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Synthesis and X-ray Crystallographic Characterization of the Gold(II) Ylide Dimers $[Au(CH_2)_2PPh_2]_2(CH_2CN)Br$ and $[Au(CH_2)_2PPh_2]_2(CH_2C(O)Ph)Br$. Unusually Stable Functionalized Alkyl Halide Adducts

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Abstract

The reaction of bromoacetonitrile and $[Au(CH_2)_2PPh_2]_2$, **1**, in benzene gives $[Au(CH_2)_2PPh_2]_2(CH_2CN)Br$, **2**, in near quantitative yield. Bromoacetophenone reacts with **1** in dichloromethane to give $[Au(CH_2)_2PPh_2]_2(CH_2C(O)Ph)Br$, **3**, in high yield. These gold(II) functionalized alkyl halide adducts are very stable. Their structural, physical and chemical properties are compared with $[Au(CH_2)_2PPh_2]_2(Me)Br$, **4**. For **2**, $C_{30}H_{30}Au_2BrP_2N$, triclinic, $P\bar{1}$; a = 11.030(3), b = 16.016(4), c = 10.3639(2) Å, α = 92.310(20), β = 107.950(18), γ = 106.730(19)°, V = 1651.4(7) Å^3 with Z = 2. The structure refined to R = 0.040, R_w = 0.040 for 3195 reflections with $I \geqslant 3.0\sigma(I)$. For **3**, $C_{36}H_{35}Au_2BrP_2O$, monoclinic, Pc; a = 13.684(4), b = 9.667(15), c = 25.765(3) Å, β = 100.95(16)°; V = 3346(1) Å^3 with Z = 4. The structure refined to R = 0.049, R_w = 0.045 for 2852 reflections with $I \geqslant 3.0\sigma(I)$. Both compounds have Au–Au single bonds. In solution each shows a much lower tendency to reductively eliminate alkyl halide than the non-functionalized alkyl adduct.

Introduction

The oxidative addition of the gold(I) ylide dimer $[Au(CH_2)_2PPh_2]_2$, **1**, by alkyl halides (RX; R = Me, Et, $PhCH_2$, X = Br, I) gives asymmetrically substituted Au(II) adducts. This overall two-center two-electron oxidative addition product of **1** has been shown by ^1H NMR spectroscopy to be in equilibrium [1a] with RX and **1**. Few other examples [1b] of an oxidative addition reaction of a dimeric complex in equilibrium with the oxidizing substrate have been reported. Simply heating the Au(II) alkyl halide adduct in the solid state causes reductive elimination giving **1** and RX (MeBr, MeI, EtI).

Asymmetrically substituted Au(II) complexes of the general form $[Au(CH_2)_2PPh_2]_2(R)X$ have been reported with alkyl [2a], benzyl [2a] trimethylsilylmethylene [2a], or fluorinated hydrocarbons [2b]. The only functionalized alkyls reported to date [3] of the dimeric Au(II) adducts are obtained from the reaction of **1** with CH_2ClI or CHClBr, giving $[Au(CH_2)_2PPh_2]_2(CH_2X)X'$ (X = Cl, X' = Br, I).

We report here the synthesis, reactivity and X-ray structural investigation of $[Au(CH_2)_2PPh_2]_2(CH_2CN)Br$ and $[Au(CH_2)_2PPh_2]_2(CH_2C(O)Ph)Br$, two Au(II) ylide adducts with functionalized alkyl substituents. Modification of the reactivity of the functionalized group is the underlying objective for these studies.

Experimental

All reactions were carried out in oven-dried Schlenk-glassware using standard inert atmosphere techniques. All solvents were dried before use according to standard methods. Bromoacetonitrile and 2-bromoacetophenone were purchased from Aldrich and used as received. All ^1H NMR spectra were obtained in $CDCl_3$ at 90 MHz (CW mode) with a Varian EM-390 at 35 °C using TMS as an internal standard. All IR spectra were obtained using a Perkin-Elmer 783 at 20 °C with NaCl cells. All gas chromatography was carried out using a Hewlett Packard 5793A, 6 ft column, 0.085 in internal diameter, stationary phase carbowax 20M, support chrom. w-HP 80/100 mesh. The diphenyl gold(I) ylide dimer $[Au(CH_2)_2PPh_2]_2$, **1**, was prepared in a manner similar to Schmidbaur's method [4] for the dimethyl analogue. The appropriate ylide, $Ph_2P(CH_2)Me$, was obtained from the deprotonation of the phosphonium salt $[Ph_2PMe_2]Br$ with KH in THF. The gold ylide dimer was separated from $[Ph_2PMe_2]Cl$ (a product from the transylidation reaction) by washing the precipitate with methanol, then THF, followed by recrystallization from hot benzene.

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[Au(CH$_2$)$_2$PPh$_2$]$_2$(CH$_2$CN)Br

To 40 mg (0.05 mmol) of [Au(CH$_2$)$_2$PPh$_2$]$_2$ in 4 ml of benzene was added 120 μl (1.7 mmol) of BrCH$_2$CN. The solution changed from a turbid white to a translucent yellow–orange color. After 30 min of reaction at 25 °C the solvent was removed *in vacuo* until it was about one quarter of its original volume. Hexane (15 ml) was added to the benzene–bromoacetonitrile solution causing the desired product to precipitate. The hexane layer was decanted and the yellow–orange precipitate was washed (3 × 15 ml) with hexane giving [Au(CH$_2$)$_2$PPh$_2$]$_2$(CH$_2$CN)Br (41 mg, 0.04 mmol) in 90% yield. IR(C≡N) ν(CH$_2$Cl$_2$, 2200 cm^{-1}) IR of BrCH$_2$CN, (CH$_2$Cl$_2$, 2250 cm^{-1}), ^{1}H NMR (CDCl$_3$, 90 MHz, 35 °C) δ = 1.54 and 1.90(d, $^2J_{PH}$ = 9.17 and 10.5 Hz respectively) AuCH$_2$P; 2.11(s, AuCH$_2$CN); 7.8–7.2(m, PPh$_2$). Melting Point 205–207 °C (decomposition).

