Activation of Two Carbon–Hydrogen Bonds of Nitromethane by a Dinuclear Gold(II) Ylide Complex. The Formation of a $CHNO_2$-Bridged A-Frame Complex

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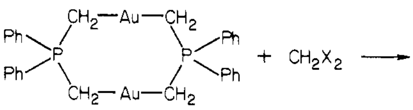
Summary: The reaction of CH_3NO_2 (neat) with the dinuclear gold(II) ylide complex $Au_2[(CH_2)_2PPh_2]_2(O_2CPh)_2$ leads to the rupture of two C–H bonds and the formation of an A-frame species with a $CHNO_2$ bridge. The X-ray molecular structure and the 500-MHz solution ^{1}H NMR spectrum establish the formation of the species.

Although CH_2-bridged A-frame species[2-4] are well established in the chemistry of dinuclear Pd and Pt complexes of diphos ($Ph_2PCH_2PPh_2$), their presence in dinuclear gold ylide chemistry is limited to very recent studies of Schmidbaur.[5,6] They are generally formed from dinuclear gold(I) ylide complexes 1 by addition of CH_2X_2, X = Cl, Br, or I (reaction 1) although we have established[7]



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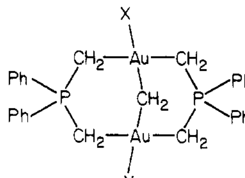

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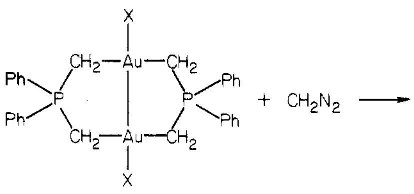

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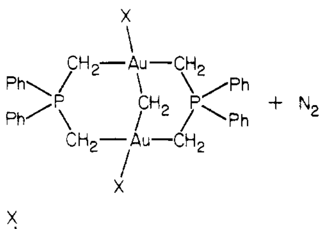

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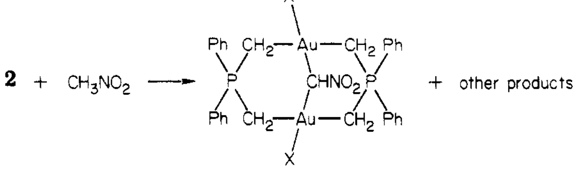

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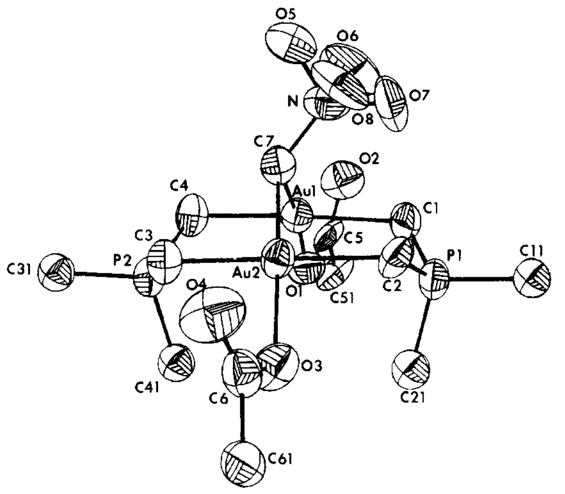

Figure 1. The molecular structure of the A-frame species [Au((CH$_2$)$_2$PPh$_2$)(OC(O)Ph)]$_2$CHNO$_2$. The complete phenyl rings are not drawn. Rotational disorder about N–C7 is observed. Important lengths (Å): Au1···Au2 = 3.073 (1), Au1–O1 = 2.073 (7), Au1–C7 = 2.034 (11), Au2–C7 = 2.033 (13), Au1–C4 = 2.106 (13), Au1–C1 = 2.122 (13), P1–C1 = 1.779 (13), P1–C11 = 1.814 (10), N–O(av) = 1.21 (14), C7–N = 1.484 (17).

that the addition of CH_2N_2 to gold(II) dimers 2 also produces methylene-bridged species (reaction 2) in high yield. We report here the novel addition of CH_3NO_2 to 2, X = benzoate, to produce (reaction 3) the first example of an A-frame species with the unsymmetrical $CHNO_2$ bridge. *Two C–H bonds must be broken to form the product.*

