Conclusions

The ligands $RN(P(OMe)_2)_2$ (R = Me, Ph) do not appear to be as generally useful as DPM for forming binuclear, A-frame type complexes. With the exception of 9 the only binuclear complexes formed contained a single bridging ligand. Among the mononuclear complexes prepared a number appear to adopt highly fluxional, trigonal-bipyramidal structures as a consequence of the short bite of the chelating ligand. One useful result of this work has been the direct determination of values, some of which are quite large, for ${}^2J_{P-P}$ between trans-disposed phosphorus atoms in four- and five-coordinate rhodium and iridium complexes.

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Registry No. 1, 112968-94-2; 2, 112947-29-2; 3, 112947-31-6; 4, 112947-33-8; 5, 112947-35-0; 6, 112947-37-2; 7, 112947-39-4; 8, 112947-41-8; 9, 112947-43-0; 10, 112947-45-2; 11, 112947-47-4; 12, 112947-49-6; 13, 112947-51-0; 14, 112947-53-2; 15, 112947-55-4; BDPPF, 12150-46-8; [RhCl(COD)]₂, 12092-47-6; [Rh(COD)-(DPPE)]ClO₄, 32799-70-5; [Rh₂(COD)₂(μ -Ph₂PC₄H₂OPPh₂)₂]-(ClO₄)₂, 112947-57-6; [Ir₂(COD)₂(μ -Ph₂PC₄H₂OPPh₂)₂]-(ClO₄)₂, 112947-57-6; [Ir₂(COD)₂(μ -Ph₂PC₄H₂OPPh₂)₂]ClO₄, 112947-59-8; [Ir(COD)(PPh₃)₂]ClO₄, 52657-94-0; [Ir(CO)₃ (PPh₃)₂]ClO₄, 15738-08-6; [IrCl(COD)]₂, 12112-67-3; PhN(P-(OMe)₂)₂, 112947-58-7; MeN(P(OMe)₂)₂, 34244-05-8; P(OMe)₃, 121-45-9.

Supplementary Material Available: Tables of anisotropic thermal parameters, rms amplitudes of anisotropic displacement, intraligand bond distances and interbond angles, torsion angles, and calculated hydrogen atom positions for 9 and 12 (31 pages); listings of F_o vs. F_c for 9 and 12 (139 pages). Ordering information is given on any current masthead page.

Oxidative Addition of Nitroalkanes to Dinuclear Gold(I) Ylide Complexes. The Characterization by X-ray Crystallography of $Au_2(ylide)_2(NO_2)_2$, a Nitro Complex of Gold(II)

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The Au^I ylide complex $[Au((CH_2)_2PPh_2)]_2$ (1) reacts oxidatively with nitroalkanes to form a Au^{II} product, $[Au((CH_2)_2PPh_2)NO_2]_2$ (2-NO₂). This complex was characterized by IR, NMR, and X-ray crystallography. The identity of the product was confirmed by the quantitative formation of 2-NO₂ from I and N₂O₄ "brown gas". The product crystallizes in a monoclinic system C2/c: a = 12.159 (2) Å, b = 14.638 (2) Å, c = 16.536 (2) Å, $\beta = 103.757$ (11)°, and Z = 4 with R = 0.036 and $R_w = 0.033$.

Introduction

The two-center oxidative addition chemistry of [Au- $((CH_2)_2PPh_2)]_2$ (1) is well-established.¹ Reactions with halogens,² benzoyl peroxide,³ and thiuram disulfide^{3b} gives symmetrical gold(II)-gold(II) dimers [Au($(CH_2)_2PPh_2)X]_2$ (2-X, X = Cl, Br, I, OC(O)C₆H₅, SeC₆H₅, etc.). Methyl halides also react⁴ with 1 to form metal-metal bonded adducts [Au($(CH_2)_2PPh_2)]_2CH_3X$ (X = I, Br). These studies have revealed that 1 reacts with many solvents.

