

CRYSTAL STRUCTURE AT -35°C OF (2,6-DIMETHOXYPHENYL)- (TRIPHENYLPHOSPHINE)GOLD(I)

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(Received November 2nd, 1979)

Summary

The crystal structure of (2,6-dimethoxyphenyl)(triphenylphosphine)gold(I) has been determined by single crystal X-ray diffraction techniques using three-dimensional data gathered at -35°C by counter methods. Colorless crystals form as thin plates in the monoclinic space group $P2_1/n$, with a 13.040(2), b 19.268(3), c 9.0153(8) Å, β 96.98(1) $^{\circ}$. A measured density (19°C) of 1.73 g cm^{-3} agrees with the calculated value (-35°C) of 1.769(1) g cm^{-3} , assuming four molecules of $(\text{C}_6\text{H}_3(\text{OCH}_3)_2)\text{Au}(\text{P}(\text{C}_6\text{H}_5)_3)$ per unit cell. Full-matrix least-squares refinement of the structure has converged with a conventional R index (on $|F|$) of 0.030 using the 5052 symmetry-independent reflections with $4 < 2\theta < 60^{\circ}$ which have $I_0 > 2\sigma(I_0)$. The molecule consists of a Au^{I} ion bonded to the P atom of a triphenylphosphine ligand and to the C(1) atom of a 2,6-dimethoxyphenyl group. The P–Au–C(1) angle of 172.7(1) $^{\circ}$ is significantly different from linearity, probably as a result of a weak bonding interaction between Au and one of the two methoxy oxygen atoms (Au...O = 2.961(4) and 3.231(4) Å).

Introduction

Although Au^{I} forms complexes of various coordination numbers, it apparently has a preference for two-coordinate linear geometry, a tendency which persists even for higher coordination numbers. Hence, trigonal planar and tetrahedral complexes such as $[\text{Au}(\text{PPh}_3)_3]^+$, $\text{AuCl}(\text{PPh}_3)_2$ and $[\text{Au}(\text{PMe}_3)_4]^+$ are known, but these complexes are also known to lose phosphine ligands readily to form the more stable (linear) two-coordinate species [1]. In contrast, the other Group IB metal ions of oxidation state I, Cu^{I} and Ag^{I} , prefer higher coordination numbers and more regular molecular geometries. This is exemplified

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by the study [2] of the three-coordinate complexes $MCl(PP)$, where $M = Cu^I$, Ag^I or Au^I and $(PP) = 2,11$ -bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene, a rather rigid bidentate ligand. The P—M—P angle is 132° when $M = Cu^I$, 141° when $M = Ag^I$ and 176° when $M = Au^I$, clearly an illustration of the preference of Au^I for linear coordination. In addition, conductivity studies of these complexes in polar solvents [2] indicate that the Au^I complex has the greatest tendency to release Cl^- to achieve two-coordination. Explanations for these differences in behavior among Group IB metals of oxidation state I (e.g., electrostatic effects and energy separations of the metal bonding orbitals) are offered elsewhere [1].

The complex (2,6-dimethoxyphenyl)(triphenylphosphine)gold(I), prepared by van Koten and Noltes [3], provides an opportunity to examine the molecular structure of a Au^I complex in which the Au ion is bonded to an aryl carbon atom (of which few structural studies have been reported) which is *ortho* to two potential donor oxygen-containing substituents; thus, Au^I has the opportunity through the proximity of donor oxygen atoms to be three-coordinate. Reported herein are the results of the crystal structure analysis of this complex.

Experimental section

Single crystals of $(C_6H_3(OMe)_2)Au(PPh_3)$ ($Me = CH_3$, $Ph = C_6H_5$) form as thin, colorless hexagonal-like plates by evaporation at room temperature of a cyclohexane solution. Based upon Weissenberg photography and preliminary X-ray diffraction experiments with a Syntex $P2_1$ autodiffractometer, the crystals were found to have the symmetry and systematic reflection absences of monoclinic space group $P2_1/n$. Intensity data collection details are given in Table 1. Standard deviations were assigned to the data (with $p = 0.02$) and the usual corrections applied, including that for absorption (see Table 1), as described elsewhere [4].