[Au(CH$_2$)$_2$PPh$_2$]$_2$(CH$_2$C(O)Ph)Br

To 21 mg (0.0256 mmol) of [Au(CH$_2$)$_2$PPh$_2$]$_2$ in 3 ml of CH$_2$Cl$_2$ was added 8.8 mg (0.044 mmol) of PhC(O)CH$_2$Br. The color of the solution immediately changed from water white to a translucent yellow–orange color. After 10 min of stirring at 25 °C the solvent was reduced *in vacuo* to near dryness. A pale yellow product then precipitated. Unreacted 2-bromoacetophenone was removed by several washings with hexane. The complex [Au(CH$_2$)$_2$PPh$_2$]$_2$(CH$_2$C(O)Ph)Br was isolated as a yellow–orange powder in 85% yield (22 mg, 0.021 mmol). νIR(C=O) (CH$_2$Cl$_2$, 1620 cm^{-1}), IR of PhC(O)CH$_2$Br, (CH$_2$Cl$_2$, 1682 cm^{-1}, sh 1702 cm^{-1}) ^{1}H NMR (CDCl$_3$, 90 MHz, 35 °C) δ = 1.50 and 1.85(d, $^2J_{PH}$ = 10.5 and 10.5 Hz respectively) AuCH$_2$P; 3.52(s, AuCH$_2$–C(O)); 7.83–7.23(m, PPh$_2$). Melting point 185.5–187 °C, (decomposition).

Hydride Reductions

To 3–5 ml of dry THF at 25 °C was added 15 mg of the Au(II) alkyl halide adduct, (**2** or **3**). To this mixture was added approximately 10–15 mg of NaBH$_4$ or NaBH$_3$CN. The THF was then removed *in vacuo* and the solid left behind triturated with CDCl$_3$, filtered and analyzed via ^{1}H NMR and gas chromatography. As a control reaction PhC(O)CH$_2$Br and BrCH$_2$CN were reacted with NaBH$_3$CN in THF and found to be reduced easily to acetophenone and acetonitrile, respectively.

X-ray Diffraction Data Collection

Single well-formed dark orange crystals of the bromoacetophenone adduct **3** were obtained by slow diffusion of anhydrous diethyl ether into dichloromethane solutions containing the adduct. Suitable red crystals of **2** were obtained within 48 h at 10 °C by layering a concentrated dichloromethane solution with hexane. A crystal of **3** was mounted in a random orientation on a glass fiber. For *2* a sealed 0.5 mm glass capillary was used to hold the crystal. For both crystals initial centering, generation of possible unit cell vectors, and assignment of indices was carried out on a Nicolet R3m/E diffractometer using procedures which have been previously described [1, 2]. Axial photographs were used to verify correct axial lengths, and in the case of the bromoacetophenone adduct, **3**, confirm the presence of monoclinic symmetry. The ω–2θ scanning technique in bisecting geometry was used for intensity data collection, with three standard reflections measured every 100 data. The data were corrected for standard decay (<3%), Lorentz and polarization effects, including absorption. Absorption corrections were applied empirically on the basis of ω-scan data measured for several intense low-angle reflections with χ values near 90° and 270°. Crystal data and experimental conditions for both complexes are summarized in Table I.

Structure Determinations and Refinements

The crystal structures of both complexes were determined using the SHELXTL crystallographic computing package implemented on a Data General Eclipse minicomputer. The bromoacetonitrile adduct crystallized in the centrosymmetric $P\bar{1}$ space group, with two molecules in the unit cell. The gold atom positions were determined from sharpened Patterson maps, and all remaining non-hydrogen atoms were located using difference-Fourier techniques. Phenyl rings were refined as idealized hexagons incorporating individual isotropic carbon atom thermal parameters. All other non-hydrogen atoms were refined anisotropically. The structure refined well giving R = 0.041 and R_w = 0.040 for 3195 reflections with $I \geqslant 3.0\sigma(I)$ and 304 parameters.

Inspection of the bond lengths and angles obtained from this model showed an anomalously short (1.250(18) Å) carbon–carbon bond for the gold coordinated CH$_2$CN moiety. The methylene carbon of the coordinated CH$_2$CN exhibited the expected tetrahedral geometry (Au–CH$_2$–C angle 109.9(13)°). All other distances and angles were observed to be within expected limits. A disorder obtained by rotating the Br–Au–Au–CH$_2$–CN backbone by 180° about the center of the two gold atoms was suspected. Keeping the Au–Au distance fixed, the occupancy of the Br center was refined. The Au–Br distance of 2.660(2) Å placed partial occupancy of Br between the carbon–carbon bond the Au–CH$_2$–CN. Refinement converged with a 96% to 4% disorder. The short carbon–carbon bond of the initial model was due to this end to end disorder. Calculated positions are given for the CH$_2$CN of the minor component in this model which refined to R = 0.0402, R_w = 0.0402 for 3195 reflections with $I \geqslant 3.0\sigma(I)$ and 308 parameters.

