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Sterically Congested Ligands: Synthesis and Spectral Characterization of the First Pd(II) and Pt(II) Complexes of Tetra-t-butyl-substituted Biaryloxybis(1,3,2-oxazaphospholidines)

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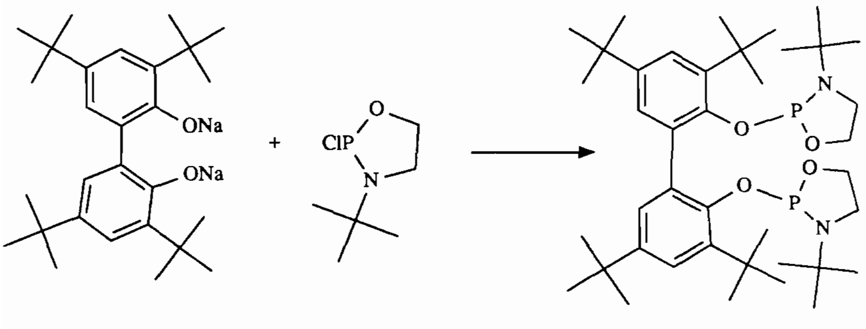
Sterically hindered trivalent phosphorus ligands are capable of providing unique coordination spheres for transition-metal-mediated reactions. Indeed, sterically hindered dibenzo[*d,g*][1,3,2]dioxaphosphocins and dibenzo[*d,f*][1,3,2]dioxaphosphepins [1] have recently been claimed to be superior ligands in transition-metal-catalyzed hydroformylation reactions [2]. Particularly interesting is the design of sterically encumbered ligands to either impart kinetic stabilization to coordinately unsaturated complexes or to control the reactivity of metal complexes [3]. Quite recently, we reported the synthesis and characterization of several hexa-t-butyl-substituted biaryloxybis(1,3,2-oxazaphospholidines) that possess intriguing spectral properties [4]. In the $^{31}P\{^1H\}$ NMR of **1**, the phosphorus atoms were observed to be chemically non-equivalent with an unprecedented seven-bond P–P coupling constant, $^7J_{PP} = 30.3$ Hz. Furthermore, of the three possible diastereomers of **1** (each of which is an enantiomeric pair) that can be formed by the reaction of **2** with **3**, only one is obtained**. The molecular structure and relative configuration of **1**, which contains two stereogenic phosphorus atoms and an axis of symmetry, were determined previously by an X-ray crystal structure. Both the observed diastereoselectivity and the spectral properties of **1** were attributed to severe geometric restraints within the molecule [4]. We report herein the first synthesis and spectral characterization of Pd(II) and Pt(II) complexes of the sterically hindered oxazaphospholidine **1**.

Experimental

All melting points were determined in open capillary tubes and are uncorrected. ^1H (300.133 MHz) and ^{31}P (121.496 MHz) NMR spectra were taken on a Bruker FT NMR spectrometer. ^{31}P NMR spectra were obtained with full proton decoupling. All ^1H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. Reagents were purchased from commercial laboratory supply houses. Solvents were dried and purged with argon prior to use. Benzene was dried either through a column of activated alumina or over sodium/lead alloy. Hexane was dried over sodium/lead alloy. Reactions were carried out in dried apparatus under a dry inert atmosphere of argon using standard Schlenk and inert atmosphere techniques. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY AG.

Dichloro[2,2'-[[3,3',5,5'-tetrakis(1,1-dimethylethyl)-[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis[3-(1,1-dimethylethyl)-1,3,2-oxazaphospholidine]]-palladium(II) (4)

To a mixture of 390 mg (0.55 mmol) of **1** and 130 mg (0.5 mmol) of bis(acetonitrile)palladium(II) chloride cooled with a ice bath was added dropwise 5 ml of benzene. The reaction mixture was allowed



2 **3** **1**

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The two phosphorus atoms of **1 are observed to be chemically non-equivalent in both the solid state (X-ray crystal structure) and in solution (NMR time scale) due to conformational differences imposed by the steric congestion within the molecule. As a result of the lower symmetry, four possible diastereomers (see ref. 4) are, in principle, possible.

