

The η^3 -Furfuryl Ligand: Plausible Catalytic Intermediates and Heterocyclic η^3 -Benzyl Analogues with Superior Binding Ability

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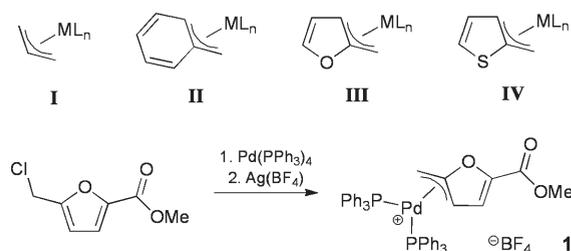
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Summary: Five-membered heterocyclic analogues of the well-known η^3 -allyl and η^3 -benzyl ligands, e.g., η^3 -thienyl and η^3 -furfuryl, have been proposed as catalytic intermediates, yet are poorly understood and have never been structurally confirmed. Herein we characterize an η^3 -furfuryl complex by multinuclear NMR spectroscopy and crystallography and offer a computational survey of allyl and allyl-like ligands. Crystallographically and computationally, we show that the η^3 -furfuryl ligand may bind more strongly than corresponding η^3 -benzyl ligands and is plausible as a catalytic intermediate.

η^3 -Allyl complexes of transition metals (**I**, Scheme 1) are an indispensable class of organometallic species, as they feature one of the simplest possible hydrocarbon π -ligands.¹ They are known to be intermediates in a number of catalytic processes, particularly the nucleophilic substitution of allylic esters, known as the Tsuji–Trost reaction.² In 1966, analogous η^3 -benzyl complexes (**II**, Scheme 1) were prepared³ and crystallographically characterized.⁴ Like its allylic cousin, the η^3 -benzyl ligand has since become the linchpin in a number of catalytic processes, particularly the Tsuji–Trost-style nucleophilic substitution of benzylic esters⁵ and the catalytic polymerization,⁶ hydroboration,⁷ hydrosilylation,⁸ and hydroamination⁹ of vinylarenes. Intermediate η^3 -benzyl complexes also influence the rates of aryl vs benzyl C–H activation of alkyl benzenes by Rh and Pt complexes.¹⁰

Given the importance of η^3 -allyl and η^3 -benzyl ligands in organometallic transformations, the scarcity of corresponding

Scheme 1. (Top) Well-Known η^3 -Allyl (**I**) and η^3 -Benzyl (**II**) Ligands and Their Five-Membered Heterocyclic Analogues (**III** and **IV**); (Bottom) Synthesis of **1**



monometallic η^3 -heterocyclic chemistry and total absence of structural data are surprising. A report from 1969 disclosed the synthesis of two η^3 -thienyl (**IV**, Scheme 1) complexes, while a paper from 1981 reported two η^3 -furfuryl (**III**) complexes.¹¹ However, in all cases structural assignment was made primarily via ¹H NMR and IR spectroscopy, while X-ray crystallographic data for heterocyclic analogues of η^3 -benzyl complexes exist only for chelating, multinuclear systems.¹² A limited number of palladium-catalyzed coupling reactions with heterocyclic “allylic” esters exist in the literature, implicating the structurally unconfirmed η^3 -coordination mode of the precursor heterocycles.¹³

Our objective was to target stable complexes containing heterocyclic analogues of the η^3 -benzyl ligand, such as η^3 -furfuryl derivatives (**III**, Scheme 1), in order to confirm their validity as catalytic intermediates or explain the infrequency of heterocyclic Tsuji–Trost reactions in the literature. Treatment of commercially available methyl 5-(chloromethyl)-2-furancarboxylate with [Pd(PPh₃)₄], followed by silver tetrafluoroborate, led to a yellow solid formulated as the η^3 -furfuryl complex **1** (Scheme 1). The compound displayed two doublets in the ³¹P{¹H} NMR spectrum (δ_P 30.6, 20.6; J_{PP} = 44.5), matching well with the comparable η^3 -benzyl complex [Pd(η^3 -benzyl)-(PPh₃)₂][PF₆] (δ_P 32.2, 22.7; J_{PP} = 41)¹⁴ and confirming the *cis* arrangement of the two phosphorus nuclei in solution.

The ¹H NMR spectrum of **1** at 298 K showed two doublet-of-doublet signals (C³H, C⁴H) and two broad singlets (CH₂).

