

Versatile Behavior of the Schiff Base Ligand 2,5-Me₂C₆H₃C(H)=N(2,4,6-Me₃C₆H₂) toward Cyclometalation Reactions: C(sp²,phenyl)-H vs C(sp³,methyl)-H Activation

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Treatment of the Schiff base ligand a with palladium(II) acetate in toluene gave 1a, with metalation of an aromatic phenyl carbon atom. Reaction at room temperature gave the trinuclear complex 4a. Treatment of a with palladium(II) acetate in refluxing acetic acid gave 1a'. The reaction of complexes 1a and 1a' with sodium chloride or lithium bromide gave the halogen-bridged complexes 2a, 3a, 2a', and 3a'.

Introduction

In the preceding decades the chemistry of cyclometalated transition-metal complexes has attracted much attention. They exhibit a good number of $applications^{1-5}$ as well as promote unusual coordination environments,⁶ and they are usually classified according to the metal, the donor atom, or the chelate ring size; by far the most well-studied examples are five-membered palladacycles containing nitrogen-Pd and C(phenyl)-Pd bonds.⁷⁻¹⁰ Analogous compounds containing alkyl C(sp³)-Pd bonds are also known; activation of the aliphatic carbon can only be achieved when the aromatic position is unavailable or sterically hindered.¹¹ Examples in which $C(sp^3)$ carbon activation is exclusive are even more exceptional.¹²⁻¹⁴

Palladium(II) acetate is one of the reagents most frequently used to prepare cyclometalated complexes, leading

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to a dimer with bridging acetate ligands in an "open book" arrangement. However, in a few cases this reaction gives cyclometalated complexes with an unusual trinuclear structure^{15,16} which exhibits interesting catalytic applications.^{17–20} We have found that this is the case with ligand **a** when the reaction is carried out at room temperature. Thus, ligand a can be metalated at an aliphatic or at a sterically hindered aromatic carbon and, in the latter case, it may give di- or trinuclear species, showing an unprecedented and versatile behavior.

Experimental Section

General Comments. Solvents were purified by standard methods.²¹ Chemicals were reagent grade. Microanalyses were carried out using a Carlo Erba Elemental Analyzer, Model 1108. IR spectra were recorded as Nujol mulls or polyethylene or KBr discs on a Satellite FTIR instrument. NMR spectra were obtained as CDCl₃ solutions and referenced to SiMe₄ (${}^{1}H$, ${}^{13}C{}^{1}H$) and were recorded on a Bruker AV-300F spectrometer. All chemical shifts were reported downfield from standards. The FAB mass spectra were recorded using a FISONS Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

Synthesis of [Pd{1-CH₂-2-[HC=N(2,4,6-Me₃C₆H₂)]-4-MeC₆H₃- $C_{N}(\mu - O_{2}CMe)]_{2}$ (1a'). A mixture of 2,5-Me₂C₆H₃C(H)=N- $(2,4,6-Me_3C_6H_2)$ (0.274 g, 1.09 mmol) and palladium(II) acetate (0.246 g, 1.10 mmol) in glacial acetic acid (40 cm^3) was refluxed under dry argon for 3 h. After the mixture was cooled to room temperature, the acetic acid was removed under vacuum. The

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Scheme 1.^{*a*}



^{*a*} Legend: (i) Pd(OAc)₂, toluene, 60 °C; (ii) NaCl (**2a**), LiBr (**3a**), ethanol-water; (iii) Pd(OAc)₂, toluene, room temperature; (iv) toluene, 80 °C; (v) Pd(OAc)₂, acetic acid, reflux; (vi) NaCl (**2a**'), LiBr (**3a**'), ethanol-/water.

