Enamine Character of a 2,3-η^2-Coordinated Pyrrole

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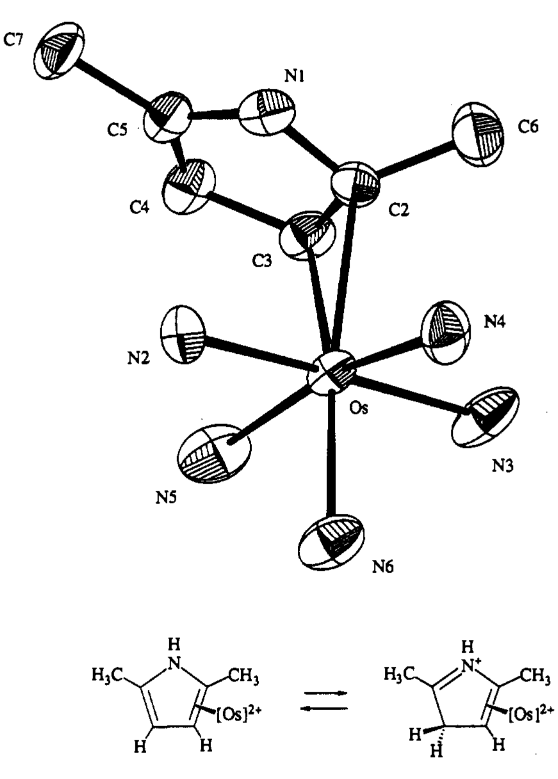
The emergence of several general synthetic routes to η^2-coordinate complexes of aromatic molecules[1–4] provides an opportunity to explore how such coordination alters the reactivity of the substrate. Although such complexes have now been reported for arenes,[1a,2] pyridines,[1b,3] pyrroles,[1c] furans,[1c] thiophenes,[1c] and selenophenes,[4] little is known about reactivity of the η^2-bound aromatic ligand. We report the first crystallographic and structural evidence that 2,3-η^2-coordination of a pyrrole transforms the ligand into an enamine.

Following a procedure similar to that earlier reported for pyrrole,[5] the complex $[Os(NH_3)_5((2,3\text{-}\eta^2)\text{-}2,5\text{-dimethylpyrrole})](OTf)_2$ (**1**) was synthesized from the free ligand and an Os(III) precursor. ^1H NMR data indicate that, at 20 °C, **1** is fluxional, showing single, broad peaks for the methyl and methine protons.[6] As a consequence of the methyl substituents, **1** has a racemization (tautomerization) rate several orders of magnitude faster than that of the parent pyrrole complex, whose NMR spectrum is chemical shift resolved at this temperature.[1c]

Crystal Structure. Air-sensitive crystals of **1a** were obtained from a DME solution. The molecular structure[7] of the cation appears in Figure 1. As postulated for the parent complex,[1c] the 2,5-dimethylpyrrole is η^2-coordinated at C2 and C3, with the Os–C distances approximately equal. Analogous to structures of other η^2-aromatic species,[3,8] the metal forms a plane with C2 and C3 which lies roughly perpendicular to that of the ligand (dihedral angle = 112.9°). The methyl carbon attached at C2 is displaced by 0.87 Å from the ring plane, approximating sp^3 geometry. The C3–C4 bond length has increased 0.05 Å, and the C4–C5 bond shortened 0.06 Å, compared to free pyrrole,[9] an observation that indicates *a significant localization of pyrrole π-electron density.*



1 **2**

Figure 1. ORTEP drawing of $[((2,3\text{-}\eta^2)\text{-}2,5\text{-dimethylpyrrole})Os(NH_3)_5]^{2+}$ (**1**) and reaction of **1** to **2**. Selected bond distances (Å) and angles (deg) are as follows: Os–C2 = 2.218 (8); Os–C3 = 2.219 (7); N1–C2 = 1.41 (1); C2–C3 = 1.41 (1); C3–C4 = 1.47 (1); C4–C5 = 1.32 (1); C5–N1 = 1.388 (9); C2–C6 = 1.51 (1); Os–N2 = 2.13 (1); Os–N3 = 2.15 (1); Os–N6 = 2.171 (8); C2–Os–C3 = 37.1 (3); N1–C2–C3 = 106.4 (7); C2–C3–C4 = 105.8 (7); C3–C4–C5 = 109.1 (6); C4–C5–N1 = 109.5 (5); C5–N1–C2 = 109.3 (6); N1–C2–C6 = 113.0 (7); N1–C5–C7 = 120.4 (7); C3–C2–C6 = 126.3 (9); C4–C5–C7 = 130.1 (7); N2–Os–N6 = 86.1 (3); N2–Os–N3 = 176.7 (5); N2–Os–N4 = 89.9 (3).