TABLE I. Crystallographic Data for Bromoacetonitrile and Bromoacetophenone Adducts of Gold(II) Ylide Dimers.

Formula	$C_{30}H_{30}Au_2BrP_2N{\cdot}CH_2Cl_2$	$C_{36}H_{35}Au_2BrP_2O$
Formula weight	1024.24	1019.42
Space group	$P\bar{1}$	Pc
Systematic absences		$h0l; l = 2n + 1$
a (Å)	11.031(3)	13.68(4)
b (Å)	16.017(4)	9.667(1)
c (Å)	10.364(2)	25.765(3)
α (deg)	92.31(2)	90.000
β (deg)	107.95(2)	100.95(2)
γ (deg)	106.73(2)	90.000
V (Å^3)	1651.4(7)	3346.4(10)
Z	2	4
d_c (g/cm^3)	1.91	2.02
Crystal size (mm)	0.25 × 0.28 × 0.30	0.4 × 0.4 × 0.1, orange
$F(000)$ (e)	964	1927.50
μ(Mo Kα) (cm^{-1})	103.37	100.47
Radiation (monochromated in Mo Kα ($\lambda\alpha$ = 0.71073 Å) incident beam)		
Orientation reflections, number, range (2θ)	25, 19° ⩽ 2θ ⩽ 28	25; 18 ⩽ 2θ ⩽ 33
Temperature (°C)	20	20
Scan method	Wyckoff–Omega	Omega
Data collection range, 2θ (deg)	3–50°	3–55°
Total reflections measured	5733	8753
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3355, 3195	2852
Check reflections	3 every 97	3 every 97
Number of parameters refined	308	267
Transmission factors, max. min.	0.439/0.249	0.032/0.016
R^a	0.0402	0.0488
$R_w{}^b$	0.0402	0.0448
Goodness-of-fit indicator^c	1.124	1.124
Largest shift/e.s.d., final cycle	−0.174	−0.006
Largest peak (e/Å^3)	0.85	1.198
g	0.0005	0.0005

$^a R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. $^b R_w = [\Sigma\sqrt{w}(|F_o| - |F_c|)]/\Sigma\sqrt{w}|F_o|$; $w^{-1} = [\sigma^2(|F_o|) + g|F_o|^2]$. ^{c}Goodness-of-fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

An alternate disorder model to the one above is one in which some $[Au(CH_2)_2PPh_2]_2Br_2$ replaces **2** in the lattice. Since the Au–Br bond of $[Au(CH_2)_2PPh_2]_2Br_2$ is 0.16 Å shorter than in **2**, the only significant difference between the two models is the Au–Br distance. Refinement of this model gave $R = 0.0402$ and $R_w = 0.042$. Therefore, this model is indistinguishable from and no better than the original disorder model employed. Regardless of which of these two models is employed, the important structural features of **2** remain unchanged. Atomic coordinates and isotropic thermal parameters for **2** and **3** are given in Tables II and III.

The bromoacetophenone complex **3** was successfully refined in the non-centrosymmetric space group *Pc* consistent with the intensity statistics and the systematic absences $h0l, l = 2n + 1$. The cell origin was defined by fixing the x and z coordinates of Au(1). Two crystallographically independent molecules were present in the asymmetric unit, and both

TABLE II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Au(CH_2)_2PPh_2]_2(CH_2CN)Br$, **2**

	x	y	z	U^a
Au(1)	2434(1)	1088(1)	1285(1)	34(1)
Au(2)	2327(1)	1623(1)	3697(1)	35( )
Br	2512(2)	678(1)	−1195(1)	48(1)
Br^b	2718(28)	2577(16)	6036(15)	23(6)
P(1)	5174(4)	1499(3)	3773(4)	39(2)
P(2)	371(4)	2129(2)	1113(4)	40(2)
C(5)	2236(15)	1972(11)	5652(12)	51(7)
C	3147(22)	2854(14)	6232(20)	61(11)
N	3916(18)	3501(12)	6687(18)	102(10)
C(1)	4286(12)	865(10)	2169(12)	43(6)
C(2)	4075(12)	1329(9)	4746(13)	43(6)
C(3)	535(13)	1932(10)	2797(14)	47(7)
C(4)	541(13)	1200(9)	327(13)	40(6)
C(11)	7153(9)	1370(7)	6085(8)	67(9)

(continued overleaf)

TABLE II. *(continued)*

	x	y	z	U[a]
C(12)	8277	1139	6802	88(11)
C(13)	8909	751	6090	49(7)
C(14)	8417	594	4661	52(7)
C(15)	7272	825	3944	50(7)
C(16)	6660	1214	4656	41(6)
C(21)	6387(13)	2878(7)	2607(12)	107(14)
C(22)	6804	3759	2417	137(17)
C(23)	6599	4400	3203	98(12)
C(24)	5978	4160	4178	95(12)
C(25)	5561	3278	4367	76(10)
C(26)	5765	2638	3582	43(6)
C(31)	−1366(10)	3059(6)	−193(10)	62(8)
C(32)	−2631	3139	−839	75(10)
C(33)	−3784	2428	−1027	81(11)
C(34)	−3671	1638	−568	68(9)
C(35)	−2406	1558	78	53(7)
C(36)	−1253	2269	265	42(7)
C(41)	2100(12)	3831(7)	2010(10)	73(9)
C(42)	3052	4589	1896	101(12)
C(43)	3519	4609	787	88(12)
C(44)	3035	3870	−207	110(14)
C(45)	2083	3111	−92	79(10)
C(46)	1616	3092	1016	53(7)
Cl(1)	−178(10)	4662(6)	7498(10)	198(7)
Cl(2)	85(12)	3477(7)	5621(15)	280(10)
C(6)	−462(40)	3874(26)	6382(45)	410(48)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. [b]Disordered atom position.

