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A Zwitterionic Palladium(II) η^3-Boratoxypentadienyl Complex: Cooperative Activation of Dibenzylideneacetone between Palladium and a Phosphine/Thioether/Borane Ligand

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*Summary: A free phosphine/thioether/borane ligand (**5**) suitable to position a Lewis acidic borane in close proximity to a coordinated late transition metal has been prepared. Reaction with 0.5 [$Pd_2(dba)_3$] gave a zwitterionic palladium(II) η^3-boratoxypentadienyl complex with the empirical formula [Pd(dba)(**5**)].*

Molecules which contain both a group 13 Lewis acid and a Lewis base have recently received increased interest, largely due to their photophysical and nonlinear optical properties or potential as cooperative Lewis acid and Lewis base catalysts for organic transformations. For the former application, the Lewis acid is typically rendered unreactive with the use of extremely bulky (usually 2,4,6-trimethylphenyl (Mes)) substituents.[1] In the latter applications, various molecules have been prepared, but many suffer from inter- or intramolecular Lewis acid−Lewis base adduct formation which can shut down reactivity,[2−4] and those which do not employ either a poor Lewis base (e.g. a triarylamine) or a relatively poor Lewis acid (e.g. $ArB(OR)_2$) to circumvent such problems.[3,5] Exceptions are bis- and tris(2-thienyl)boranes,[6] 1-phenylthieno[3,4-*d*]borepin,[7] bis(*o*-(diisopropylphosphino)phenyl)phenylborane,[8] and boron-containing polythiophenes reported recently by Jäkle et al.[9] Several Lewis acid−Lewis base molecules have also been proposed as in situ generated bifunctional catalysts, but the exact nature of these complexes has not been established.[10]

We are interested in the preparation of Lewis acid−Lewis base molecules as ligands suitable to position a strongly Lewis acidic group in close proximity to a coordinated late transition metal. Once in the coordination sphere of the metal, the borane can be expected to interact either with the metal to form a rare[8,11] transition-metal borane complex ($M \rightarrow BR_3$) or with coligands, resulting in their coordination, abstraction, or activation. To this end, 2,7-di-*tert*-butyl-5-(diphenylboryl)-4-(diphenylphosphino)-9,9-dimethylthioxanthene (**5**) (Scheme 1), which incorporates a phosphine, a thioether, and a borane group in a rigid chelating framework, was prepared. A molecule containing two donor groups was chosen to ensure that a coordinated metal is positioned in close proximity to the pendant borane, and phenyl substituents on boron and phosphorus were chosen to prevent intramolecular adduct formation as well as impart sufficient Lewis acidity to the borane.[12]

Ligand **5** was prepared in five steps from commercially available thioxanthone (Scheme 1). Reaction of thioxanthone with $AlMe_3$ in toluene gave 9,9-dimethylthioxanthene (**1**) in a manner analogous to the preparation of 9,9-dimethylxanthene.[13]

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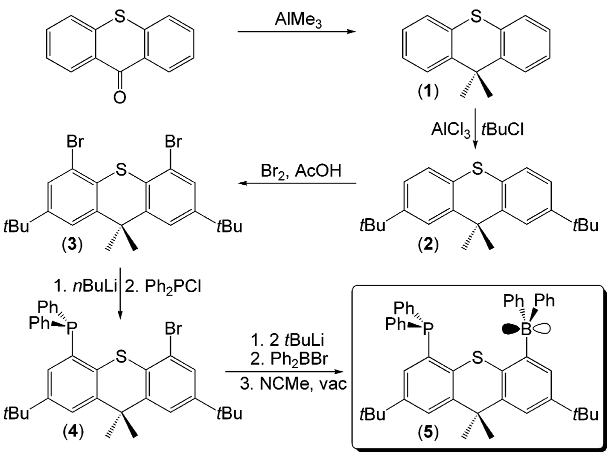
Scheme 1. Preparation of Ligand 5 from Thioxanthone