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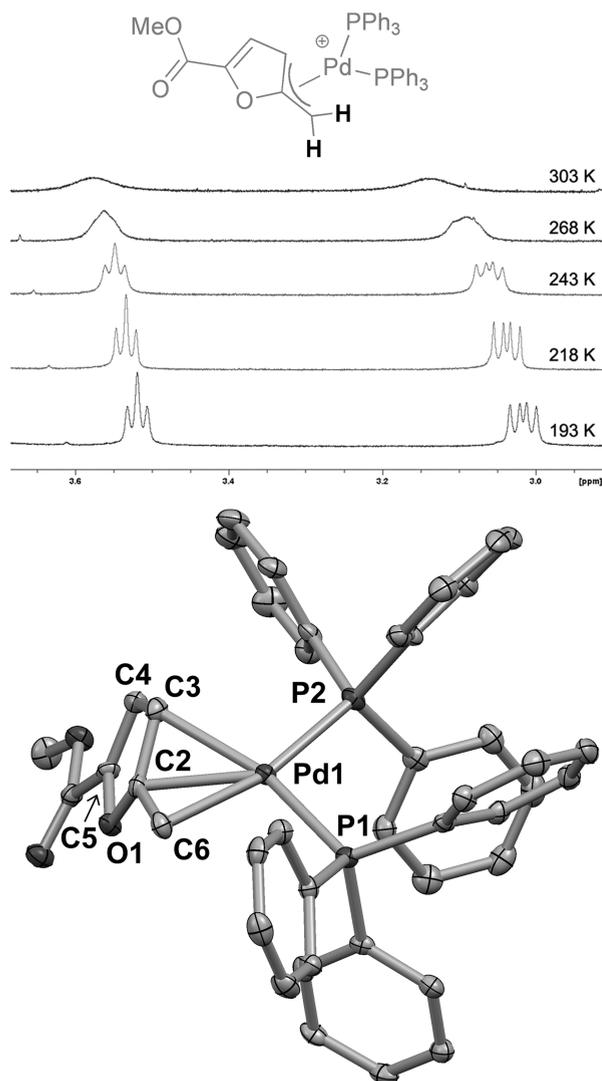


Figure 1. (Top) Section of the variable-temperature ^1H NMR spectrum of **1** showing the methylene proton signals. (Bottom) Molecular structure of the cation of **1**. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [deg] for **1**: Pd1–C6 2.163(3), Pd1–C2 2.236(2), Pd1–C3 2.289(3), C2–C3 1.402(4), C3–C4 1.438(4), C4–C5 1.342(4); C6–C2–O1 121.6(2), O1–C2–C3 109.4(2), C3–C2–C6 126.8(3).

A variable-temperature ^1H NMR experiment showed resolution of the broad methylene proton signals into doublet-of-doublet signals at approximately 243 K. However, no dynamic behavior was detected in the ^{31}P NMR spectrum of **1** (CD_2Cl_2) in the range 193–303 K. This room-temperature fluxionality can be attributed to fast $\eta^3\text{-}\eta^1\text{-}\eta^3$ rearrangement to a T-shaped intermediate (thus broadening the methylene proton signals but leaving the phosphorus nuclei inequivalent), but without accompanied flipping through a Y-shaped transition state, for which we would expect a single broad signal for the methylene protons in the ^1H NMR spectrum and broadening of the ^{31}P NMR signals.^{3,5b,9c,15}

The solid-state structure of **1** derived from crystallographic data confirmed the formulation (Figure 1). The furfuryl ligand is unsymmetrically bound, with a $d(\text{Pd}-\text{C}3)/d(\text{Pd}-\text{C}6)$ ratio (a measure of symmetry defined by Kuwano for η^3 -benzyl

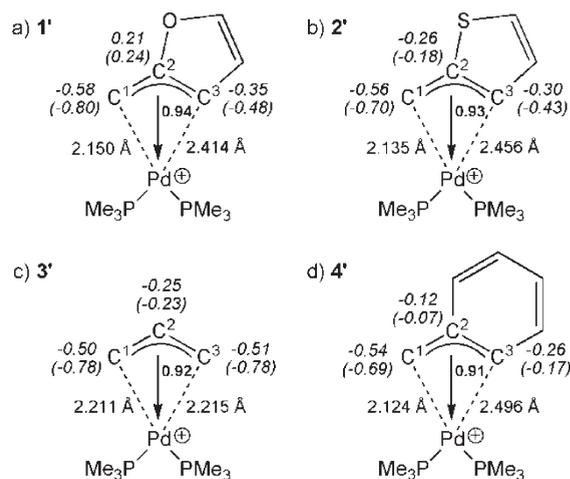


Figure 2. Selected structural parameters and NPA charges of model complexes **1'**–**4'** (RI-BP86/def2-TZVPP//RI-BP86/def2-TZVP). Atomic charges are printed in italics; values in parentheses correspond to charges in the free ligand. Charge transfer between the coordinated ligand and the metal fragment is in bold.