residue was treated with water and extracted with dichloromethane. The combined extracts were dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo to give a brown oil which was chromatographed on a column packed with silica gel. Elution with dichloromethane-ethanol (1%) afforded the final product as a yellow solid after solvent removal, which was recrystallized in dichloromethane/hexane. Yield: 77%. Anal. Found: C, 57.8; H, 5.7; N, 3.5. Calcd for $C_{40}H_{46}N_2O_4Pd_2$: C, 50.3; H, 5.0; N, 4.3. ν_{max}/cm^{-1} : 1610 s (CN), 1580 s ($\nu_{as}(COO)$), 1420 s ($\nu_{s}(COO)$). δ_{H} (300 MHz; CDCl₃; Me₄Si): 7.49 (1H, s, HCN), 7.13, 6.86 (2H, m, H₃, H₄), 6.90 (2H, s, H₉, H₁₁), 6.76 (1H, br, H₆), 3.29 (2H, br, CH₂), 2.79, 1.33 (6H, br, Me_c, Me_d), 2.26, 2.17 (6H, s, Me_b, Me_e), 1.33 (3H, s, AcO). Synthesis of $[{Pd[2,5-MeC_6H_2C(H)=N(2,4,6-Me_3C_6H_2)-}$ $C6,N](\mu-O_2CMe)_2\{Pd(\mu-O_2CMe)_2\}]$ (4a). A pressure tube containing 2,5-Me₂C₆H₃C(H)=N(2,4,6-Me₃C₆H₂) (\mathbf{a} ; 0.275 g, 1.09 mmol), palladium(II) acetate (0.245 g, 1.10 mmol), and 20 cm³ of dry toluene was sealed under argon. The resulting mixture was stirred for 76 h at room temperature and the solvent removed under vacuum to give a green solid which was recrystallized from dichloromethane-hexane. Yield: 71%. Anal. Found: C, 49.8; H, 4.7; N, 2.5. Calcd for C₄₄H₅₂N₂O₈Pd₃: C, 50.0; H, 4.9; N, 2.6. $\nu_{\text{max}}/\text{cm}^{-1}$ 1610 sh (CN), 1550s (ν_{as} (COO)), 1400 s $(\nu_{s}(COO))$. δ_{H} (300 MHz; CDCl₃; Me₄Si): 8.14, 8.13 (2H, s, H'CN/HCN), 6.81 (8H, m, H_4'/H_4 , H_5'/H_5 , H_9'/H_9 , H_{11}'/H_{11}), 2.67, 2.65 (6H, s, Me), 2.43 (9H, s, Me), 2.36, 2.27, 2.25, 2.24, 2.22 (15H, s, Me), 1.89, 1.83, 1.06, 1.01 (12H, s, AcO). m/z (FAB): 774 [(L-H)₂Pd₂(OAc)]⁺.

Results and Discussion

For the convenience of the reader the compounds and reactions are shown in Scheme 1.

The reaction of ligand \mathbf{a} with palladium acetate has been studied. The results show that the ligand incorporates two main features with which we will deal separately. First, it allows for the making of a species containing a rare $Pd_3(OAc)_4$ core, and second, the behavior of the ligand under different reaction conditions sheds new light regarding the choice of metalation at C_{sp^2} or C_{sp^3} carbon atoms, as well as on the formation of endo or exo metallacycles.

Thus, the reaction of a with palladium acetate in toluene at room temperature gave the novel trinuclear cyclometalated complex 4a. This is in agreement with similar trinuclear cyclometalated complexes previously reported,¹⁵⁻²⁰ when the reaction is carried out in weakly coordinating solvents. Treatment of a solution of 4a in toluene at 80 °C for 24 h gave 1a (see below) plus black palladium and a small amount of other decomposition products, indicating the temperature dependence of both compounds. It therefore seems that compounds of type 4a are a reaction intermediate after C-H activation, which may or may not be isolable, as has been the case in the present reaction. Change of solvent for acetic acid (see below) gave altogether different results, and compounds similar to 4a were not detected. The ¹H NMR spectrum for 4a showed two sets of signals for the syn and anti isomers (in approximately equimolar ratio) in the solution.^{15–20} The HC=N resonances were assigned at 8.14 and 8.13 ppm, shifted to lower frequency, in agreement with the N-coordination of the ligand. Four signals at ca. 1.8 and 1.0 ppm, two for each isomer, were assigned to the four acetate methyl groups.

Furthermore, treatment of **a** with Pd(OAc)₂ in toluene at 60 °C for 24 h gave, after column chromatography purification, a yellow solid identified as **1a**. In the IR spectrum of the complex the ν (C=N) stretching band, 1587 s cm⁻¹, appeared at lower frequency than the corresponding one in the free imine, 1633 m cm⁻¹, in accordance with nitrogen coordination to the metal center.²² This was supported by the upfield shift (0.67 ppm, as compared to the free ligand) of the *H*C=N

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Figure 1. Molecular structure of 4a, with labeling scheme. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)-C(6), 1.993(4); Pd(1)-N(1), 2.001(3); Pd(1)-O(1), 2.144(3); Pd(1)-O(3), 2.057(3); Pd(2)-O(2), 1.995(3); Pd(2)-O(4), 2.010(3); Pd(1)-Pd(2), 3.031(1). C(6)-Pd(1)-O(3), 99.9(1); C(6)-Pd(1)-N(1), 81.3(1); N(1)-Pd(1)-O(1), 90.8(1); O(1)-Pd(1)-O(3), 88.0(1); C(6)-Pd(1)-O(1), 172.0(1); N(1)-Pd(1)-O(3), 167.1(1).