The structure was solved by standard heavy-atom methods and refined by full-matrix least-squares techniques. A listing of computer programs used in this work is available *. The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral atom scattering factors for Au, P, O, C [5] and H [6] were used in these calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections for anomalous scattering of Mo- K_α radiation were applied to the Au and P scattering functions [5].

Least-squares convergence was attained, using only those 5052 reflections with $I_o > 2\sigma(I_o)$, for a model in which phenyl rings of the PPh_3 ligand were treated as planar rigid groups **, all other nonhydrogen atoms as anisotropic ellipsoids and the remaining hydrogen atoms as isotropic atoms, with $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.030$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.033$, and a standard deviation of an observation of unit weight = $[\sum w(|F_o| - |F_c|)^2 / (m - s)]^{1/2} = 1.79$ for $m = 5052$ observations and $s = 157$ variables. The methyl

* A listing of computer programs used in this work is given in ref. 4.

** The phenyl rings of the PPh_3 ligand were constrained as follows: 11 atoms/group, C—C = 1.392 Å, C—H = 1.00 Å, C—C—C = 120° and $B_{iso}(H_i) = (B_{iso}(C_i) + 1.0) \text{ \AA}^2$.

TABLE 1
CRYSTALLOGRAPHIC SUMMARY

Crystal Data at -35°C^a		Empirical formula	$\text{C}_{26}\text{H}_{24}\text{AuO}_2\text{P}$
a	13.040 (2) Å	Formula wt.	596.42
b	19.268 (3) Å	Crystal system	monoclinic
c	9.0153 (8) Å	Systematic absences	$0k0, k = 2n + 1$
β	96.98 (1) $^{\circ}$	Space group	$h0l, h + l = 2n + 1$ $P2_1/n^b$
V	2248 (1) Å ³		
D_m (flotation, aqueous ZnCl_2)	1.73 (1)		
D_c	1.769 (1) g cm ⁻³	Z	4
		$F(000)$, electrons	1164
Data Collection at -35°C^c		0.71069	
Radiation (Mo- K_{α}) (Å)		ω scan, recentered automatically after each batch of 1000 reflections	
Mode		Symmetrical over 1.0° about $K_{\alpha 1,2}$ maximum Offset 1.0 and -1.0° in ω from $K_{\alpha 1,2}$ maximum	
Scan range		Variable, $1.5-4.0$	
Background		4 remeasured after every 96 reflections; analysis d of these data indicated overall decreases in intensity of ca. 2% during the 138 h of data collection for which the appropriate correction was applied.	
Scan rate (deg min ⁻¹)		$4.0-60.0^{\circ}$	
Check reflections		6547	
2 θ range		$0.11 \times 0.22 \times 0.58$	
Total reflections measd		0.0160	
Data crystal dimensions (mm)		(010), (0 $\bar{1}$ 0), (101), (10 $\bar{1}$), (110), ($\bar{1}$ 10), (1 $\bar{1}$ 0), ($\bar{1}$ 10)	
Data crystal volume (mm ³)		68.63	
Data crystal faces		0.24-0.50	
Absorption coeff, $\mu(\text{Mo-}K_{\alpha})$ (cm ⁻¹)			
Transmission factor range			

^a Unit cell parameters were obtained by least-squares refinement of the setting angles of 49 reflections with $17.0 < 2\theta < 27.7^{\circ}$. ^b A nonstandard setting of space group $P2_1/c$ (no. 14) with equivalent positions $x, y, z; -x, -y, -z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$. ^c Syntex $P2_1$ autodiffractometer equipped with a graphite monochromator and a Syntex LT-1 inert gas low temperature delivery system. ^d Ref. 17.

hydrogen atoms were satisfactorily located from a difference electron density map and then, based upon these positions, were placed at idealized positions * with C-H bond lengths of 0.95 Å [7] for the final cycles of refinement. Inspection of the data at the conclusion of refinement showed no evidence of secondary extinction. A structure factor calculation with all 6547 reflections measured during data collection gave R and R_w indices of 0.047 and 0.034, respectively. In the final cycle of refinement, all shifts in parameters were less than 0.5 of a corresponding estimated standard deviation (e.s.d.). The largest peaks in a final difference map were less than $0.4 e \text{ \AA}^{-3}$ and were close to either the Au position or the positions of the phenyl ring atoms.