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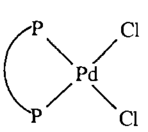
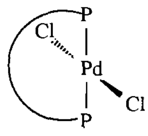
to warm to room temperature and the heterogeneous mixture was stirred at room temperature for 3 days. The solvent was removed *in vacuo* and the residue was triturated with hexane to give 310 mg (70%) of a bright yellow powder, melting point 201 °C (dec); ^{31}P NMR ($CDCl_3$)[minor isomer] δ 74.6 (d, upfield half of AB q, $^2J_{PPdP'} = 129.7$ Hz), 90.5 (d, downfield half of AB q); [major isomer] δ 94.9 (d, upfield half of AB q, $^2J_{PPdP'} = 62.7$ Hz), 100.5 (d, downfield half of AB q); MS *m/e* 875, 876, 877, 878, 879, 880, 882 ($M^{+\cdot}$). *Anal.* Calc. for $C_{40}H_{66}Cl_2N_2O_4P_2Pd$: C, 54.71; H, 7.58; N, 3.19. Found: C, 54.59; H, 7.28; N, 2.98%.

The reaction was repeated using a 20 mole percent excess of **1** (27 h reaction time) to give only the major isomer above; ^{31}P NMR ($CDCl_3$) δ 94.9 (d, upfield half of AB q, $^2J_{PPdP'} = 62.7$ Hz), 100.5 (d, downfield half of AB q); ^1H NMR (C_6D_6) δ 1.10 (s, $C(CH_3)_3$, 9 H), 1.13 (s, $C(CH_3)_3$, 9 H), 1.15 (s, $C(CH_3)_3$, 9 H), 1.57 (s, $C(CH_3)_3$, 9 H), 1.60 (s, $C(CH_3)_3$, 9 H), 1.69 (s, $C(CH_3)_3$, 9 H), 2.44 (m, 2 H), 2.52 (m, 1 H), 3.01 (m, 2 H), 3.16 (dt, 1 H), 4.14 (m, 1 H), 4.51 (m, 1 H), 6.91 (d, $^4J_{HC=C-CH} = 2.5$ Hz, 1 H), 7.00 (d, $^4J_{HC=C-CH} = 2.5$ Hz, 1 H), 7.57 (d, $^4J_{HC=C-CH} = 2.5$ Hz, 1 H), 7.60 (d, $^4J_{HC=C-CH} = 2.5$ Hz, 1 H).



cis-**4**

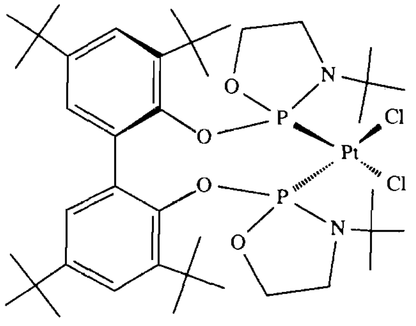


trans-**4**

where  is ligand **1**

Dichloro[2,2′-[[3,3′,5,5′-tetrakis(1,1-dimethylethyl)-[1,1′-biphenyl]-2,2′-diyl]bis(oxy)]bis[3-(1,1-dimethylethyl)-1,3,2-oxazaphospholidine]]-platinum(II) (5)