TABLE III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Au(CH_2)_2PPh_2]_2$-$CH_2C(O)Ph)Br$, 3

	x	y	z	U
Au(1)	−50(1)	1885(2)	−17(1)	42(1)[a]
Au(2)	645(2)	4439(2)	−140(1)	39(1)[a]
Au(3)	−2166(2)	947(2)	−1478(1)	39(1)[a]
Au(4)	−1427(1)	3484(2)	−1589(1)	44(1)[a]
Br(1)	−823(5)	−618(4)	58(3)	60(2)[a]
Br(2)	−637(5)	5966(4)	−1614(3)	61(2)[a]
P(1)	−1520(7)	4397(11)	238(4)	44(4)[a]
P(2)	2283(8)	2159(10)	160(4)	48(4)[a]
P(3)	−3808(7)	3395(10)	−1804(4)	43(4)[a]
P(4)	−60(8)	891(11)	−1752(4)	47(4)[a]
C(1)	−693(22)	5371(31)	−103(11)	27(7)
C(2)	−1576(32)	2639(46)	−58(17)	71(13)
C(3)	1406(39)	840(44)	22(20)	65(15)
C(4)	1995(27)	3606(36)	−253(14)	35(10)
C(5)	1097(27)	6523(36)	−239(14)	38(9)
C(6)	2165(48)	6714(51)	93(24)	80(17)
C(7)	−3643(34)	1773(45)	−1501(18)	64(14)
C(8)	−2749(34)	4479(39)	−1488(18)	49(12)
C(9)	−42(22)	2619(29)	−1600(11)	23(7)
C(10)	−727(29)	54(44)	−1302(16)	62(12)
C(11)	−2716(27)	−979(37)	−1220(13)	38(9)
C(12)	−3645(34)	−1397(37)	−1604(16)	40(10)

TABLE III. *(continued)*

	x	y	z	U
O(1)	2921(26)	6490(29)	−102(13)	61(9)
O(2)	−4472(28)	−1336(34)	−1379(14)	77(10)
C(13)	−2768(14)	5065(27)	118(11)	67(12)
C(14)	−2965	6434	−38	58(11)
C(15)	−3937	6938	−116	76(14)
C(16)	−4712	6073	−38	72(13)
C(17)	−4515	4704	119	65(12)
C(18)	−3543	4200	196	54(10)
C(19)	−1037(21)	4518(28)	940(7)	54(10)
C(20)	−1715	4538	1282	68(12)
C(21)	−1375	4655	1826	61(12)
C(22)	−357	4752	2028	60(11)
C(23)	321	4732	1686	107(18)
C(24)	−19	4616	1142	80(14)
C(25)	2397(20)	2544(27)	839(7)	51(10)
C(26)	2959	3699	1036	65(12)
C(27)	3125	3994	1576	64(12)
C(28)	2728	3136	1918	61(11)
C(29)	2166	1981	1722	92(16)
C(30)	2000	1686	1182	60(11)
C(31)	3477(19)	1447(31)	72(14)	65(12)
C(32)	4131	798	481	76(14)
C(33)	5053	329	398	121(21)
C(34)	5321	508	−94	78(15)
C(35)	4666	1156	−503	93(16)
C(36)	3744	1626	−420	123(21)
C(37)	2252(22)	7256(27)	624(8)	53(10)
C(38)	1428	7445	863	59(11)
C(39)	1559	7915	1384	85(15)
C(40)	2513	8196	1665	71(13)
C(41)	3337	8007	1427	91(16)
C(42)	3206	7537	906	86(15)
C(43)	−5045(17)	4039(32)	−1763(12)	53(11)
C(44)	−5878	3620	−2130	80(15)
C(45)	−6826	4053	−2076	75(14)
C(46)	−6941	4905	−1655	75(14)
C(47)	−6109	5325	−1288	78(14)
C(48)	−5161	4892	−1342	124(21)
C(49)	−3805(9)	3268(26)	−2508(7)	63(12)
C(50)	−3589	1998	−2717	54(10)
C(51)	−3638	1860	−3261	58(11)
C(52)	−3903	2990	−3594	60(11)
C(53)	−4119	4260	−3384	74(13)
C(54)	−4071	4398	−2841	51(10)
C(55)	1220(16)	118(27)	−1631(11)	55(11)
C(56)	1485	−1017	−1300	47(9)
C(57)	2446	−1556	−1232	50(10)
C(58)	3143	−960	−1495	54(10)
C(59)	2878	175	−1826	89(16)
C(60)	1916	714	−1894	108(18)
C(61)	−475(19)	642(26)	−2438(7)	56(11)
C(62)	−352	−655	−2655	52(10)
C(63)	−626	−860	−3199	90(16)
C(64)	−1023	232	−3526	83(15)
C(65)	−1145	1528	−3310	91(16)
C(66)	−872	1733	−2766	53(10)
C(67)	−3803(25)	−1588(30)	−2167(8)	61(12)