Our initial studies of reactions of CH_3NO_2 with gold ylide complexes focussed on reactions with the Au^{II} complex $[Au((CH_2)_2PPh_2)OC(O)C_6H_5]_2$ (2-OBz). As reported,³

a nitromethane solution of 2-OBz at 0 °C produces the A-frame complex wherein CHNO₂ bridges two Au(III) centers. At room temperature a somewhat different chemistry takes place. When left standing in a THF/CH₃NO₂ (12:1) solvent mixture, 2-OBz gives the title compound 2-NO₂.



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Figure 1. A thermal ellipsoid drawing of [Au((CH₂)₂PPh₂)NO₂]₂.

Table I. Crystallographic Data for [Au((CH₂)₂PPh₂)NO₂]₂

formula	$Au_2C_{28}H_{28}P_2N_2O_4$
fw	912
space group	C2/c
systematic absences	hkl, h + k = 2n; h0l, l = 2n; 0k0, 2n
a, Å	12.159 (2)
b, Å	14.638 (2)
c, Å	16.536 (2)
α , deg	90.00
β , deg	103.75 (1)
γ , deg	90.00
V, Å ³	2858.8 (6)
Ζ	4
$d_{\rm calcd}$, g cm ⁻³	2.120
cryst size, mm	$0.15 \times 0.20 \times 0.35$
<i>F</i> (000), e	1720
μ (Mo K α), cm ⁻¹	103.71
radiatn	monochromated in Mo K α ($\lambda = 0.71073$ Å) incident beam
orientatn reflectns, no., range (2θ)	25, 20 < θ < 30°
temp, °C	22
scan method	Ω
data collectn range, 2θ ,	3, 50
deg	KH 00
total reflectns measd	5706
no. of unique data, total with $F_0^2 > 3\sigma(F_0^2)$	2528, 1516
check reflctns	3 every 97
no. of parameters refined	100
trans. factors, max, min	0.96, 0.54
R^a	0.036
R_{w}^{b}	0.033
goodness-of-fit indicator ^c	1.082
largest shift/esd, final cycle	0.022
largest peak, $e/Å^3$	0.90
g	0.000 28

 ${}^{a}R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b}R_{w} = \sum w^{1/2} (|F_{o}| - |F_{c}|) / \sum w^{1/2}F_{o}; w^{-1}$ = $[\sigma^{2}|F_{o}| + |g|F_{o}^{2}]. {}^{c}$ Goodness-of-fit = $[\sum w(|F_{o}| - |F_{c}|)^{2} / (N_{o} - N_{p})]^{1/2}.$

It is known³ (by ³¹P NMR) that the reaction of **2-OBz** with CH_3NO_2 gives 1 as one of the byproducts. In weakly acidic media, compound 1, benzoic acid, and other products result from **2-OBz**. In order to begin to understand various aspects of this complex reaction, 1 was reacted directly with nitromethane and other nitroalkanes.

Reactions of Cu^I complexes with nitroalkanes⁵ and dimethylformamide⁶ DMF have been known for many years.

Table II.	Atom Coor	dinates (×104) a	and Temperature
Facto	ors (Å $^2 imes 10^3$) for [Au((CH ₂	$_{2}^{2}PPh_{2}^{2}NO_{2}]_{2}$