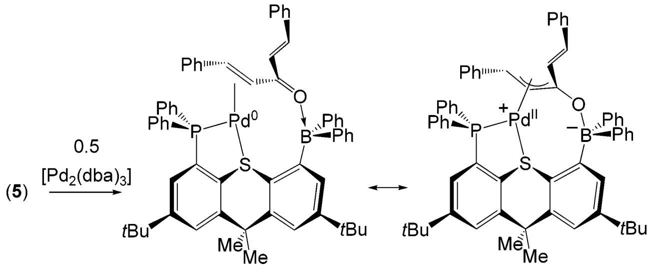


tert-Butyl groups were then installed in the 2- and 7-positions to give **2** by a Friedel−Crafts reaction with 2-chloro-2-methylpropane and AlCl$_3$. Subsequent reaction of **2** with Br$_2$ in AcOH furnished 2,7-di-*tert*-butyl-4,5-dibromo-9,9-dimethylthioxanthene (**3**), which can be selectively monolithiated using *n*-butyllithium at −45 °C and then reacted with Ph$_2$PCl to give the desired bromo/phosphine precursor (**4**). Lithiation of **4** using *tert*-butyllithium and then quenching with Ph$_2$BBr afforded crude **5**, which could not be purified directly due to its extremely high solubility. However, dissolution of crude **5** in MeCN resulted in precipitation of the acetonitrile adduct of the ligand (**5**·NCMe) as a white solid. Under dynamic vacuum, the adduct regenerates base-free **5**, which is isolated in 66% yield as an air-sensitive lemon yellow powder.

Ligand **5** was characterized by NMR spectroscopy, HRMS, and CHS elemental analysis. In solution, **5** shows a sharp singlet at −8.65 ppm in the ^{31}P NMR spectrum and a broad singlet at +69 ppm in the ^{11}B NMR spectrum. The ^{11}B chemical shift is characteristic of a free triarylborane, and the sharp ^{31}P signal is indicative of a free triarylphosphine. The monomeric nature of **5** is further supported by mass spectrometry and its high solubility in hexanes and hexamethyldisiloxane. In the ^{1}H and ^{13}C NMR spectra of **5**, the two methyl groups of the ligand backbone are equivalent and there is no change in the ^{1}H NMR spectrum between +20 and −80 °C. This could result from a planar thioxanthene ligand backbone or from a bent backbone with rapid inversion on the NMR time scale. Attempts to grow X-ray-quality crystals of **5** were unsuccessful, due to the extreme solubility of **5** in noncoordinating solvents. However, a bent thioxanthene backbone is more likely, by analogy with related alkylidene-9*H*-thioxanthenes and phenothiazines.[14]

To test the efficacy of **5** as a ligand in late-transition-metal chemistry and the ability of **5** to position the borane in close proximity to a coordinated transition metal, the reaction of **5** with 0.5 equiv of [Pd$_2$(dba)$_3$] (dba = *trans*,*trans*-dibenzylideneacetone) in CH$_2$Cl$_2$ was carried out, forming orange [Pd(dba)(**5**)]·CH$_2$Cl$_2$ in 79% yield after crystallization from CH$_2$Cl$_2$/hexanes and drying in vacuo (Scheme 2). This complex was studied by NMR spectroscopy and X-ray crystallography. Selected spectroscopic features include a sharp singlet at +30.25 ppm in the ^{31}P NMR spectrum and a broad singlet at +5.3 ppm in the ^{11}B NMR spectrum, characteristic of a four-coordinate borane or borate.

Scheme 2. Reaction of Ligand 5 with [Pd$_2$(dba)$_3$][a]



[a] Two limiting structures of the product are shown.