(continued on facing page)

TABLE III. *(continued)*

	x	y	z	U
C(68)	−4754	−1531	−2478	74(13)
C(69)	−4882	−1704	−3025	76(13)
C(70)	−4059	−1934	−3260	73(13)
C(71)	−3107	−1990	−2949	71(13)
C(72)	−2979	−1817	−2402	87(16)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

molecules were refined using anisotropic thermal parameters for all non-hydrogen atoms except the carbon atoms of the phenyl rings. The phenyl rings were refined as regular hexagons using isotropic carbon atom thermal parameters. It was not possible to refine this structure in the centrosymmetric space group $P2/c$ when the cell origin was shifted to an apparent center of symmetry located midway between the two independent molecules in the asymmetric unit. A non-centrosymmetric cell was consistent with the Patterson map, which showed no Au $2x\ 2y\ 2z$ peaks of appropriate weight. Final refinement in the space group Pc converged to R values of $R = 0.0488$ and $R_w = 0.0448$. Refinement with opposite phasing gave $R = 0.0550$ and $R_w = 0.0513$.

Results

The reaction of **1** with excess bromoacetonitrile in benzene at 25 °C gives $[Au(CH_2)_2PPh_2]_2(CH_2CN)Br$, **2**, in near quantitative yield. In neat bromoacetonitrile the gold(II) dibromide $[Au(CH_2)_2PPh_2]Br_2$ is the main product. A perspective drawing of **2** is shown in Fig. 1. The ^1H NMR spectrum of this product is that of an asymmetrically substituted gold(II) alkyl halide. Similarly, the reaction of excess 2-bromoacetophenone with **1** gives $[Au(CH_2)_2PPh_2]_2(CH_2C(O)Ph)Br$, **3**, in >80% yield. A diagram of **3** in perspective is given in Fig. 2. Complex **3** is an asymmetrically substituted Au(II) adduct, as determined from the ^1H NMR spectrum and the single crystal X-ray structural investigation.

The ^1H NMR spectra of **2** and **3** in solution ($CDCl_3$, 35 °C, 90 MHz) does not show the presence of **1** and the free alkyl halides. From this, we estimate a lower limit for K_{eq} for the reaction [**1**] + [RX] = [Au(II)RX] to be 9.0×10^3 M^{-1}, assuming greater than 90% formation of the Au(II) alkyl halide adduct.

The addition of excess $NaBH_4$ to **2** in THF regenerates **1**, (observed via ^1H NMR spectroscopy). Acetonitrile was detected in the solution via gas chromatography. Complex **3** can be rapidly reduced

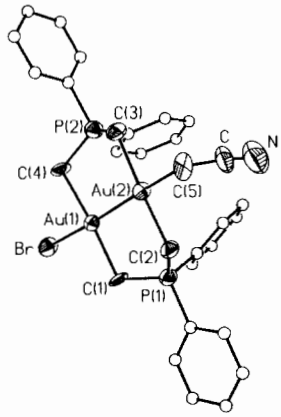

Fig. 1. Molecular structure of **2**, $[Au(CH_2)_2PPh_2]_2(CH_2CN)Br$. Hydrogen atoms omitted for clarity (50% probability thermal ellipsoids). Selected bond lengths: Au(1)–Au(2) = 2.658(1) Å; Au(1)–Br = 2.660(2) Å; Au(2)–C(5) = 2.120(14) Å; CN = 1.106(24) Å; Au(1)–C(1) = 2.105(14) Å. Selected angles: Au(2)–Au(1)–Br = 175.2(1)°; Au(1)–Au(2)–C(5) = 176.6(0.5)°; Au(2)–Au(1)–C(1) = 93.1(0.4)°; C(5)–C≡N = 174.8(2.8)°; Au(2)–C(5)–C = 109.9(1.3)°.

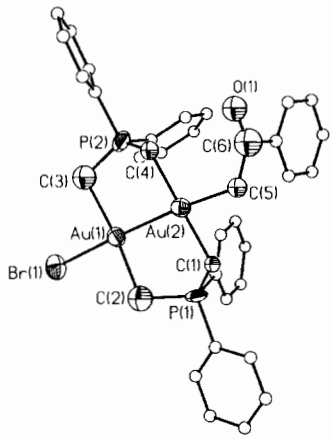

Fig. 2. Representative molecular structure of **3**, $[Au(CH_2)_2PPh_2]_2(CH_2(O)Ph)Br$. (50% probability thermal ellipsoids). Selected bond lengths: Au–Au = 2.687(2) and 2.689(2) Å; Au–Br 2.637(5) and 2.662(5) Å; Au–$CH_2C(O)Ph$ = 2.137(36) and 2.159(37) Å; C=O, 1.25(8) and 1.36(6) Å Selected bond angles: Au–Au–Br = 176.7(2)° and 175.2(2)°; Au–Au–CH_2 = 176.1(10)° and 168.3(9)°; CH_2–C=O = 121.4(5) and 111.0(3)°.

to **1** with either $NaBH_4$ or $NaBH_3CN$ in THF at 25 °C. The ^1H NMR spectrum of the reaction mixture shows the presence of acetophenone as well as **1**.