Factors (A ~ 10) for [Au((CH2)21 1 h2)1(O2)]2				
atom	x	У	z	U ^a
Au	1552 (1)	2908 (1)	4669 (1)	40 (1)
Р	1628 (3)	800 (2)	4168 (2)	39 (1)
N	-56 (10)	3550 (8)	4197 (8)	74 (5)
O(1)	-636 (9)	3821 (8)	4626 (8)	120 (6)
O(2)	-354 (12)	3581 (9)	3425 (10)	139 (7)
C(1)	2241 (10)	4211 (7)	4941 (7)	47 (5)
C(2)	709 (9)	1669 (7)	4305 (8)	45 (5)
C(11)	903 (9)	-295 (7)	3994 (7)	37 (4)
C(12)	1469 (10)	-1098 (7)	4320 (8)	51(5)
C(13)	914 (12)	-1931 (9)	4150 (9)	61 (6)
C(14)	-167(12)	-1984 (10)	3666 (8)	63 (6)
C(15)	-737(12)	-1189 (10)	3345 (8)	62 (6)
C(16)	-218 (11)	-357 (8)	3506 (7)	49 (5)
C(21)	2185 (9)	996 (7)	3265(7)	40 (4)
C(22)	2906 (11)	329 (9)	3092 (7)	51 (5)
C(23)	3355 (12)	448 (9)	2381(8)	65 (6)
C(24)	3073 (11)	1196 (11)	1897 (8)	67 (6)
C(25)	2373 (13)	1842 (9)	2077 (9)	66 (6)
C(26)	1922 (10)	1746 (8)	2762 (8)	51 (5)

^a Equivalent isotropic U defined as one-third of the trace of the orghogonalized U_{ij} tensor.

Table III. Selected Bond Lengths (Å) for [Au((CH₂)₂PPh₂)NO₂]₂

Au-N	2.142 (11)	Au-C(1)	2.088 (10)	
Au-C(2)	2.100 (11)	Au–Au _a	2.596 (1)	
P-C(2)	1.743 (12)	P-C(11)	1.818 (11)	
P-C(21)	1.803 (13)	P-C(1a)	1.761(11)	
N-O(1)	1.181 (20)	N-O(2)	1.242 (20)	

Table IV. Selected Bond Angles (deg) for [Au((CH₂PPh₂)NO₂]₂

N-Au-C(1)	87.9 (4)	N-Au-C(2)	86.2 (4)	
C(1)-Au- $C(2)$	173.7 (4)	An-Au-Au _a	175.9 (4)	
C(1)-Au-Au _a	93.4 (3)	C(2)-Au-Au	92.7 (3)	
C(2) - P - C(11)	111.2 (5)	C(2) - P - C(21)	111.7 (6)	
C(11)-P-C(21)	105.9 (5)	C(2)-P-C(1a)	107.1 (6)	
C(11) - P - C(1a)	112.2(5)	C(21)-P-C(1a)	108.8 (6)	
Au-N-O(1)	123.5(10)	Au-N-O(2)	114.1 (11)	
O(1) - N - O(2)	122.3(13)	$Au-C(1)-P_a$	111.5(5)	
Au-C(2)-P	112.6 (6)			

In these solvents Cu^I is oxidized by oxygen to Cu^{II}. With nitroalkanes the product is an N-bonded copper(II) nitrate. Several other metal-catalyzed oxidations involving nitro compounds are well-established.⁷

This paper describes the reaction of 1 with nitroalkanes and the structure of the product obtained with CH_3NO_2 , the first example of a Au(II) nitro complex.

Experimental Section

X-ray Crystallography. Intensity data for [Au-((CH₂)₂PPh₂)NO₂]₂ were collected on the Nicolet R3m/E system. A crystal (0.10 mm \times 0.15 mm \times 0.35 mm) was mounted on a glass fiber and optically aligned in the beam. Cell constants were obtained from 25 high-angle reflections ($20^{\circ} < 2\theta < 30^{\circ}$). Reflection conditions (hkl, h + k = 2n; h0l, l = 2n; 0k0, k = 2n)indicate C_2/c or C_c space group. C_2/c (No. 15) was confirmed by successful refinement. The SHELXTL package installed on the Data General Eclipse S140 computer was used. Decay, Lorentz, polarization, and empirical absorption corrections were applied. The position of the gold atom was located from the direct methods (SOLV). Coordinates of all the other non-hydrogen atoms were found from the successive least-squares refinements and difference Fourier maps. Hydrogen atom positions were calculated according to sp² or sp³ hybridization and fixed at 0.96 Å from C. All non-hydrogen atoms were refined anisotropically.