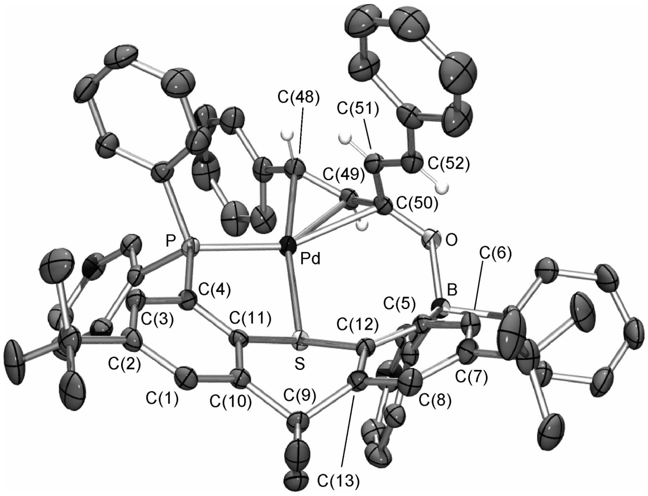


Figure 1. ORTEP drawing of [Pd(dba)(**5**)]·3CH$_2$Cl$_2$ with solvent and most hydrogen atoms omitted for clarity (50% thermal ellipsoids). Selected bond distances (Å) and angles (deg): Pd−P = 2.268(1), Pd−S = 2.344(1), Pd−C(48) = 2.139(3), Pd−C(49) = 2.149(3), Pd−C(50) = 2.337(3), C(48)−C(49) = 1.425(5), C(49)−C(50) = 1.397(5), C(50)−C(51) = 1.473(5), C(51)−C(52) = 1.334(5), C(50)−O = 1.319(4), B−O = 1.537(4); P−Pd−S = 87.15(3).

X-ray-quality crystals of [Pd(dba)(**5**)]·3CH$_2$Cl$_2$ were grown by diffusion of hexanes into a CH$_2$Cl$_2$ solution of the complex at −30 °C.[15] The solid-state structure (Figure 1)[16] shows that ligand **5** is coordinated to palladium via phosphorus and sulfur and the borane group of **5** is bonded to the oxygen atom of a dba molecule ligated to palladium. Considerable distortion of ligand **5** is clearly required in order to allow boron−oxygen bond formation; boron lies 1.14 Å below the S−C(9)−C(13) plane, and the S−C(12)−C(5)−B torsion angle is 17.7(5)°.

For a complex with the empirical formula [Pd(dba)(**5**)], two limiting structures are conceivable: (1) a palladium(0) alkene

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(15) In addition to [Pd(dba)(**5**)]·3CH$_2$Cl$_2$, crystals of [Pd(dba)(**5**)] with a different amount of (disordered) solvent were also formed and investigated by X-ray crystallography. The structures of the [Pd(dba)(**5**)] core are to all intents and purposes identical in both crystals.

(16) Crystal data for [Pd(dba)(**5**)]·3CH$_2$Cl$_2$: $C_{67}H_{68}BCl_6OPPdS$, 0.35 × 0.25 × 0.10 mm^3, mol wt 1282.15, triclinic, $P\bar{1}$, a = 14.4708(9) Å, b = 15.2820(8) Å, c = 17.4377(11) Å, α = 69.479(3)°, β = 77.378(3)°, γ = 61.798(3)°, V = 3176.3(3) Å^3, Z = 2, ρ_{calcd} = 1.341 g cm^{-3}, $2\theta_{\max}$ = 55.02°, λ(Mo Kα) = 0.710 73 Å, T = 173(2) K, 28 166 measured reflections, 14 111 unique (R_{int} = 0.0522), 14 111 reflections included in the refinement, $I > 2\sigma(I)$, μ = 0.644 mm^{-1}, minimum transmission 0.719, maximum transmission 0.938, 703 parameters, final R indices ($I > 2\sigma(I)$) R1 = 0.0522, wR2 = 0.1209, GOF = 1.029, residual electron density 0.098 (rms). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-290380. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

complex with the borane unit coordinated to the ketone and (2) a zwitterionic palladium(II) η^3-boratoxypentadienyl complex (Scheme 2). The crystal structure of [Pd(dba)(**5**)] is only consistent with the palladium(II) η^3-boratoxypentadienyl structure, for the following reasons. (1) The C(49)−C(50) distance of 1.397(5) Å is considerably shorter than a C−C single bond (cf. C(50)−C(51) at 1.473(5) Å) but is typical for an allyl unit. (2) The C(50)−O distance of 1.319(4) Å is longer than expected for a borane−ketone adduct (typically 1.25−1.28 Å) but falls within the usual range for an alkoxyborate (typically 1.27−1.33 Å). (3) The Pd−C(50) distance of 2.337(3) Å is only slightly longer than that expected for a typical palladium(II) allyl complex (2.0−2.3 Å).