Final positional and thermal parameters with e.s.d.s as obtained from the least-squares inverse matrix are presented in Table 2, along with the rigid group parameters. Positional and thermal parameters for the rigid group atoms and a

(Continued on p. 288)

* Idealized hydrogen atomic positions were calculated by the local program HIDEAL, written by R.C. Collins.

TABLE 2a
 FRACTIONAL COORDINATES AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^3$) FOR NONGROUP NONHYDROGEN ATOMS ^a

Atom	X	Y	Z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Au ^b	0.14551 (1)	0.12452 (1)	0.29744 (2)	281 (1)	236 (1)	293 (1)	42 (1)	52 (1)	-25 (1)
P ^b	0.23129 (8)	0.03013 (6)	0.22058 (13)	245 (5)	226 (5)	256 (5)	18 (4)	31 (4)	-24 (4)
O(1)	0.1617 (3)	0.2296 (2)	0.5785 (4)	45 (2)	36 (2)	39 (2)	8 (2)	-5 (1)	-7 (2)
O(2)	-0.0183 (3)	0.1978 (2)	0.1021 (4)	72 (3)	48 (2)	40 (2)	21 (2)	-12 (2)	-3 (2)
C(1)	0.0703 (3)	0.2144 (2)	0.3396 (5)	30 (2)	22 (2)	33 (2)	0 (2)	9 (2)	0 (2)
C(2)	0.0879 (3)	0.2545 (2)	0.4679 (5)	30 (2)	23 (2)	40 (3)	-1 (2)	7 (2)	4 (2)
C(3)	0.0343 (4)	0.3164 (3)	0.4874 (6)	42 (3)	27 (2)	49 (3)	2 (2)	12 (2)	-6 (2)
C(4)	-0.0397 (4)	0.3378 (3)	0.3700 (7)	43 (3)	23 (2)	66 (4)	8 (2)	13 (3)	8 (2)
C(5)	-0.0598 (4)	0.2992 (3)	0.2422 (6)	38 (3)	29 (2)	48 (3)	6 (2)	2 (2)	11 (2)
C(6)	-0.0033 (4)	0.2388 (2)	0.2287 (6)	39 (3)	29 (2)	37 (3)	-1 (2)	7 (2)	-1 (2)
C(7)	-0.0839 (5)	0.2208 (3)	-0.0235 (6)	67 (4)	57 (4)	43 (3)	-8 (3)	-10 (3)	5 (3)
C(8)	0.1757 (5)	0.2677 (3)	0.7168 (7)	73 (4)	59 (4)	50 (3)	11 (3)	-8 (3)	-23 (3)

TABLE 2b
 FRACTIONAL COORDINATES AND ISOTROPIC THERMAL PARAMETERS (\AA^2) FOR NONGROUP HYDROGEN ATOMS ^a

Atom ^c	X	Y	Z	B
H(3)	0.035 (4)	0.342 (3)	0.592 (6)	4 (1)
H(4)	-0.079 (4)	0.382 (2)	0.378 (5)	3 (1)

H(6)	-0.104 (4)	0.309 (3)	0.172 (6)	3 (1)
H(7, 1)	-0.087	0.197	-0.101	6
H(7, 2)	-0.152	0.227	0.003	6
H(7, 3)	-0.060	0.263	-0.059	6
H(8, 1)	0.229	0.246	0.784	6
H(8, 2)	0.197	0.314	0.697	6
H(8, 3)	0.114	0.269	0.760	6