Comparison of the complexes **2** and **3** with $[Au(CH_2)_2PPh_2]_2(CH_3)Br$, **4**, reveals the effect the CN and C(O)Ph substituents have upon the physical and chemical properties of the gold(II) alkyl halide adducts. Both **2** and **3**, as well as **4**, undergo facile halogen exchange in $CDCl_3$ in the presence of excess

CH_3I. This exchange was detected by the observation (^1H NMR spectroscopy) of the CH_3Br generated. We have previously demonstrated that upon heating, **4** undergoes a reductive elimination reaction in the solid state to give CH_3Br and **1**. Under similar conditions, the thermolysis of **2** and **3** leads only to decomposition.

Discussion

The gross structural features of complexes **2** and **3** are quite similar. The Au–Au distance in both complexes is indicative of a gold–gold bond. The Au–Au distances in **2** and **3** are statistically significantly different ((2.658(1) Å for **2** and 2.687(2) Å, 2.689(2) Å for **3**). However, the values observed here for the gold–gold distances are within the range of other Au(II) dimers examined. Formally, the gold centers of **2** and **3** are described as Au(II) d^9 centers. The observed diamagnetism of these complexes is consistent with Au–Au bonding.

In complexes **2** and **3** the Au–C bond lengths (Au–CH_2CN of **2** and Au–CH_2–C(O)Ph of **3**) are not significantly different (2.120(14) Å; 2.137(36) Å and 2.119(40) Å respectively). Furthermore, when compared with the methyl bromide adduct, **4**, where the Au–CH_3 bond length is found to be 2.13(12) Å, no significant bond length differences are found [2a]. This suggests that the cyanide substituent in **2** and the C(O)Ph substituent in **3** have little effect on the Au–CH_2 bond distance of the non-ring methylene moiety.

The Au–Br bond lengths in **2** (2.660(2) Å) and **3** (2.662(5) and 2.637(15) Å) are 0.013–0.016 Å longer than the Au–Br bond length of $[Au(CH_2)_2PPh_2]_2Br_2$. The structural *trans* effect (STE) seen here has been described [2a]. The point to be made here is that the magnitude of the STE decreases with the addition of the electronegative cyanide and ketone substituents. The Au–Br distances of 2.500(4) Å found in $[Au(CH_2)_2PPh_2]_2Br_2$ are 0.195 Å shorter than the 2.695(9) Å Au–Br distance found in **4**.

The observed decrease in the magnitude of the STE in **2** and **3** compared with **4** can best understood by qualitatively considering the differences in the polarization of the R–Au–Au–Br sigma bonded backbone. In **2**, (R = CH_2CN) and **3**, (R = CH_2-C(O)Ph) the extent of polarization is expected to be less than that in **4** (R = Me) because of the difference in electron withdrawing ability of CN and C(O)Ph *vs.* H. The backbone CH_2–Au–Au–Br sigma bond (HOMO) of **2** and **3** are both more like Br–Au–Au–Br than is H_3C–Au–Au–Br.

The decrease in the STE as a function of the polarization of the R–Au–Au–X sigma bond is also observed when comparing the gold–halide bond lengths of the MeI and MeBr adducts with their analogous dihalides [2a]. The Au–I bond of $[Au(CH_2)_2PMe_2]_2(Me)I$ is 0.20 Å longer [2a] than the Au–I bond of $[Au(CH_2)_2PPh_2]_2I_2$ while the Au–Br bond of $[Au(CH_2)_2PPh_2]_2(Me)Br$ is only 0.17 Å longer than the Au–Br bond of $[Au(CH_2)_2PPh_2]_2Br_2$. This modest decrease (0.03 Å) is consistent with the reduced electronegativity of I compared with Br and the resultant decrease in the overall polarization of the CH_3–Au–Au–X sigma bond.

The reduction of **2** to **1** and CH_3CN with $NaBH_4$ as well as the facile reduction of **3** to **1** and acetophenone with $NaBH_3CN$ is important to this work. A cautious mechanistic interpretation of this observation is necessary, however, since other alkyl halide Au(II) adducts of **1** (*i.e.*, **4** specifically) have been shown [1a] to be in equilibrium with free alkyl halide and **1**. $NaBH_3CN$ was observed to reduce bromoacetophenone to acetophenone in approximately 10 min at 25 °C in THF, conditions similar to those used with **3**. Since acetophenone could have been generated either via the direct reduction of **3** or by reaction with the bromoacetophenone in equilbrium with **3**, one cannot state without further study that direct nucleophilic attack of BH_3CN^- on the Au bound $CH_2C(O)Ph$ moiety has occurred.

The stabilizing effect of an electron withdrawing substituent on an alkyl ligand of a transition metal alkyl complex is now well established [5–7]. However, the first Au(II) alkyl halide adducts of $[Au(CH_2)_2PMe_2]_2$ were with MeI [4a, 4b, 8]. In addition, few examples of structurally characterized [9–13] metal coordinated methyl cyanide (M–CH_2CN) complexes [9]* have been reported. Therefore we compare here the results we have obtained with published data.

Structurally, the M–CH_2CN unit of **2** (M = Au) is similar to that found in the platinum complexes reported by A. Del Pra *et al.* [10, 11] and Burgi *et al.* [12]. In the neutral platinum complexes [10, 11] (*trans*-$(PPh_3)_2Pt(X)CH_2CN$, X = Cl, H) and the cationic platinum structure [12] for ($[(PMe_2Ph)_3PtCH_2CN][PF_6]$) the C≡N distances are in the range of 1.15(2) Å to 1.12(3) Å, and 1.18(3) Å respectively. Although the cationic complex shows the greatest C≡N distance, statistically, none are significantly different from the 1.11(3) Å observed in **2**. Furthermore, the C≡N distances in the Pt complexes and **2** are not significantly different (statistically) from the C≡N distance of acetonitrile (1.16 Å) [15].