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Final refinement of 100 parameters gave R = 0.0364 and $R_w = 0.0331$. The largest residual peak was 0.9 e/Å³.

Synthesis. The reagent grade nitroalkanes and the deuteriated NMR solvents were dried over molecular sieves. Gold label nitromethane, Aldrich (impurities suggested by GC 0.6%), and distilled nitromethane and nitrobenzene were tried initially, but no differences in reactivity were observed. *p*-Nitrotoluene from Aldrich was used without further purification. The purity of *p*-nitrotoluene was checked by melting point. Fresh THF, distilled over Na/benzophenone, was always used.

Preparation of $[Au((CH_2)_2PPh_2)NO_2]_2$ from Reactions with Nitroalkanes. In a large excess (20 mL) of nitroalkane, 20 mg of 1 was dissolved. When the mixture was left standing in air, for varying lengths of time, CH₃NO₂ about 3 weeks, CH₃CH₂NO₂ about 2 days, (CH₃)₂CHNO₂ about 3 weeks, and CH₃CH₂CH₂NO₂ about 2 weeks, the color changed from green to intense orange. With CH₃CH₂NO₂ a yellow precipitate appeared (84% yield). The solvent was allowed to evaporate slowly, and orange crystals were formed (yield ~50%). Crystals of X-ray quality obtained by dissolving 2-NO₂ in chloroform and slowly evaporating the solvent; mp 216.5 °C. Anal. Calcd for Au₂H₂₈P₂N₂O₄: C, 36.84; H, 3.07; N, 3.07. Found: C, 36.90; H, 3.02; N, 3.01. ¹H NMR (CDCl₃); δ 7.45 and 7.65 (m, phenyl protons), 1.87 (d, J_{P-H} = 9.9 Hz, CH₂).

Preparation of [Au((CH₂)₂PPh₂)NO₂]₂ from Reaction with N₂O₄ "Brown Gas". In a 25-mL Schlenk flask 25 mg of 1 was suspended in 5 mL of toluene. This flask was degassed and connected via cannula to a three-necked round-bottomed flask containing about 5 mL of (concentrated) nitric acid. An outlet needle was inserted in the stopper on the 25-mL Schlenk flask. Ethanol (95%) was slowly added to the nitric acid by syringe, approximately 0.5-mL total over a period of 30 min. The brown gas, containing N₂O₄, was bubbled through the suspension of 1, producing a yellow precipitate (90% yield). The identification of this compound as 2-NO₂ was confirmed by its melting point.

Preparation of $[Au((CH_2)_2PPh_2)(NO_2)]_2$ from the Reaction of 1 and *p*-Nitrotoluene in THF. To a stirred solution of 1, 30 mg (0.036 mmol) in THF (10 mL), was added p-nitrotoluene (0.01 g, 0.072 mmol) in one portion at room temperature. The resultant reaction mixture was stirred several days (15–20 days). During this time an orange-yellow solid precipitated. After separation of solid, 2-NO₂, by filtration, the organic products from the filtrate were extracted with diethyl ether. The Et_2O layer was washed with water (10 mL, twice) and dried with MgSO₄. The solvent was evaporated to dryness yielding a viscous yellow liquid. The liquid was purified by preparative TLC (silica/40% EtOAc in hexane) and was found to contain toluene and polymerized THF. ¹H NMR of yellow liquid in $CDCl_3$; δ 7.2 (m, 5 H, phenyl protons), 2.3 (s, 3 H, CH₃) assigned for toluene; 5.65 (d, J = 10 Hz, 1 H, olefinic protons), 4.3 (m, 2 H, olefinic protons), 4.1 (m, 1 H, 4-H), 4.0 (m, 3-H), 2.1-1.9 (br m, 5-H) assigned for oligomerized THF. MS (electron impact): m/e 92 (M⁺, toluene), 210 (M⁺, oligomerized product of THF). The purity of the orange yellow Au^{II} complex obtained from this reaction was checked by ¹H NMR and mixed melting point with authentic material.