Reactivity. The uncoordinated portion of the 2,3-η^2 tautomer of **1** may be viewed as an enamine. In marked contrast to the behavior observed for free pyrrole, which protonates at the α-position preferentially and under forcing conditions ($pK_a = -1$),[10] the treatment of **1** with anilinium ion ($pK_a = +4.6$) in methanol (10 min, ether precipitation) yields a β-protonated (i.e., C4) species, exclusively (**2**).[11] ^1H, ^{13}C, and DEPT NMR data indicate inequivalent methyls along with a methine and a methylene group. The same product is obtained by treatment of **1** with 1 equiv of triflic acid in methanol (10 min, ether precipitation). Protonation of the parent pyrrole complex with triflic acid in methanol also produces a β-protonated product. Treatment of **2** with a slight excess of diisopropylethylamine completely restores **1**. Preliminary data indicate that carbon electrophiles such as methylacetonitrilium triflate also react preferentially at C4 with no indication of a competitive process at an α-position.[12]

With dipolarophiles such as maleic anhydride, **1** does not show enamine reactivity, but acts as an azomethine ylide yielding

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(5) A solution of 2,5-dimethylpyrrole (2.90 g, 30 mmol), $Os(NH_3)_5(OTf)_3$ (0.90 g, 1.25 mmol) 1,2-dimethoxyethane (7.0 g), and *N,N*-dimethylacetamide (3.0 g) was treated with activated Mg^0 powder (2.9 g). After 100 min, addition of CH_2Cl_2 (150 mL) to the filtered reaction mixture resulted in a light yellow precipitate (**1**, 0.60 g, 0.90 mmol, 72% yield). A sample of **1** (0.35 g) was purified by ion-exchange chromatography and precipitated as a tetraphenylborate salt (**1a**, 0.47 g, 92%). Anal. ($C_{54}H_{64}B_2N_6Os$) C, H, N; C: calcd, 64.38; found, 63.91.

(6) Characterization of **1**: (a) ^1H NMR (20 °C, acetone-d_6) 6.98 (NH, br, 1 H), 5.17 (CH, br, 2 H), 4.41 (*t*-NH_3, br, 3 H), 3.30 (*c*-NH_3, br, 12 H), 1.80 (CH_3, br, 6 H); ^1H NMR (−50 °C, acetone-d_6) 7.05 (NH, s, 1 H), 5.32 (C(4)H, s, 1 H), 4.88 (C(3)H, s, 1 H), 4.54 (*t*-NH_3, br, 3 H), 3.40 (*c*-NH_3, br, 12 H), 1.98 (CH_3, s, 3 H), 1.53 (CH_3, s, 3 H); (b) ^{13}C NMR (proton decoupled, 20 °C, acetone-d_6) 102 (C(2,5), br), 60 (C(3,4), br), 15 (CH_3, br); (c) cyclic voltammetry ($\nu = 200$ mV/s; CH_3CN/TBAH) $E_{1/2} = +0.05$ V; NHE. (d) Anal. ($C_9H_{25}N_6OsO_9S_3F_9$) C, H, N.

(7) Crystallographic data: $C_{54}H_{64}B_2N_6Os\cdot 3CH_3OCH_2CH_2OCH_3$; $M = 1279.32$; triclinic, space group $P1$ (No. 1); $a = 11.966$ (4) Å, $b = 13.677$ (3) Å, $c = 11.132$ (3) Å; $\alpha = 98.08$ (2)°, $\beta = 104.94$ (4)°, $\gamma = 110.46$ (2)°, $V = 1595$ (2) Å^3; $Z = 1$, $d_{calcd} = 1.33$ g·cm^{-3}. The structure was solved by direct methods using TEXSAN 5.0. Full-matrix least-squares refinement yielded $R(F) = 0.032$ and $R_w(F) = 0.048$ for 11 120 absorption-corrected reflections with $I > 3\sigma(I)$ measured within the full sphere up to $2\theta = 50°$ on a Rigaku AFC6S diffractometer (Mo Kα radiation, λ = 0.710 69 Å; $T = -120$ °C). The refinement of the enantiomer with the inverted coordinates gave $R(F) = 0.047$ and $R_w(F) = 0.067$.