*Although fumaronitrile and tetracyanoethylene could be considered as cyanide substituted alkyls, the structures of the complexes are sufficiently different such that these complexes will not be discussed here.

The C–C 'single bond' of the $M–CH_2–C{\equiv}N$ units in *trans*-$(PPh_3)_2Pt(X)CH_2CN$ (X = H, Cl) [10, 11], $(PPh_3)_3PtCH_2CN$ [12] and **2** are 1.43(2) Å, 1.44(2) Å, 1.42(3) Å and 1.45(2) Å. Clearly, these distances are all within one e.s.d and therefore not significantly different. A. Del Pra *et al.* [10, 11] suggest that this formal C–C single bond actually contains approximately 25% C=C double bond character. Presumably this effect is due to the C=N and not the metal since the C–C bond in acetonitrile also is reported [14] * to be 1.4 Å.

In **2** as well as the three Pt complexes discussed, the $C–C{\equiv}N$ angle is very nearly linear and shows no unusual interactions. Also the $M–CH_2–C$ angle of the coordinated methyl cyanide are all within expected values for sp^3 carbon centers.

The large estimated standard deviations of the bond lengths and angles in the structure of $Ph_3PAu(CCl_2CN)$ as reported by Perevalova *et al.* [13] regrettably precludes making any meaningful comparison with our own or any other structural results. Both Perevalova *et al.* and ourselves observe a decrease of 50 cm^{-1} in the $C{\equiv}N$ stretching frequency (to 2200 cm^{-1}) upon coordination of the $CH_2C{\equiv}N$ to the gold center. Similarly, Michelin, Napoli and Ros [15] report the $C{\equiv}N$ stretch in a large variety of Pt alkoxides (*cis*-$L_2Pt(OR)CH_2CN$, L_2 = diphosphine or PPh_3) to be in the region of 2200 cm^{-1}.

Compared to the metal coordinated methyl cyanide complexes, considerably more information is available on $M–CH_2C(O)R$. Nonetheless, there is surprisingly little known about their chemistry [16]. In the literature these metal-coordinated ketones ($M–CH_2C(O)R$) are referred to as 'acylmethyl' [16] and 'oxoalkyl' [17] complexes. From their chemistry, Doney, Bergman and Heathcock [16] suggested that they are best described as carbon-bound transition metal enolates. These functionalized metal alkyl complexes are presumably of importance as intermediates in the reaction of α-halocarbonyl compounds with low valent metal complexes [18]. Milstein [19] has demonstrated that *cis* hydrido carbon-bound metal enolates (referred to only as *cis*-hydrido alkyl complexes) are involved in the isomerization of epoxides to ketones.

In **3**, the eight membered heterocyclic ring containing the gold atoms forms a boat configuration. The carbon-bound metal enolate is coordinated to a square planar gold center. The oxygen of the carbonyl does not appear to interact with other atoms in the complex. The infrared C=O stretching frequency of **3** is approximately 60 cm^{-1} lower (1620 cm^{-1}) than observed for the non-coordinated bromoacetophenone *vide supra.* This observation is consistent with other data on carbon-bound metal enolates [20]. In cases where there is a clear interaction between the metal center and the carbonyl, even greater differences have been seen in the C=O stretching frequency of the coordinated and non-coordinated substrate [21].

Since **3** crystallized in the space group *Pc* with two crystallographically independent molecules in the asymmetric unit, two values for each bond distance and angle are available. The closest intramolecular approach between the Au center and the oxygen of the carbon-bound enolate is 3.677(3) Å. This is taken as a non-interacting distance. The closest inter-molecular approach between a Au center and oxygen atom is 7.061(2) Å.

The C=O distances** observed in **3** are 1.25(8) Å and 1.36(6) Å. These distances are somewhat longer but not statistically different from C=O bonds in complexes [17, 20a, 22] containing similar coordination. Weiss *et al.* [17] observe a 1.216(7) Å C=O distance in $CH_3C(=O)CH_2Mn(CO)_4PPh_3$. Kastner and Scheidt report a C=O distance of 1.224(4) Å for an acetonyl-$\alpha,\beta,\gamma,\sigma$-tetraphenyl-porphinato $Co^{(III)}$ complex. Russell and Tucker [22] report a C=O distance of 1.21(3) Å in *cis*-$((Ph_3P)_2ClPt(CF_2C(O)CF_2Cl)$. In the 1:2 diacetone alcohol-μ-peroxo Pd adduct reported by H. Suzuki *et al.* [21], the C=O distance was observed to be 1.28 Å. Even in this case where there is an intramolecular interaction between the oxygen of the C=O and the Pd centers (Pd–O 2.15 Å) the C=O distance is not significantly changed. The carbonyl carbon is trigonal planar while the methylene of the carbon bound metal enolate is tetrahedral (Au–C–C angle 108(3)° and 109(2)°) and shows no unusual features.

Supplementary Material

Tables of bond lengths, bond angles, anisotropic thermal parameters, H-atom coordinates, observed and calculated structure factors for complexes **2** and **3** (43 pages). Deposited with Cambridge Crystallographic Data Centre, Cambridge, U.K.

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*Specifically Costain [14b] is cited: CH_3CN: C–H (1.10250 Å); C–C–C (1.45836); C–N (1.5710); <HCC (109.5°).