The extent to which the zwitterionic palladium(II) structure dominates in [Pd(dba)(**5**)] is remarkable in comparison with structures of complexes formed upon reaction of [$(PPh_3)_2$Pd(η^2-PhHC=CHC(O)R)] (R = H, Me) with strong Lewis acids such as BF_3, $B(C_6F_5)_3$, and $AlCl_3$. For this intermolecular variant studied by Ogoshi and Kurosawa et al., considerably longer Pd−CO bond lengths were observed in all cases, and a palladium(II) boratoxyallyl like complex was only observed by combination of BF_3 with the more easily activated enal (R = H).[17] In this work, we employ a far less Lewis acidic borane (similar to BPh_3)[12] and an enone which should be more difficult to activate (R = PhHC=CH versus R = H, Me).[18] The unusual ability of the pendant borane in [Pd(dba)(**5**)] to activate enones is perhaps due to entropic factors which favor initial palladium−alkene and borane−ketone coordination and steric constraints imposed by the rigidity of **5**, which force the carbonyl carbon into closer proximity with the metal. The rigidity of **5** is also manifested in the exclusive formation of [Pd(dba)(**5**)] with trans-disposed substituents around the C(49)−C(50) bond. In contrast, the Ogoshi/Kurosawa complexes are formed as cis isomers with one exception; the trans isomer of [$(PPh_3)_2$Pd{CHPhCHCHOB($C_6F_5)_3$}] was observed as a minor component in solution (less than 5%) but crystallized preferentially.[17]

NMR data for [Pd(dba)(**5**)] also support an η^3-boratoxypentadienyl structure in solution. At −75 °C in CD_2Cl_2, the $^{13}C\{^1H\}$ NMR spectrum shows a doublet at 144.08 ppm ($^2J_{C,P}$ = 10 Hz) for *C*(50). The magnitude of this coupling constant falls within the range observed for phosphine-ligated palladium(II) alkyl complexes, and the identity of the peak and origin of the coupling has been confirmed by $^1H/^{13}C$-HMBC NMR and $^{13}C\{^1H\}$ NMR at both 126 and 75.5 MHz. C(50) is therefore coordinated to palladium and remains so on the NMR time scale at −75 °C, which is not consistent with a simple palladium(0) alkene complex. The C(50) peak is shifted 44 ppm upfield of that for free dba, which is a larger shift than has been observed for any of the Ogoshi/Kurosawa complexes,[17] in keeping with the solid-state data, which suggest a more activated enone.

Despite the structural and spectroscopic evidence to suggest that [Pd(dba)(**5**)] is best regarded as a complex of palladium(II), preliminary reactivity studies have shown that reactivity typical of a palladium(0) alkene complex is still accessible. For example, coordinated dba undergoes exchange with free d_2-dba at room temperature. In contrast, no reaction was observed with PhC_2H, norbornylene, or $HNEt_2$, even after several days in refluxing benzene. Future work will examine the effect of varying the nature of the enone, the steric and electronic properties of ligand **5**, and the potential for this work to allow α,β-unsaturated ketones to undergo palladium(II) allyl like reactivity.

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Supporting Information Available: Text giving full experimental details for all new compounds and characterization details and a CIF file giving X-ray crystallographic data. This material is available free of charge via the Internet at http:/pubs.acs.org.

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(17) A continuum from palladium(0) enone−Lewis acid adducts to zwitterionic palladium(II) complexes was observed, with increased palladium(II) character for stronger Lewis acids and enones less able to stabilize the positive charge generated on the carbonyl carbon upon Lewis acid coordination: Ogoshi, S.; Yoshida, T.; Nishida, T.; Morita, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 1944.

(18) The increased ability of dba (R = CH=CHPh versus R = Me, H) to stabilize the positive charge generated on the carbonyl carbon upon Lewis acid coordination (cf. IR ν(CO) for free RC(O)H > RC(O)Me > RC(O)-CH=CHPh) will render dba more difficult to activate toward the palladium(II) boratoxyallyl extreme than *trans*-benzylideneacetone or *trans*-cinnamaldehyde.