Physical Measurements. The NMR spectra were obtained in the CDCl_3 (TMS reference) or $\text{THF-}d_8$ solutions by using Varian Instruments EM390 (90 MHz) and XL-200 (200 MHz) spectrometers.

IR spectra were obtained with IBM FTIR/85 and Perkin-Elmer 783 infrared spectrometers. Samples were prepared as CsI solid pellets. Elemental analysis were performed by Galbraith Laboratories Inc.

Results

Upon reaction of 1 with nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane, an orange-yellow product is formed. Long reaction times are required (a few days to several weeks), depending on the nitroalkane and on the concentration of the gold complex. Once the product was isolated, it is sufficiently stable for characterization. It decomposes in air in a few weeks. Reaction with nitrotoluene in THF gives interesting observations. If the reaction is stirred for about 2 days in diffuse light, no color change is observed. In light the solution color changes to orange color within a few hours. This observation suggested that the reaction is light-sensitive and probably free radical in nature.

The ¹H NMR spectra of the title compound 2-NO₂ and $[Au((CH_2)_2PPh_2)Cl]_2$ (2-Cl) show similar chemical shifts in CDCl₃, for the phenyl and methylene protons. This observation is due to the very similar electron-withdrawing properties of Cl and NO₂. The ¹H NMR clearly indicated that 2-NO₂ is a Au^{II}-Au^{II} dimer.

The formation of 2-NO₂ from 1 was followed by ¹H NMR. The solubility of 1 in pure nitroalkanes is too low to observe an NMR signal; thus a different solvent system was required. When 5 mg of 1 was dissolved in 0.5 mL of CDCl₃ and a 10-fold excess $(3.3 \ \mu L)$ of CH₃NO₂ was added, no reaction was observed within the first 24 h. The experiment was repeated with a 100-fold excess of CH₃NO₂. Initially no reaction was observed. When the mixture was left standing overnight, a green flocculent and later polymeric precipitate appeared but the solution NMR spectra showed only the starting materials. Similar results were obtained in CDCl₃ with a 10- and a 100-fold excess of CH₃CH₂NO₂. The solution was observed by ¹H NMR for up to 1 week.

In 0.5 mL of THF only about 3 mg of 1 could be dissolved. A twofold excess of CH₃NO₂ showed by ¹H NMR a reaction forming an asymmetrical gold product (two doublets at δ (CH₂) 1.89 ($J_{PH} = 12.4$ Hz) and δ (CH₂) 1.29 ($J_{PH} = 12.6$ Hz)). A peak slightly shifted from the CH₃NO₂ (δ 4.32) at δ 4.11 appeared also. Only about two-thirds of the Au^I ylide starting material (δ 1.22 ($J_{PH} = 12.4$ Hz)) was used up in the reaction in the first 2 h. No visible progress was observed after 2 h, but the reaction did seem to go to completion in about 3 months.

Solid pellet CsI IR spectra of 2-NO₂ obtained both from CH_3NO_2 and $(CH_3)_2CHNO_2$ were compared to the spectra of 1 and 2-Cl. All high-frequency bands present in 2-Cl were also present in 2-NO₂. In the nitroalkane addition product two additional bands, assigned to asymmetric and symmetric vibrations of the NO₂ group, were present at 1262 and 1600 cm⁻¹. These positions are similar to bands found⁸ in nitroalkanes as expected since gold has nearly the same electronegativity as carbon. X-ray crystallography shows the title compound on a center of symmetry. The Au–Au bond is very short, 2.596 (1) Å, while the Au–N bond distance, 2.14 (1) Å, is comparable to the Pt–N distance in PtNO₂ complexes.⁹ The eight-membered ring containing the two metal atoms is in the sterically preferred chair configuration. The average gold carbon bond is 2.1 Å long, a normal distance for Au^{II} ylide¹¹ complexes.