To a mixture of 350 mg (0.5 mmol) of **1** and 190 mg (0.5 mmol) of dichloro(1,5-cyclooctadiene)-platinum(II) [5] cooled with an ice bath was added dropwise 5 ml of benzene. The reaction mixture was allowed to warm to room temperature and the heterogeneous mixture was stirred at room temperature for 72 h during which time the reaction became homogeneous. The solvent was removed *in vacuo* and the residue was triturated with hexane (3 X 3 ml) to give 360 mg (75%) of a white powder, melting point 260 °C (dec); ^{31}P NMR (benzene-d_6) δ 73.1 (d, upfield half of AB q, $^1J_{PPt} = 5668.1$ Hz; $^2J_{PPtP'} = 26.4$ Hz), 81.0 (d, downfield half of AB q, $^1J_{P'Pt} = 5667.2$ Hz, $^2J_{PPtP'} = 26.4$ Hz); ^{195}Pt satellites observed at δ 49.8 (d), 96.4 (d) [upfield pair] and δ 57.7 (d), 104.3 (d) [downfield pair]; ^1H NMR (benzene-d_6) δ 1.06 (s, $C(CH_3)_3$, 9 H), 1.15 (s, $C(CH_3)_3$, 9 H), 1.18 (s, $C(CH_3)_3$, 9 H), 1.55 (s, $C(CH_3)_3$, 18 H), 1.70 (s, $C(CH_3)_3$, 9 H), 2.43 (m, 2 H), 2.62 (m, 1 H), 2.86 (m, 1 H), 3.01 (m, 2 H), 4.01 (m, 1 H), 4.31 (m, 1 H), 6.89 (d, 1 H), 7.00 (d, 1 H), 7.53 (d, 1 H), 7.58 (d, 1 H); ^1H NMR ($CDCl_3$) δ 1.03 (s, $C(CH_3)_3$, 9 H), 1.20 (s, $C(CH_3)_3$, 18 H), 1.51 (s, $C(CH_3)_3$, 9 H), 1.59 (s, $C(CH_3)3$, 9 H), 1.61 (s, $C(CH_3)_3$, 9 H), 2.83 (m, 1 H), 3.08 (m, 1 H), 3.26 (m, 2 H), 3.43 (m, 2 H), 4.54 (m, 2 H), 6.79 (d, 1 H), 6.83 (d, 1 H), 7.50 (d, 2 H). *Anal.* Calc. for $C_{40}H_{66}Cl_2N_2O_4P_2Pt$: C, 49.69; H, 6.88; N; 2.90. Found: C, 49.35; H, 6.92; N, 2.97%.



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Results and Discussion

The tetra-t-butyl-substituted oxazaphospholidine **1** was prepared by the reaction of the disodium bis-phenolate **2** with the phosphorochloramidite **3** as previously described [4]. The reaction of **1** with bis-(acetonitrile)palladium(II) chloride in benzene gave two compounds whose spectral data are consistent with a mixture of *cis* and *trans* isomers of **4**. In the $^{31}P\{^1H\}$ NMR spectrum of the mixture, two AB quartets were observed with two bond P–P coupling of 129.7 and 61.9 Hz, respectively. As in the free ligand **1**, the phosphorus atoms are observed to be chemically non-equivalent. The resonance of the major isomer present was assigned the *cis* structure based upon the generally observed correlation that the isomer with the smaller coupling constant ($^2J_{PPdP'} = 61.9$ Hz) generally has the *cis* configuration [6]. The signs of the observed $^2J_{PP}$ coupling constants were not determined, however, Verkade *et al.* [6] have shown that the sign of $^2J_{PP}$ can be different for the *cis* and *trans* complexes. The upfield chemical shift observed in the $^{31}P\{^1H\}$ NMR of **4** and the corresponding platinum complex, *vide infra*, relative to the uncomplexed ligand **1** is similar to that observed by Verkade for phosphite ligands and opposite to that generally observed for phosphine ligands [6].

The reaction of bis(acetonitrile)palladium(II) chloride with a 20 mole percent excess of **1** gave exclusively the *cis* complex. Consistent with the observation of non-equivalent phosphorus atoms in the ^{31}P NMR spectrum of *cis*-**4**, in the ^{1}H NMR of the pure *cis* complex, six resonances were observed that were assigned to the protons of the six non-equivalent t-butyl groups. Similarly, four distinct resonances were observed for the non-equivalent aromatic protons.

The pure *cis* compound, which was a bright yellow solid, was stable in the solid state, but a solution of **4** rapidly darkened to give an orange–red solution when exposed to atmospheric oxygen. Examination of the $^{31}P\{^{1}H\}$ NMR spectrum of the solution exposed to oxygen suggested that the phosphorus atoms had been rapidly oxidized, as evidenced by the disappearance of the doublet resonances at δ 94.9 and δ 100.5 and the appearance of new resonances at δ 67.5 and δ 12.5*.