Mixing equimolar quantities of 1 with benzoyl peroxide in benzene or toluene gives a yellow-green precipitate of 2, X = benzoate, in yields greater than 90%. A similar reaction with dibenzoyl disulfide produces the Au–S bonded complex 2, X = SC(O)C$_6$H$_5$, the X-ray structure of which has been completed.[8] When 2, X = benzoate, is added to excess CH_3NO_2, a blood-red solution forms from which light yellow crystals of 3 separate after several weeks at near 0 °C. The estimated yield is about 30% based on starting materials. Preliminary studies of the solution ^{1}H and ^{31}P NMR spectra, as well as the optical spectrum of the reaction in THF, suggest that other gold-containing species, in addition to 2 and 3, are present during the course of the reaction.

Although spectral and structural analyses adequately confirm the formation 3, reaction 3 is quite complex and involves a number of intermediates as identified by ^{31}P NMR and UV–vis spectrometry. The chemistry is in some ways, reminiscient of the reaction reported by Halbert et al.[9] Our best representation of the stoichiometry at this time is as follows

$$2Au_2(ylide)_2(O_2CPh)_2 + CH_3NO_2 = Au_2(ylide)_2(O_2CPh)_2CHNO_2 + Au_2(ylide)_2 + 2HO_2CPh$$

With 2, X = Cl, CH_3NO_2 induces isomerization to a new heterovalent Au(III)/Au(I) species.[10]

The X-ray structure[11] of 3 (Figure 1) establishes the

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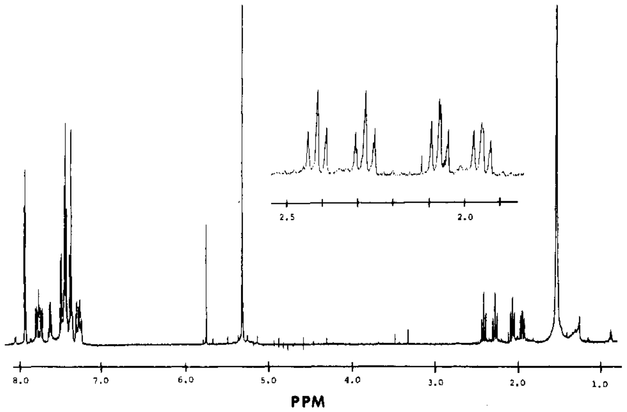

Figure 2. The 500-MHz ^1H NMR spectrum of the $CHNO_2$-bridged complex in CD_2Cl_2. The insert contains the CH_2 region with both ^{31}P and ^1H coupling to each hydrogen atom.

formation of the A-frame species. Disorder of the NO_2 group (occupancy about 1:1) left some uncertainty with regard to the constitution of the bridge. Therefore a proton NMR spectrum at 500 MHz in CD_2Cl_2 was obtained.[12] The four observed 3-line resonances (Figure 2) in the CH_2 region (1.8–2.5 ppm) and the single uncoupled resonance at 5.75 ppm unequivocally establish the presence of the unsymmetrical $CHNO_2$ bridge. Integration verifies the 8:1 intensity ratio expected for this structure.

The geometry about each gold(III) atom is typical of an A-frame species with a Au···Au separation of 3.073 (1) Å. A Au–Au distance of ~2.6 Å is obtained generally for **2**, X = Cl, Br, I, $SC(S)N(C_2H_5)_2$, SC(O)Ph, etc. Thus Au–Au bond rupture occurs during the formation of **3**. This must be accompanied by some chemical reduction of either **2** or the CH_3NO_2 solvent itself. Studies underway are directed to a resolution of this question. No H_2 evolution has been detected, although its formation cannot yet be ruled out conclusively.[13]

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Registry No. 1, 81457-56-9; 2 (X = $OC(O)C_6H_5$), 90990-50-4; 2 (X = $SC(O)C_6H_5$), 90968-87-9; 3, 90968-88-0; CH_3NO_2, 75-52-5; benzoyl peroxide, 94-36-0; dibenzoyl disulfide, 644-32-6.

Supplementary Material Available: Tables of atom coordinates (Table I), bond lengths (Table II), bond angles (Table III), isotropic temperature factors (Table IV), hydrogen atom coordinates (Table V), and observed and calculated structure factors (Table VI) (24 pages). Ordering information is given on any current masthead page.