resonance in the ¹H NMR spectrum.²³ The ν_{as} (COO) and ν_{s} (COO) values were consistent with bridging acetate groups,²⁴ and a singlet resonance at ca. 1.6 ppm in the ¹H NMR spectrum, assigned to the equivalent methyl acetate protons, was consistent with a trans geometry of the cyclometalated moieties.²⁵ The FAB mass spectrum showed a cluster of peaks assigned to [(L-H)₂Pd₂(OAc)]⁺, thereby confirming the dinuclear nature of the complex.²⁶

Crystal Structures of 1a and 4a. Suitable crystals of **1a** and **4a** were grown by recrystallization from dichloromethane—n-hexane solutions. The structure of **4a** is given in Figures 1 and 2; the structure of **1a** and crystallographic data are given in the Supporting Information. Selected interatomic distances and angles for **4a** are given in the caption to Figure 1. The crystals consist of discrete molecules separated by normal van der Waals distances. The asymmetric unit comprises one molecule for **1a** and a half-molecule for **4a**; the latter exhibits a crystallographic inversion center located at the central palladium atom Pd(2).

The molecular configuration of complex **1a** is a dimeric form with the cyclopalladated moieties in an "open book" arrangement linked by two acetate bridging ligands, as observed in the related dimers.^{25,27} As a result of two mutually cis μ -acetato ligands bridging the Pd(1) and Pd(2) atoms,



Figure 2. Molecular structure of 4a, depicting the S-shape of the $Pd_3(OAc)_4$ core. Hydrogen atoms have been omitted for clarity.

the chelated organic ligands are forced to lie above one another in the dimeric molecule. This leads to interligand repulsions on the "open" side of the molecule and results in the coordination planes of the palladium atoms being tilted at an angle of 51.0°. The tripalladium complex 4a shows a $Pd_3(OAc)_4$ core with the two terminal palladium atoms, Pd(1) and Pd(3), bonded to a Schiff base ligand and to the central palladium atom Pd(2) through four bridging acetate ligands, resulting in an S-shaped complex (Figure 2), in which the three palladium atoms are in a linear disposition (Pd-Pd-Pd angle 180°). Such structural arrangements are rather rare, and to our knowledge it is the sixth example in a still short list of structurally characterized $Pd_3(OAc)_4$ species;^{17–20} however, it is the first example containing a monodentate imine. The dihedral angle between the palladium coordination planes of Pd(1) and Pd(2) is 39.0°; however, the coordination planes of the symmetry-related terminal palladium atoms are in an exactly parallel arrangement. Each palladium atom is in a slightly distorted squareplanar coordination environment consisting of a C=N nitrogen atom, the phenyl ring ortho carbon, and two oxygen atoms from the bridging acetate; the most noticeable distortion of the ideal coordination sphere corresponds to a C-Pd-N bite angle of 81.3(1)°. The coordination geometry at Pd(2) is defined by four oxygen atoms from the bridging acetate groups, and the coordination angles at palladium atom are close to the ideal value of 90°. All bond distances are within the expected values, with allowance for lengthening of the Pd-O bond trans to carbon, due to the differing trans influence of the carbon and nitrogen atoms. The palladium-palladium distance of 3.031(1) Å is close to the upper value of the range found in related structures, 3.0457(5)-2.864(1) Å,¹⁹ and may be regarded as nonbonding.

The second interesting feature stemming from the reactivity of **a** is the choice of the metalation site on the phenyl ring. Metalation may be prompted through C–H activation at an aromatic or at aliphatic carbon atoms. Even though activation of the sp² carbon is usually preferred, the reaction conditions play an essential role in the regioselectivity of the cyclometalation reaction.^{12–14} Nevertheless, the ligand portrays quite distinct metalation possibilities, as opposed to

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those of previously considered imines where endo/exo five- or six-membered metallacycles were feasible.¹³ To begin with, **a** may be metalated at the C6 carbon to give an endo fivemembered ring, via a $C_{aromatic}$ -Pd bond, or at the C(2)*Me* carbon to give an endo six-membered ring, via a $C_{aliphatic}$ -Pd bond, both cases pertaining to the benzylidene ring. Alternatively, **a** could undergo metalation at the C(8)*Me* or C(12)*Me* carbons to give an exo five-membered ring bearing a $C_{aliphatic}$ -Pd bond, with exo $C_{aromatic}$ -Pd bonds being obviously precluded. Nevertheless, all attempts to produce the exo fivemembered palladacycle through either of the aniline methyl groups failed, putting forward the preference in formation of the endo six-membered species. Therefore, in spite of the fact that it has been suggested that there is a strong tendency to form five-membered metallacycles,²⁸ the six-membered ring is the final choice with the present ligand.