The reaction of **1** with dichloro(1,5-cyclooctadiene)platinum(II) gave the platinum complex **5**. In the ^{1}H NMR of **5**, six upfield resonances were observed that were assigned to the protons of the six non-equivalent t-butyl groups. In the $^{31}P\{^{1}H\}$ NMR spectrum of **5** in deuteriobenzene, two phosphorus resonances were observed that were coupled both to each other and to ^{195}Pt. The appropriate coupling constants in the $^{31}P\{^{1}H\}$ NMR spectrum are $^{2}J_{PP'}$ = 26.7 Hz, $^{1}J_{PPt}$ = 5667.2 Hz and $^{1}J_{P'Pt}$ = 5668.1 Hz. The observed P–P ^{2}J coupling constant was the same in both deuteriochloroform and deuteriobenzene, whereas a small solvent-induced change in chemical shift was observed ($\Delta\delta = 5$ ppm). The P–^{195}Pt ^{1}J coupling constants were found to be slightly larger in deuteriochloroform (5788.7 and 5749.9 Hz, respectively). The observation of a small change in chemical shift with a significantly larger variation in $^{1}J_{PPt}$ is similar to that reported by Dixon *et al.*, which was suggested to be the result of solvation effects due to a weak solvent interaction with the d_{z^2} orbital on platinum [8]**.

The small $^{2}J_{PP}$ coupling and large values of the $^{1}J_{PPt}$ coupling strongly suggest a *cis* geometry for the phosphorus ligands [6, 9]. A *cis* geometry is also consistent with both the tendency of Pt(II) to form *cis* complexes with bidentate phosphorus ligands [10] and the larger radius of Pt(II) compared to Pd(II). Caution must be taken with regard to this assignment, however, because exceptions are known due to the geometric requirements and the *trans* influence of the ligands as in, for example, the *trans* spanning ligands studied by Vernanzi *et al.* [11]. The magnitude of the $^{1}J_{PPt}$ coupling is quite large and unusual for Pt(II) complexes, although isolated cases of similar magnitude are known in the literature [11b–13].

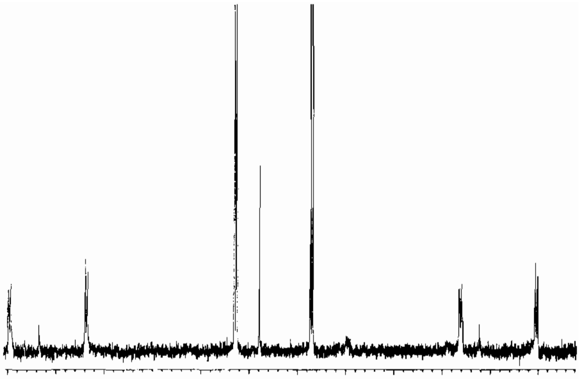

Fig. 1. $^{31}P\{^{1}H\}$ spectrum of **5**.

A large Pt–P ^{1}J coupling constant often reflects a high percentage of s character in the phosphorus orbital bonded to platinum [14]. Given the assumption that pyramidal geometry is achieved when the sum of the requisite bonds are near 270°, both phosphorus atoms of **1** in the solid state approach a pyramidal structure because the sum of the appropriate bond angles is close to 292° for each phosphorus atom [4]. If the geometry of the phosphorus atom in the Pt(II) complex **5** is similar to that in the free ligand **1** (in the solid state), a high degree of s character would be expected in the phosphorus orbital that contains the non-bonded pair of electrons used to bond to platinum. Efforts are currently underway to obtain an X-ray crystal structure of these complexes and investigate their chemistry.

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*For the ^{31}P chemical shift of a 1,3,2-oxaphospholidine *P*-oxide, see ref. 7.

**For a discussion of the effect of solvents on ^{195}Pt chemical shifts, see ref. 8b.

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