TABLE 2c

GROUP PARAMETERS ^a

Group ^d	x_0	y_0	z_0	ϕ	θ	ρ
Ph(1)	0.2075 (2)	0.0214 (2)	0.0178 (2)	-2.988 (4)	-2.048 (2)	-1.170 (4)
Ph(2)	0.3076 (1)	0.0412 (2)	0.2663 (3)	1.707 (2)	2.874 (2)	-2.182 (2)
Ph(3)	0.2008 (2)	-0.0544 (1)	0.2939 (3)	-0.272 (2)	2.696 (2)	-0.315 (2)

^a See Figure 1 for identity of the atoms. Numbers in parentheses throughout the table are estimated standard deviations in the units of the last significant digits for the corresponding parameter. The U_{ij} are the mean square amplitudes of vibrations in Å^2 from the general temperature factor expression $\exp[-2\pi^2(U_1h^2a^*2 + U_2k^2b^*2 + U_3l^2c^*2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. ^b For Au and P atoms the anisotropic thermal parameters are given $\times 10^4$. ^c The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound. ^d See Figure 1 for identity of the group. For a description of these group parameters see ref. 18. Angular coordinates are in radians. The internal coordinate system of phenyl ring has been defined elsewhere [19].

tabulation of observed and calculated structure factor amplitudes are available*.

Discussion

The crystal structure of $(C_6H_3(OMe)_2)Au(PPh_3)$ consists of discrete molecules in which no intermolecular distance is less than that of the accepted Van der Waals' distance. The Au^I ion is bonded to the C(1) atom of the 2,6-dimethoxyphenyl ring and to the P atom of the PPh_3 ligand in an essentially linear manner with a C(1)—Au—P angle of $172.7(1)^\circ$. Figure 1 is a view of the molecule and indicates the atom-numbering scheme used in this paper. A compilation of bond lengths and angles is given in Table 3.

The Au—P bond length here of $2.284(1) \text{ \AA}$ is similar to the distances found in other linear, two-coordinate Au^I complexes: $2.243(4) \text{ \AA}$ in $AuCl(PPh_3)$ [8], $2.286(3) \text{ \AA}$ in $[Au(PPh_3)_2]^+$ [8], $2.279(8) \text{ \AA}$ in $(Me)Au(PPh_3)$ [9], $2.27(1) \text{ \AA}$ in $(C_6F_5)Au(PPh_3)$ [10], and $2.28(1) \text{ \AA}$ (average of two values) in $(Ph_3P)Au(C(CF_3)=C(CF_3))Au(PPh_3)$ [11]. As noted elsewhere [1], these values are substantially shorter than the predicted single bond length of $\sim 2.44 \text{ \AA}$ ($r_{Au} = 1.34 \text{ \AA}$, $r_P = 1.10 \text{ \AA}$ [12]) and may indicate some degree of $Au(d_\pi) \rightarrow P(d_\pi)$ back bonding in these linear complexes [13].

The Au^I —C(1) bond length of $2.050(4) \text{ \AA}$ is comparable to that in $(C_6F_5)Au(PPh_3)$ ($2.07(2) \text{ \AA}$) [10] and to the mean distance of $2.05(6) \text{ \AA}$ noted in $(Ph_3P)Au(C(CF_3)=C(CF_3))Au(PPh_3)$ [11], in which the Au^I ions are bonded not to aryl carbon atoms but to sp^2 -hybridized carbon atoms. The geometry of the $C_6H_3(OMe)_2$ ring is virtually that of an idealized phenyl ring; i.e., the ring is planar (see Table 4) and the mean C—C distance ** of $1.390 \pm 0.013 \text{ \AA}$ is in agreement with the established aromatic C—C distance of 1.395 \AA [14]. Thus, despite evidence [9] which may suggest $Au \rightarrow C$ back bonding in acetylide and cyanide complexes of Au^I , there appears to be no structural evidence for this in $(C_6H_3(OMe)_2)Au(PPh_3)$.