complexes) of 1.06.^{5b} Thus, the η^3 -furfuryl ligand of **1** is roughly equivalent to the most symmetrical examples of known η^3 -benzyl ligands on palladium (with ratios ranging from 1.05 to 1.29). A further feature of the structure of **1** is the increase of the furan C2–C3 double bond length (1.402(4) Å) compared to the unbound C4–C5 bond (1.342(4) Å). This lengthening is approximately 5% of the shortest distance, presumably reflecting back-donation from palladium into the $\text{C}^2\text{-C}^3$ π^* antibonding orbital. Overall, the crystallographic data of complex **1** show that the η^3 -furfuryl ligand can match even the most “allyl-like” of known η^3 -benzyl ligands in terms of symmetry and bond lengths.

To obtain a consistent comparison of the structural and electronic features of allyl-type ligands **I**–**IV** (Scheme 1), we performed calculations based on density functional theory (DFT) at RI-BP86/def2-TZVPP//RI-BP86/def2-TZVP levels with a quasirelativistic pseudopotential on palladium (Figure 2). The calculations were undertaken with a simplified model of **1** (**1'**, class **III**), the analogous thienyl complex **2'** (class **IV**), parent allyl complex **3'** (class **I**), and benzyl complex **4'** (class **II**). The calculations explicitly included BF_4^- counterions.

Computed energies of ligand exchange reactions show the heterocyclic complexes **1'** and **2'** to be of similar stability. Both are about 41–43 kJ mol^{-1} more stable than benzyl complex **4'** and about the same amount (46–48 kJ mol^{-1}) less stable than the parent allyl complex **3'**. The energy required to computationally force the ligands from η^3 to η^1 binding modes by imposing BF_4^- coordination to Pd (this mode represents a local minimum on the potential energy surface in all three cases) is smallest for the benzyl ligand and again similar for the furfuryl and thienyl ligands, i.e., **4'** (25.0 kJ/mol) < **2'** (41.5 kJ/mol) \approx **1'** (45.3 kJ/mol). Trends in the bonding may be inferred from key optimized structural parameters (Figure 2). The aforementioned $d(\text{Pd}-\text{C}^3)/d(\text{Pd}-\text{C}^1)$ ratio becomes more symmetrical going from the benzyl to the allyl system: **4'** (1.18) > **2'** (1.15) > **1'** (1.12) > **3'** (1.00). The overestimated Pd–C³ bond lengths reflect the neglect of dispersion interactions in the RI-BP86/def2-TZVP optimizations. Inclusion of semiempirical dispersion corrections shortens the Pd–C³ bonds for all systems with aromatic ligands but does not alter any of the main conclusions drawn.

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Computed natural atomic (NPA) charges provide insight into the two main aspects affecting the symmetry and strength of the η^3 coordination: the competition between aromaticity and metal coordination at the C^3 atom, and the electronegativity of the heteroatom, which partly determines the charge on the exocyclic methylene carbon. Thereby, the benzyl complex **4'**, clearly the most aromatic, exhibits the least negative charge on C^3 and thus the weakest and longest C^3 -Pd contact. The heterocyclic ligands in **1'** and **2'** have diminished cyclic delocalization and thus allow a more negative charge on C^3 and consequently stronger coordination of this site. On the other hand, the electronegativity of the oxygen heteroatom in **1'** leads to a pronounced $O-C^2-C^3$ charge alternation (Figure 2), giving the largest negative charge on the methylene carbon in the free ligand. As a consequence, the furfuryl complex **1'** (followed closely by **2'**) exhibits the most symmetrical η^3 coordination of the three ligands, leading to an overall stronger bond.

In summary, a stable mononuclear η^3 -furfuryl complex, long assumed to be an intermediate in catalytic transformations of

heterocycles,¹³ has been synthesized, crystallographically characterized, and studied computationally. The metrics garnered from the crystallographic and computational study of **1** strongly suggest that when bound to suitable palladium(II) fragments, η^3 -furfuryl (and -thienyl) ligands may lead to significantly more stable complexes than η^3 -benzyl ligands, an effect partly due to the reduced aromaticity of the heterocycles. Further studies on the synthesis, reactivity, and electronic structure of η^3 -furfuryl (and related heterocyclic) complexes are in progress.

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Supporting Information Available: Experimental, spectroscopic, and computational details. This information is available free of charge via the Internet at <http://pubs.acs.org>