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Synthesis and Structural Characterization of $Au_4(MNT)(dppee)_2(Cl)_2 \cdot {}^1/_4CH_2Cl_2$ (MNT = 1,2-Dicyanoethene-1,2-dithiolate-*S,S'*; dppee = *cis*-Bis(diphenylphosphino)ethylene): A Gold(I) Metal–Olefin Complex in Which the Olefin Orientation Relative to the Coordination Plane Involving the Metal Is Defined

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Summary: The reaction of 1 equiv of $Na_2(MNT)$ *(MNT = 1,2-dicyanoethene-1,2-dithiolate-S,S') with 2 equiv of* $Au_2(dppee)(Cl)_2$ *(dppee = cis-bis(diphenylphosphino)ethylene) produces* $Au_4(MNT)(dppee)_2(Cl)_2$*, (1). The molecular structure of 1 shows the Au atom of the* $[Au(MNT)]^-$ *moiety coordinated to the olefinic center of one of the dppee ligands with a coplanar orientation of the olefin with respect to* AuS_2*.*

The synthesis of stable gold(I)–olefin complexes has proven to be a difficult task. In contrast to the rich metal–olefin chemistry displayed by neighboring elements in the periodic table, the literature available on reactions of gold with unsaturated reagents shows that these complexes tend to have low thermal stability.[1] In most cases only spectroscopic information serves as evidence for the existence of these complexes.[2]

In 1987 Strähle and co-workers[3] reported the synthesis and structural characterization of AuCl(*cis*-cyclooctene). This complex showed AuCl coordination to the olefinic center of the cyclooctene ligand. Unlike the situation which occurs when group 10 triad elements[4] with d^{10} configurations (16e) bond to olefins, wherein the ML_2 and olefin double bond are coplanar, bonding information via the ligand orientation is not present for the 14e AuX(olefin). With AuX_2(olefin) coordination, however, the AuX_2 plane can orient either perpendicular to the olefin–metal plane as in Zeise's anion,[4] $[PtCl_3(olefin)]^-$, or coplanar to it as found with L_2Cu^I(olefin) or L_2M^0(olefin) (M = group 10 element, L = phosphine). To our knowledge no monoolefin structure of $[L_2M^I(olefin)]$ (M = Ag^I, Au^I) has been reported.[5] Structures of Cu^I and Ag^I complexes with the diolefin cyclooctadiene show ML_2 coordination to both olefin centers in a distorted-tetrahedral geometry about the metal atom.[5]

Continuing studies of gold(I) complexes, we have observed the gold–olefin coordination shown in Figure 1, a S_2Au(olefin) species. The complex $Au_4(MNT)(dppee)_2(Cl)_2$ (1) is only the second gold(I)–olefin complex characterized structurally and the first to demonstrate that in-plane coordination is preferred.

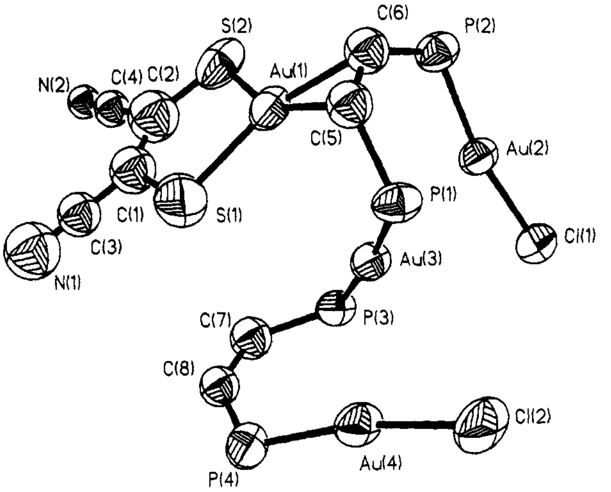

Figure 1. Molecular structure of 1 with thermal ellipsoids at 50% probability (phenyl rings have been omitted for clarity). Relevant bond distances (Å) and angles (deg): Au(1)–Au(3) = 3.367(3); Au(3)–Au(4) = 3.027(3); Au(2)–Au(3) = 3.013(3); Au(1)–C(5) = 2.14(4); Au(1)–C(6) = 2.11(4); C(1)–C(2) = 1.31(7); C(5)–C(6) = 1.38(6); C(7)–C(8) = 1.30(6); S(1)–Au(1)–S(2) = 90.5(5).

Complex 1 is obtained from the reaction of 1 equiv of Na_2MNT with 2 equiv of $Au_2(dppee)(Cl)_2$ in THF.[6] The product has been characterized by IR, ^1H NMR, one-dimensional and two-dimensional $^{31}P\{^1H\}$ NMR,[7] FAB-MS, and X-ray diffraction analysis. The IR spectrum of complex 1 confirms the presence of the MNT ligand by the appearance of a sharp band at 2195 cm^{-1} corresponding

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[3] Dell'Amico, D. B.; Calderazzo, F.; Dantona, R.; Strähle, J.; Weiss, H. *Organometallics,* **1987,** *6,* 1207.