Although Au^I forms few complexes with oxygen ligands [1] and prefers two-coordination, there is a hint of a weak $Au^I \cdots O$ interaction in $(C_6H_3(OMe)_2)Au(PPh_3)$. The C(1)—Au—P angle is $\sim 173^\circ$, compared to the value of 178° in the closely analogous complex $(C_6F_5)Au(PPh_3)$ [10]. Furthermore, the $Au \cdots O(1)$ and $Au \cdots O(2)$ distances of $3.231(4)$ and $2.961(4) \text{ \AA}$, respectively, differ significantly, although both distances exceed the Van der Waals' distance of 2.74 \AA for the Au^I and O species [12]. Presumably to accommodate this weak $Au \cdots O(2)$ interaction, the Au—C(1)—C(6) angle has contracted to 117° , while the Au—C(1)—C(2) angle has expanded to 126° . A similar effect was noted in the structure of $((C_2H_5)_2NC(S)S)Au(PPh_3)$ [15], which contains the potentially bidentate *N,N*-diethyldithiocarbamate ligand. One sulfur atom, S(1), is strongly bonded to Au at a distance of 2.338 \AA , while the second sulfur atom, S(2),

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** An average bond length, \bar{l} , for n bond lengths is given by $\bar{l} = \Sigma l_i/n$, and its standard deviation as $\sigma(\bar{l}) = [\Sigma (l_i - \bar{l})^2 / (n - 1)]^{1/2}$.

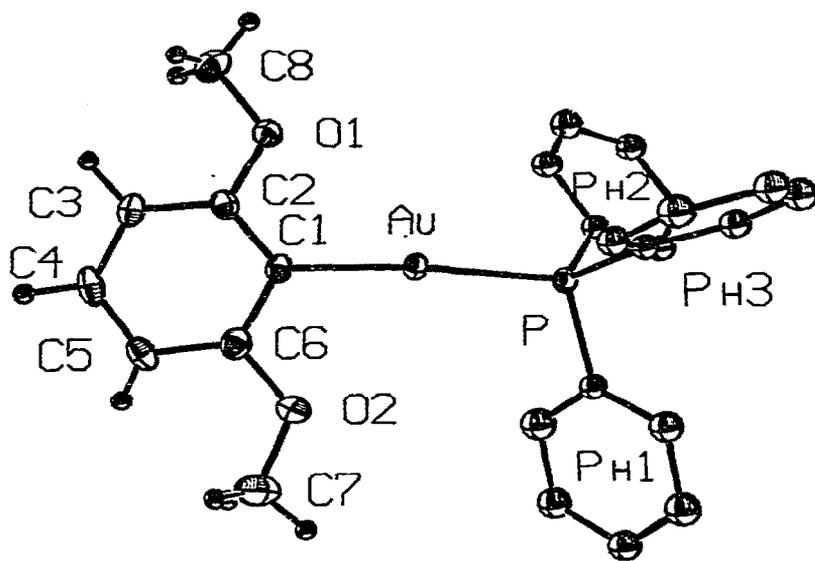


Fig. 1. View of the $(C_6H_3(OMe)_2)Au(PPh_3)$ molecule illustrating the atom numbering scheme used herein. Atoms are drawn as ellipsoids of 30% probability. Hydrogen atoms, except those of the PPh_3 ligand which have been omitted for clarity, are shown as spheres of radius 0.5 Å.