Since there was an initial question crystallographically as to whether $-NO_2$ or $-N(O)CH_3$, was coordinated to the Au in 2-NO₂ formed from CH₃NO₂, both models were refined. The two possibilities were found to be indistinguishable. The N–O bond lengths (or N–O and N–C) are 1.18 (2) and 1.24 (2) Å, but this difference is not statistically significant. It is also not unusual, however, for the two N–O distances in coordinated NO₂ to be somewhat different.¹⁰ The ¹H NMR spectrum as well as the synthesis of 2-NO₂ using N₂O₄ settled any crystallographic ambiguity.

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Discussion

In view of the ease of oxidation¹¹ of 1, it is not surprising that it reacts with nitroalkanes and N_2O_4 "brown gas". The symmetrical addition of N2O4 is analogous to the oxidative addition of halogens or pseudohalogens to 1. The product formed is the symmetrical Au^{II}-Au^{II} species, not a mixed-valent Au^{III}-Au^I species.

The reaction of nitroalkanes with 1 to form $2-NO_2$ in some ways appears similar to the oxidative addition observed with alkyl halides. However, no adduct, 3, has been isolated. Presumably either such an intermediate is not formed or it is destroyed as it is formed.



Nitroalkanes support radical reactions; therefore, we believe that a radical¹² chain process forms the stable dinitro product 2-NO2 and various other organic components of alkyl or aryl radicals. Our data have substantiated a radical reaction for 1 with p-nitrotoluene in THF. This reaction produces 2-NO₂ as a main product with organic radical products including toluene and oligomerized THF. The organic products have been characterized by GC, GC-mass spectrometry, and NMR spectroscopy.

Several possible reaction sequences involving radical formation can be written. One such scheme is shown below. With p-nitrotoluene, termination gives toluene as a major organic product. This type of stable arene formation from an aryl radical in a protic solvent^{13e} is very common. The THF radical formed by H atom abstraction can undergo a coupling reaction^{13b,c} with additional THF or available radicals. The coupling reaction between THF

radicals produces oligomerized products. מו יו ת ווי

$$\mathrm{RNO}_2 + 1 = \mathrm{R}^{\bullet} + \mathrm{Au}_2 \mathrm{NO}_2^{\bullet}$$

 Au_2NO_2 + RNO_2 = R + $Au_2(NO_2)_2$ product

$$R^{\bullet} + THF \rightarrow THF$$
 oligomers + RH

The structure of one oligomerized THF product assigned on the basis of mass and NMR spectroscopy is shown as ิ.



Additional evidence for the radical nature of the reaction of 1 with nitroalkanes relates to the nature of the R group. Nitroethane reacts more rapidly than CH₃NO₂ and the other alkyl nitrates studied. This observation is consistent with a radical process with an initiation step which follows the order R = Et > R = Me. Nucleophilic oxidative addition should show reactivity,¹⁴ $CH_3 > Et >$ secondary alkyls, paralleling reactivities observed with alkyl halide additions to 1, an order different from the one formed here. The alkyl halides addition reaction also is reversible while alkyl and aryl nitrates react irreversibly.

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Registry No. 1, 81457-56-9; 2-NO₂, 113008-27-8; CH₃NO₂, 75-52-5; CH₃CH₂NO₂, 79-24-3; (CH₃)₂CHNO₂, 79-46-9; CH₃C-H₂CH₂NO₂, 25322-01-4; N₂O₄, 10544-72-6; p-nitrotoluene, 99-99-0.

Supplementary Material Available: Complete listings of atomic coordinates and isotropic and anisotropic thermal parameters for complex 2-NO2 (2 pages); a table of observed and calculated structure factors for complex 2-NO2 (9 pages). Ordering information is given on any current masthead page.

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