The two independent (C=O) distances reported for **3 are within 3 e.s.d. of each other.

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References

1 (a) J. P. Fackler, Jr., H. H. Murray and J. D. Basil, *Organometalics, 3,* 821 (1984); (b) E. Guilmet, A. Maisonnet and R. Poilblanc, *Organometallics, 2,* 1123 (1983).

2 (a) J. D. Basil, H. H. Murray, J. P. Fackler, Jr., J. Tocher A. M. Mazany, T. J. Delord, B. Trzcinska-Bancroft, H. Knachel, D. Marler and D. S. Dudis, *J. Am. Chem. Soc., 107,* 6908 (1985); (b) H. H. Murray, J. P. Fackler, Jr. and B. Trzcinska-Bancroft, *Organometallics, 4,* 1633 (1985); (c) H. Schmidbaur and R. Franke, *Inorg. Chim. Acta, 13,* 85 (1975).

3 (a) H. H. Murray, J. P. Fackler, Jr. and A. M. Mazany, *Organometallics, 3,* 1310 (1984); (b) H. H. Murray, J. P. Fackler, Jr. and D. A. Tocher, *Chem. Commun.,* 1278 (1985).

4 (a) H. Schmidbaur and R. Franke, *Inorg. Chim. Acta, 13,* 79 (1975); (b) *3,* 85 (1975); (c) H. Schmidbaur, J. Adlkofer and M. Heimann, *Chem. Ber., 107,* 3697 (1974).

5 G. E. Coates, M. L. H. Green and L. Wade (ed.), 'Organometallic Compounds', Vol. II, Methven, London, 1968, p. 224.

6 (a) J. Chatt and B. L. Shaw, *J. Chem. Soc.,* 705 (1959); (b) 4020 (1959); (c) 1718 (1960).

7 (a) R. Ros, R. A. Michelin, R. Bastaillard and R. Roulet, *J. Organomet. Chem., 139,* 355 (1977); (b) *165,* 107 (1979); (c) R. A. Michelin, U. Belluco and R. Ros, *Inorg. Chim. Acta, 24,* L33 (1977).

8 J. P. Fackler, Jr. and J. D. Basil, *Organometallics, 1,* 871 (1982).

9 A. McAdam, J. N. Francis and J. A. Ibers, *J. Organomet. Chem. 149,* 24 (1971); (b) C. Panattoni, R. Graziani, G. Bandoli, D. A. Clemente and U. Belluco, *J. Chem. Soc. B,* 371 (1970).

10 A. Del Pra, E. Forsellini, G. Bombieri, R. A. Michelin and R. Ros, *J. Chem. Soc., Dalton Trans.,* 1862 (1979).

11 A. Del Pra, G. Zanotti, G. Bombieri and R. Ros, *Inorg. Chim. Acta, 36,* 121 (1979).

12 P. S. Pregosin, R. Favez, R. Roulet, T. Boschi, R. A. Michelin and R. Ros, *Inorg. Chim. Acta, 45,* L7 (1980); H. B. Burgi, 'X-ray Structure of Cyanomethyltris(dimethylphenylphosphine)platinum(II)hexafluorophosphate', personal communication.

13 E. G. Perevalova, Y. T. Struchkov, V. P. Dyadchenko, E. I. Smyslova, Y. L. Slovokhotov and K. I. Grandberg, *Izv, Akad, Nauk SSSR, Ser. Khim., 12,* 2818 (1983); Engl. transl. *Bull. Acad. Sci. USSR, Div. Chem. Sci., 32,* 2529 (1983).

14 (a) L. E. Sutton (ed.), 'Tables of Interatomic Distances and Configuration in Molecules and Ions', Special Publ. No. 18, Suppl. 1956–1959, The Chemical Society, London, 1965, p. M77s., C. C. Costain, *J. Chem. Phys., 29,* 864 (1958).

15 R. A. Michelin, M. Napoli and R. Ros, *J. Organomet. Chem., 175,* 239 (1979).

16 J. J. Doney, R. G. Bergman and C. H. Heathcock, *J. Am. Chem. Soc., 107,* 3724 (1985).

17 J. Engelbrecht, T. Greiser and E. Weiss, *J. Organomet. Chem., 204,* 79 (1981).

18 (a) H. Alper and D. Des Roches, *J. Org. Chem., 41,* 806 (1976); (b) D. Milstein, O. Buchman and J. Blum, *J. Org. Chem., 42,* 2299 (1977); (c) M. Suzuki, Y. Oda and R. Noyori, *J. Am. Chem. Soc., 101,* 1623 (1979).

19 D. Milstein, *Acc. Chem. Res., 17,* 221 (1984).

20 (a) M. Kastner and W. R. Scheidt, *J. Organomet. Chem., 157,* 109 (1978); (b) R. B. King, M. B. Bisnette and A. Fronzaylia, *J. Organomet. Chem., 5,* 341 (1966); (c) V. Galamb, G. Pa'lyi, F. Cser, M. G. Zurmanova and Y. T. Struchkov, *J. Organomet. Chem., 209,* 183 (1981).

21 H. Suzuki, Y. Moro-Oka, T. Ykawa, T. Miyajima, I. Tanaka and T. Ashida, *Chem. Lett.,* 1369 (1982).

22 D. Russell and P. A. Tucker, *J. Chem. Soc., Dalton Trans., 20,* 2222 (1975).