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(11) Characterization of **2**: (a) ^1H NMR (20 °C, acetone-d_6) 5.07 (*t*-NH_3, br, 3 H), 4.66 (C(3)H, d (5.7 Hz), 1 H), 3.83 (*c*-NH_3, br, 12 H), 3.28 (C(4)H, d (24.6 Hz), 1 H), 3.05 (C(4)H, dd (5.7, 24.6 Hz), 1 H), 2.55 (C(5)CH_3, s, 3 H), 1.85 (C(2)CH_3, s, 3 H); (b) ^{13}C NMR (20 °C, acetone-d_6) 187.1 (C(5)), 74.3 (C(2)), 46.2 (C(4)), 42.1 (C(3)), 17.8 (CH_3), 16.1 (CH_3); (c) cyclic voltammetry ($\nu = 200$ mV/s; CH_3CN/TBAH) $E_{p,a} = +1.09, +1.35$ V; $E_{p,c} = -1.03$ V; NHE. (d) Anal. ($C_9H_{25}N_6OsO_9S_3F_9$) C, H, N.

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2,5-cycloaddition products, as earlier reported for $[Os(NH_3)_5(\eta^2\text{-pyrrole})]^{2+}$.[1c] A full report of electrophilic substitution and dipolar cycloaddition reactivity for η^2-pyrrole and substituted pyrrole complexes is forthcoming.

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Supplementary Material Available: Tables of experimental details, atomic positional parameters, thermal parameters, and bond distances and angles and an ORTEP drawing of the asymmetric part of the unit cell for **1a** (15 pages); table of observed and calculated structure factors for **1a** (75 pages). Ordering information is given on any current masthead page.

Synthesis and Structural-Bonding Analysis of the $[Au_6Ni_{12}(CO)_{24}]^{2-}$ Dianion Containing an Unprecedented 18-Vertex Cubic T_d Metal Core Composed of Five Face-Fused Octahedra: The First Example of a Discrete Gold/Nickel Bimetallic-Bonded Species

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Continuing efforts in our laboratory[1] have been directed toward the syntheses of new high-nuclearity nickel carbonyl clusters through reactions of various transition-metal and main-group compounds with the $[Ni_6(CO)_{12}]^{2-}$ dianion.[2] Here we report the synthesis and structural determination of the novel $[Au_6Ni_{12}(CO)_{24}]^{2-}$ dianion (**1**). This cluster, which represents the first example of a molecular gold/nickel bimetallic-bonded species, possesses a heretofore unknown 18-vertex T_d polyhedron composed of five face-fused metal octahedra.

The Au_6Ni_{12} cluster (**1**) was obtained from a 2:3 molar reaction of $[PPh_3Me]^+{}_2[Ni_6(CO)_{12}]^{2-}$ (0.50 g, 0.40 mmol) and Ph_3PAuCl (0.30 g, 0.60 mmol) in THF at ambient temperature for 18 h under a N_2 atmosphere. After removal of a brown precipitate by filtration, the THF solution was reduced under vacuum to a volume of 15 mL and chromatographed on a SiO_2 gel column. **1** was isolated in ca. 5% yield as the third band eluted from the column. This red, air-unstable cluster, which was crystallized as the $[PPh_3Me]^+$ salt by slow diffusion of diisopropyl ether into a concentrated THF solution, was characterized by infrared and electrochemical measurements and by a single-crystal X-ray diffraction analysis.[3]

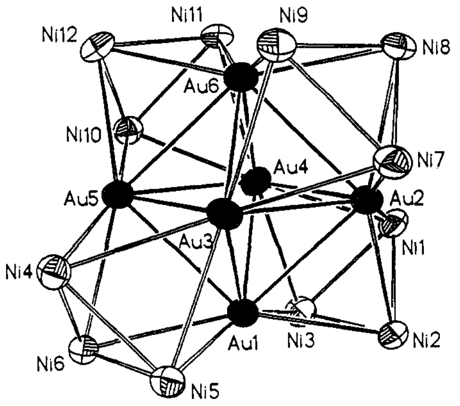

Figure 1. Au_6Ni_{12} core of the 236-electron $[Au_6Ni_{12}(CO)_{24}]^{2-}$ dianion (**1**). This 18-vertex polyhedron of cubic T_d-$\bar{4}3m$ symmetry may be viewed as a face-to-face condensation of four octahedral Au_3Ni_3 fragments at alternate faces of a central Au_6 octahedron.