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[5] A search of the Cambridge crystallographic data file has been conducted.

[6] Data for 1: To a THF solution (5 mL) of $Au_2(dppee)(Cl)_2$ (0.1001 g, 0.1161 mmol) was added Na_2MNT (0.0108 g, 0.0581 mmol). The initially colorless solution changed to light yellow upon the addition. After the mixture was stirred for 3 h, the THF was evaporated through vacuum and the yellow solid redissolved in CH_2Cl_2 (10 mL). The CH_2Cl_2 solution was concentrated under vacuum, and addition of Et_2O produced precipitation of a light yellow solid. The solid was filtered and dried under vacuum; yield 0.0780 g (75.1%). IR (cm^{-1}): 2195 (s, C≡N); 1575, 1563 (w, C═C, Ph); 340, 330 (broad, Au—Cl). ^1H NMR ($CDCl_3$, 25 °C; δ): 7.50 (m, Ph). FAB-MS ($(M/Z)^+$): 1755, 1343, 1127, 825, 748. Anal. Calcd: C, 37.54; H, 2.48; N, 1.56. Found: C, 36.45; H, 2.17; N, 1.60.

[7] The 2-D COSY $^{31}P\{^1H\}$ NMR spectrum was obtained using $CDCl_3$ as the solvent and recorded at room temperature on a Varian XL 200 MHz broad-band Fourier transform spectrometer. The spectrum was referenced against external H_3PO_4.

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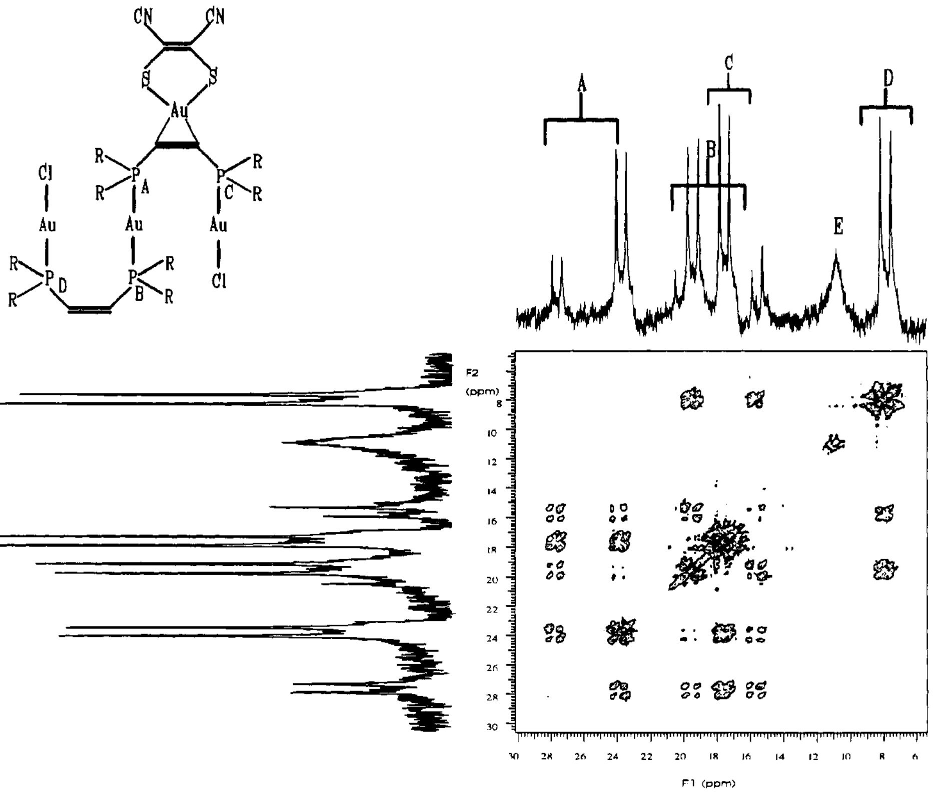

Figure 2. 2-D COSY $^{31}P\{^1H\}$ NMR spectrum for 1 in $CDCl_3$.

to the CN stretch of the ligand. The spectrum also shows a Au–Cl stretch as two broad bands between 340 and 330 cm^{-1}. The complexity of the $^{31}P\{^1H\}$ NMR and that of the FAB-MS suggested a complex polynuclear structure.

Yellow needlelike crystals[8] suitable for X-ray diffraction were obtained from the slow evaporation and diffusion of Et_2O into a CH_2Cl_2 solution of 1. The molecular structure (Figure 1) shows 1 to be a tetranuclear gold(I) species. Au(2) and Au(4) each coordinate in a linear fashion to a Cl atom and to one of the phosphorus atoms of the two dppee ligands present in the structure: P(2)–Au(2)–Cl(1) = 168.2(5)° and P(4)–Au(4)–Cl(2) = 169.7(5)°. The coordination around Au(3) is nearly linear. Au(1) is bonded to a chelating MNT unit and to the olefinic portion of one of the dppee ligands. Selected bond lengths and angles are given in Figure 1.