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES $^\circ$

Au—P	2.284 (1)	O(2)—C(7)	1.405 (7)
Au—O(1)	3.231 (4)	C(1)—C(2)	1.388 (6)
Au—O(2)	2.961 (4)	C(2)—C(3)	1.404 (7)
Au—C(1)	2.050 (4)	C(3)—C(4)	1.405 (8)
P—C(11) *	1.826 (2)	C(5)—C(6)	1.393 (7)
P—C(21) *	1.826 (2)	C(6)—C(1)	1.382 (7)
P—C(31) *	1.819 (3)	C(3)—H(3)	1.07 (6)
O(1)—C(2)	1.386 (6)	C(4)—H(4)	1.01 (5)
O(1)—C(8)	1.440 (7)	C(5)—H(5)	0.82 (5)
O(2)—C(6)	1.381 (6)		
P—Au—C(1)	172.7 (1)	C(2)—C(3)—H(3)	124 (3)
Au—P—C(11) *	117.8 (1)	H(3)—C(3)—C(4)	118 (3)
Au—P—C(21) *	110.3 (1)	C(3)—C(4)—C(5)	121.3 (5)
Au—P—C(31) *	110.3 (1)	C(3)—C(4)—H(4)	121 (3)
C(11) *—P—C(21) *	106.2 (1)	H(4)—C(4)—C(5)	118 (3)
C(11) *—P—C(31) *	105.3 (1)	C(4)—C(5)—C(6)	118.6 (5)
C(21) *—P—C(31) *	106.3 (1)	C(4)—C(5)—H(5)	124 (4)
Au—C(1)—C(2)	126.3 (3)	H(5)—C(5)—C(6)	117 (4)
Au—C(1)—C(6)	117.4 (3)	C(5)—C(6)—C(1)	123.3 (5)
C(2)—C(1)—C(6)	116.3 (4)	C(5)—C(6)—O(2)	121.8 (5)
C(1)—C(2)—C(3)	123.0 (4)	O(2)—C(6)—C(1)	114.9 (4)
C(1)—C(2)—O(1)	115.9 (4)	C(2)—O(1)—C(8)	116.8 (4)
O(1)—C(2)—C(3)	121.2 (4)	C(7)—O(2)—C(6)	119.9 (4)
C(2)—C(3)—C(4)	117.5 (5)		

$^\circ$ Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 1 for identity of the atoms. Atoms marked with * are rigid-group atoms.

TABLE 4
DEVIATIONS FROM SELECTED LEAST-SQUARES PLANES ^a

Atom	Deviations (Å) ^b
$-0.8399X - 0.4271Y - 0.3348Z + 3.2394 = 0$	
Au*	0
P*	0
C(1)*	0
O(1)	-1.622 (4)
O(2)	1.600 (4)
$0.7556X + 0.5155Y - 0.4042Z - 1.3151 = 0$	
C(1)*	-0.003 (4)
C(2)*	-0.001 (4)
C(3)*	-0.001 (5)
C(4)*	0.005 (5)
C(5)*	-0.009 (5)
C(6)*	0.008 (5)
Au	0.0363 (2)
O(1)	-0.013 (4)
O(2)	0.015 (4)
H(3)	-0.21 (6)
H(4)	0.02 (5)
H(5)	-0.32 (5)
C(7)	0.156 (6)
C(8)	-0.111 (6)

^a Orthonormal (Å) coordinate system with axes *X*, *Y* and *Z* parallel to unit cell vectors *a*, *b* and *c**. A negative deviation from the plane indicates that the atom with coordinates given in Table 2 lies between the plane and the unit cell origin. See Figure 1 for identity of the atoms. ^b Numbers in parentheses are the estimated standard deviations in the least significant digits.

completes the four-membered $\text{Au}-\text{S}(1)-\text{C}-\text{S}(2)$ ring at a distance of 3.015 Å, a distance which is ~ 0.17 Å less than the Van der Waals' distance. As a consequence of this weak $\text{Au}\cdots\text{S}(2)$ interaction, the $\text{P}-\text{Au}-\text{S}(1)$ bond angle has decreased by 4.3° from linearity.

The deviation from a symmetrical structure in $(\text{C}_6\text{H}_3(\text{OMe})_2)\text{Au}(\text{PPh}_3)$ in which the two $\text{Au}\cdots\text{O}$ distances would be equal implies that Au^{I} has an affinity for three-coordination, even if the third ligand is an oxygen donor. More satisfactory trigonal coordination for the Au^{I} ion, however, is apparently obtained with the more polarizable phosphine ligands, e.g. $\text{ClAu}(\text{PPh}_3)_2$ [8] and $[\text{Au}(\text{PPh}_3)_3]^+$ [16], both of which possess bond angles of $\sim 120^\circ$ about Au.

Acknowledgement

This work was supported by the Robert A. Welch Foundation (Grant No. F-233). We are also indebted to the National Science Foundation for purchase of the Syntex P2₁ diffractometer (Grant No. GP-37028) and to Drs. Gerard van Koten and Jan G. Noltes for providing a sample of $(\text{C}_6\text{H}_3(\text{OMe})_2)\text{Au}(\text{PPh}_3)$.

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