The idealized T_d configuration of the $[Au_6Ni_{12}(CO)_{24}]^{2-}$ dianion (**1**) can be formally considered to arise from the condensation of four $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ fragments in antiprismatic orientations on four alternate faces of a central Au_6 octahedron. Alternatively, the Au_6Ni_{12} core can be described as a composite of four vertex-sharing Au_3Ni_3 octahedra (Figure 1). Each equilateral nickel triangle retains the architecture of the three terminal carbonyl and three doubly bridging carbonyl ligands found in the two $Ni_3(CO)_3(\mu_2\text{-}CO)_3$ moieties comprising the trigonal-antiprismatic $[Ni_6(CO)_{12}]^{2-}$ precursor. Electron counting in this face-fused polyoctahedral cluster, which may be considered to possess globally delocalized metal-metal bonding, gives a total of 236 electrons, which agrees with the predicted cluster valence electron count for four octahedra sharing six vertices (i.e., 4 × 86 − 6 × 18 = 236 electrons).[4,5] The 12 independent, Au-Au distances in the central Au_6 octahedron vary from 2.786 (2) to 2.882 (2) Å; the mean value of 2.835 Å is shorter than the corresponding mean Au-Au distance of 2.98 Å on the "surfaces" of the $Au_{11}X_3(PAr_3)_7$ clusters (where X = I, SCN)[6] but comparable to the mean Au-Au distance of 2.81 Å on the "surface" of the $[Au_9(P\{p\text{-tol}\}_3)_8]^{3+}$ cluster.[7] To our knowledge, there are no previous examples of a noncentered Au_6 octahedron. The yellow $[Au_6(P\{p\text{-tol}\}_3)_6]^{2+}$ dication (where *p*-tol denotes 4-methylphenyl), originally formulated[8] as a noncentered octahedral cluster, was recently shown by Schmidbaur and co-workers[9] to be the $[Au_6(P\{p\text{-tol}\}_3)_6(\mu_6\text{-}C)]^{2+}$ dication with octahedral coordination of the $AuPPh_3$ fragments around an interstitial carbon atom; thus, the carbide-centered atom in this cluster results in a normal electron count[10] and accounts for the unusually long Au-Au distances of 3.02 Å (average).[11-17] In

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(3) $[PPh_3Me]^+{}_2[Au_6Ni_{12}(CO)_{24}]^{2-}\cdot C_4H_8O$: orthorhombic, *Pbca*, a = 17.730 (5) Å, b = 29.518 (6) Å, c = 30.676 (14) Å, V = 16054 (9) Å^3, Z = 8. The crystal structure (with the independent unit consisting of one dianion, two monocations, and one THF molecule) was determined by direct methods (SHELXTL) followed by successive Fourier and difference syntheses. Anisotropic least-squares refinement converged at $R_1(F) = 8.38\%$, $R_2(F) = 7.74\%$ for 7657 independent absorption-corrected reflections ($|F| > 3.0\sigma(F)$) obtained at room temperature via a Siemens (Nicolet) P3/F diffractometer with Mo Kα radiation.

(4) Application of the topological electron-counting (TEC) model[5] to **1** also gives a total valence cluster electron count (N) of 236, as calculated from the equation $N = 2(8V - F + 2 + X)$ where V = 18 vertices, F = 32 exposed triangular (metal-metal bonding) faces, and X = 4 (based upon four vertex-sharing octahedra). The fact that this and other electron-counting procedures do *not* predict the correct electron total for five face-fused metal octahedra emphasizes from a bonding viewpoint that **1** is best considered as the composite of four vertex-sharing Au_3Ni_3 octahedra.

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