.4 mg, 36.6 mmol) was added to yellow solid (dppe)$Pt(ONp)_2$[33] (10.8 mg, 12.3 μmol), producing a yellow solution. ^{31}P NMR showed quantitative formation of a symmetric Pt complex (δ 36.1, $^1J_{P-Pt}$ = 3830 Hz).

Reaction of (*R*-BINAP)Pt(*S*-BINOL) with 1 Equiv of HOTf. Using the same procedure for generation of **A** from **1**, 1.3 μL of HOTf (14.7 μmol) was added to 16.0 mg of (*R*-BINAP)Pt(*S*-BINOL) (14.5 mmol) in CD_2Cl_2, producing a yellow solution. ^{31}P NMR showed 50% (*R*-BINAP)$Pt(OTf)_2$ and 50% (*R*-BINAP)Pt(*S*-BINOL).[34]

Acknowledgment. We thank the NIH (Grant No. GM60578), the Petroleum Research Fund, administered by the American Chemical Society, and Union Carbide for support of this research. N.M.B. also thanks the UNC Board of Governors and the ACS Division of Organic Chemistry (as well as sponsor Rohm and Haas) for Graduate Fellowships. M.R.G. is a Camille-Dreyfus Teacher-Scholar (2000–2004).

Supporting Information Available: Tables of complete ^1H and ^{13}C NMR chemical shifts for **1** and **A**; $^1H/^1H$ correlations (from COSY data) for **1** and **A**; one-bond $^{13}C/^1H$ correlations (from HMQC data) for **1** and **A**; long-range $^{13}C/^1H$ correlations (from HMBC data) for **1** and **A**. Experimental details of the synthesis of (dppe)$Pt(ONp)_2$ (**7**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) At 195 K, complete conversion is attained in <5 min when 10 mol % HOTf is used to catalyze the Diels–Alder reaction in eq 1, whereas $[P_2Pt]^{2+}$-catalyzed reactions require several hours to reach completion under identical conditions.[2]

(30) Cai, D.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *Tetrahedron Lett.* **1995**, *36*, 7991–7994. Also, note that using *rac*-BINOL rather than *S*-BINOL for the experiments described in this paper gave identical results.

(31) Andrews, M. A.; Gould, G. L.; Klooster, W. T.; Koenig, K. S.; Voss, E. J. *Inorg. Chem.* **1996**, *35*, 5478–5483.

(32) See the Supporting Information from ref 2a.

(33) See the Supporting Information for preparation of (dppe)Pt(ONp)$_2$.

(34) Reference 2a contains NMR data for these complexes.