Henceforth, reaction between **a** and palladium(II) acetate in refluxing acetic acid gave, even after column chromatography and recrystallization, a mixture of compounds. The ¹H NMR spectrum showed the presence of an unidentified compound, a small amount of **1a**, and the major complex, which was formulated as **1a**', derived from C-H activation at the C2-methyl group. Although the IR and the ¹H NMR spectra (see the Experimental Section and Scheme 1) were in agreement for **1a**', unambiguous proof for this species was obtained after preparation of the corresponding pure chloride-bridged derivative **2a**' from the aforementioned mixture.

Complexes **1a** and **1a**' reacted smoothly with sodium chloride or bromide in ethanol-water to give the halidebridged species **2a**, **3a**, **2a**', and **3a**'. The MS-FAB spectra showed peaks assigned to $[(L-H)_2Pd_2X_2]^+$ or $[(L-H)_2Pd_2X)]^+$ (X = Cl, Br). The resonance for the metalated $-CH_2$ - group was at 3.38 and 3.37 ppm for **2a**' and **3a**', respectively.

Crystal Structures of 2a and 2a'. Suitable crystals were grown by recrystallization from dichloromethane—*n*-hexane solutions of **2a** and **2a'**. The structure of **2a'** is given in Figure 3; the structure of **2a** and crystallographic data are given in the Supporting Information. Selected interatomic distances and angles for **2a'** are given in the caption for Figure 3. The crystals consist of discrete molecules separated by normal van der Waals distances. The asymmetric unit comprises half of the molecule with a crystallographic inversion center located at the center of the $Pd_2(\mu-Cl)_2$ moiety (**2a**). The molecules are dimeric, and the coordination sphere around each palladium atom consists of two halogen atoms, a C=N nitrogen atom, and the C(6) carbon atom (**2a**) or the methylene C(2) carbon atom (**2a**').

The coordination environment at the metal center is slightly distorted square planar, with the most noticeable deviation corresponding to the C-Pd-N bite angle of $81.29(13)^\circ$ in **2a**. For complex **2a**' the C-Pd-N angle, $86.7(2)^\circ$, is closer to the ideal value of 90°, due to the smaller ring strain of the six-membered cyclometalated ring as opposed to the five-membered ring.

The $[(C-N)Pd(\mu-Cl)_2Pd(C-N)]$ fragment adopts a planar configuration in **2a**, with an angle between the palladium



Figure 3. Molecular structure of 2a', with labeling scheme. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)–C(15), 2.008(5); Pd(1)– N(1), 2.043(3); Pd(1)–Cl(1), 2.327(1); Pd(1)–Cl(1a), 2.501(1); C(15)–Pd(1)–N(1), 86.7(2); N(1)–Pd(1)–Cl(1a), 93.8(1); Cl(1a)–Pd(1)–Cl(1), 87.9(1); Cl(1)–Pd(1)–Cl(15), 91.5(1); C(15)–Pd(1)–Cl(1a), 177.0(1); N(1)–Pd(1)–Cl(1), 178.2(1); Cl(1)–Pd(1)–Cl(1a), 92.1(4).

coordination plane and the Pd_2Cl_2 ring of 3.6°. This situation is the most common configuration observed in related species.²⁹ In complex **2a**' the six-membered palladacycle adopts a half-skew chair conformation, with the palladium atom out of the plane (1.052 A) defined by the remaining atoms, and the C(2)–C(15)–Pd(1) bond angle of 109.3(3)° is in agreement with the sp³ hybridization of the C(15) carbon.

All bond distances are within the expected values, with allowance for lengthening of the Pd-X bond trans to carbon, due to the differing trans influence of the carbon and nitrogen atoms, resulting in an asymmetric $Pd(\mu-X)_2Pd$ moiety,

In conclusion, the ligand presents a versatile behavior dependent on the reaction conditions. In noncoordinating solvents such as toluene, activation of the $C_{aromatic}$ -H bond proceeds smoothly at room temperature to give the five-membered trinuclear metallacyclic species **4a**. Higher temperatures are needed to produce the dinuclear compound either from the trinuclear species or by direct metalation of the ligand itself. This would be in agreement with $C_{aromatic}$ -H bond cleavage requiring a low activation energy and should be the kinetically controlled process: a possible intermediate step in the formation of the dimer complex.³⁰ Under more intense conditions, refluxing acetic acid, va ery stable endo six-membered metallacycle containing $C_{aliphatic}$ -H bonds seems to be the thermodynamically favorable product under these conditions.

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Supporting Information Available: Figures, tables, and CIF files giving crystal structure data and structure refinement de-

tails for **1a**, **4a**, **2a** and **2a**' and text giving details of the syntheses of new compounds and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. 718085 (**1a**), 718086 (**2a**), 718087 (**2a**'), and 718089 (**4a**).