The coordination around Au(1) is nearly planar. The dihedral angle between the planes defined[9] by S(1)–Au(1)–S(2) and C(5)–Au(1)–C(6) is 6.4°. Similar small deviations from the in-plane olefin coordination have been observed in other d^{10} systems such as $Pt(PPh_3)_2(C_2H_4)$ (dihedral angle 1.6°) and $Ni(PPh_3)_2(C_2H_4)$ (dihedral angle 6.0°).[10,11]

NMR studies suggest that the olefin coordination is maintained in solution. To properly assign the signals observed in the $^{31}P\{^1H\}$ NMR, a 2-D COSY experiment was performed. Figure 2 shows the 2-D COSY $^{31}P\{^1H\}$ NMR spectrum for complex 1 in $CDCl_3$. Doublets C (7.90 ppm) and D (17.55 ppm) correspond to P_C and P_D, respectively. P_C is coupled to P_A with J_{AC} = 49.32 Hz, and P_D is coupled to P_B with J_{BD} = 51.39 Hz. P_A and P_B appear as a typical AB quartet pattern, with a trans coupling constant of J_{AB} = 360.60 Hz. The broad singlet at 10.84 ppm has been assigned to the starting diphosphine reagent $Au_2(dppee)(Cl)_2$.

A combination of factors appear to produce the gold–olefin coordination in 1: the nonlinear S–Au–S structure opens up the Au^I atom to σ donation from the olefin; the coordination of the olefin carbon atoms to P–Au centers appears to create a favorable energy match between the olefin pπ^* orbitals and the dπ orbitals of the metal; relativistic Au···Au interactions[12] (<3.1 Å) help stabilize the overall structure. The S–Au–S angle in complex 1 is 90.5(5)°. This value is smaller than those observed for the analogous L–M–L angle in platinum(0) and nickel(0) phosphine complexes. The lengthened C═C bond distance of 1.38(6) Å compared with that of the uncoordinated olefin in the same complex (1.30(6) Å) indicates that back-donation (Dewar–Chatt–Duncanson type, but in-plane)[13] is important. The lengthening of the C═C bond is

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[8] X-ray structure determination for 1: Data were collected on a Nicolet R3m/E diffractometer controlled by a Data General Nova 4 minicomputer using graphite-monochromated Mo Kα radiation (0.710 73 Å) at ambient temperature over the range $4 < 2\theta < 45°$. The data were corrected for decay, absorption, Lorentz, and polarization effects. All data processing was performed by a Data General Eclipse S140 minicomputer using the SHELXTL crystallographic computational package (version 5.1). The compound crystallizes in the space group $P2_1/n$ with a = 12.712(4) Å, b = 13.541(3) Å, c = 35.661(9) Å, β = 92.86(2)°, V = 6131(3) Å^3, Z = 4, D_c = 1.964 g/cm^3, and μ = 97.84 cm^{-1}. The structure was solved from 2635 reflections with $F_o^2 > 3\sigma(F_o^2)$. Initial gold atom positions were obtained from the direct methods program solution. An interstitial CH_2Cl_2 molecule was found in the asymmetric unit, refined initially to approximately one-fourth occupancy and subsequently refined at 25% occupancy. This solvent molecule is highly disordered. The CN groups from the MNT ligands have been "fixed" to a linear geometry. All non-hydrogen atoms with the exception of ethylene and phenyl ring carbons were refined anisotropically. The final agreement factors were R = 0.0605 and R_w = 0.0719.

[9] The dihedral angle between the S–Au–S and C–Au–C planes was calculated using the CAChe (CAChe Scientific, Inc., Beaveton, OR) molecular modeling program.

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comparable with the increases observed[13] in Ni(0) and Pt(0) systems. Goddard has stated[14] that "bending" of the L–M–L angle in $Pt(PR_3)_2$ complexes promotes metal oxidative addition of H_2 by lowering steric interactions and increasing the Pt 5d to σ^* overlap. The small L–M–L angle also allows an increase in the overlap of the Pt 6s orbital with the filled σ H_2 bonding orbital. A similar bonding situation prevails with the S_2Au(olefin) complex, with the olefin pπ and pπ^* orbitals functioning as the H_2 σ and σ^* orbitals.

While we expect that other L_2Au(olefin) species can be synthesized, ongoing efforts in this regard in our group have repeatedly failed to form crystalline products. The contribution of the weakly attractive relativistic Au···Au bonding forces to the stability of the product may be the key factor which has allowed the title compound to be isolated and structurally characterized.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and bond lengths and angles for 1 (12 pages). Ordering information is given on any current masthead page.

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