(11) Crystallographic data: $C_{43}H_{39}Au_2NO_6P_2$; monoclinic, space group $P2_1/n$ (No. 14); a = 10.7806 (14) Å, b = 17.643 (2) Å, c = 21.739 (3) Å, β = 101.351 (11)°, Z = 4, 3158 unique reflections with $I \geq 3\sigma(I)$. With 338 parameters R = 0.0391, R_w = 0.0397, and goodness of fit = 1.179; maximum shift/error = 0.008. Data collected on Nicolet P3F diffractometer at ambient temperature with graphite-monochromated Mo Kα radiation. Data corrected for Lorentz, decay, polarization, and absorption effects. All calculations were performed with SHELXTL crystallographic programs.

(12) We wish to thank Professor Ian Scott and Dr. Paul Fagerness, Center for Biological NMR, Texas A&M University, for these measurements.

(13) Note added in proof. The UV-vis spectrum changes observed during the reaction suggest the presence of at least three gold-containing species.

(Pentamethylcyclopentadienyl)trioxorhenium, $(\eta^5-C_5Me_5)ReO_3$

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Summary: $(\eta^5-C_5Me_5)ReO_3$ has been synthesized from the reaction of $(\eta^5-C_5Me_5)Re(CO)_2(THF)$ with O_2 at 450 psi. It is a rare example of a group 7A organometallic compound having the metal in the maximum group oxidation state *and* an 18-electron configuration.

One aspect of the use of pentamethylcyclopentadienyl ligands that has recently been given attention is the ability to stabilize higher formal oxidation states in organometallic complexes.[1] We here wish to report an extreme instance of this in the synthesis of the air-stable rhenium(VII) complex $(\eta^5-C_5Me_5)ReO_3$. It will be noted coincidentally that despite the maximum group oxidation state being achieved this is nevertheless an 18-electron complex. In the VI and VII oxidation states for rhenium, the occurrence of metal–carbon bonds is very rare indeed and is limited largely to the methyls $ReMe_6$,[2,3] Me_4ReO,[4] Me_3ReO_2,[3] and $MeReO_3$.[5] Conversely, cyclopentadienyl- or (pentamethylcyclopentadienyl)rhenium compounds are numerous[6] but are typically found with low oxidation states.

$(\eta^5-C_5Me_5)ReO_3$ (**1**) was first observed by us serendipitously in an attempt to replace the MeCN ligand in $[(\eta^5-C_5Me_5)Re(CO)(MeCN)(p-N_2C_6H_4OMe)]^+$[7] with dinitrogen and was identified readily from its elemental analysis and IR, mass, and ^1H NMR spectra. The MeCN complex in THF was pressurized with 1500 psi of undeoxygenated nitrogen for 3 days. IR spectroscopy then showed the absence of any carbonyl complexes, and **1** was isolated after chromatography on neutral alumina as the only rhenium compound that eluted. It was similarly produced as a coproduct in the synthesis of $(\eta^5-C_5Me_5)Re(CO)_2(N_2)$ from $(\eta^5-C_5Me_5)Re(CO)_2(THF)$ in THF also using undeoxygenated nitrogen at 1500 psi of pressure. Reaction of these carbonyl complexes with dioxygen impurity in the dinitrogen was implicated and was confirmed by the direct synthesis of **1** in 55% yield from $(\eta^5-C_5Me_5)Re(CO)_2(THF)$[8] in THF under 450 psi of dioxygen for 1 day. Chromatography on silica gel first eluted organic products (see below) using hexane and then a yellow band of **1** using ether, which was recrystallized as yellow needles that melt without decomposition at 192 °C.[9]

The spectroscopic properties of **1** are simple indeed and in agreement with its formulation as a mononuclear complex as illustrated. The 70-eV electron-impact mass spectrum gave the parent ion isotopic cluster in close to

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(8) Synthesized in situ by UV irradiation of $(\eta^5-C_5Me_5)Re(CO)_3$ in THF. The tricarbonyl itself in THF was observed not to react in 3 days with O_2 under the same conditions (450 psi).

(9) Anal. Calcd for $(\eta^5-C_5Me_5)ReO_3$: C, 32.43; H, 4.05. Found: C, 32.31; H, 3.95.

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