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[(ClAu)$_3$(triphos)] as a Building Block for the Synthesis of Heterometallic Clusters. Crystal Structure of [{Fe$_2$(μ-CO)(CO)$_6$(μ-HC═CPhH)Au}$_3$(triphos)]: A Compound Containing Three Independent Cluster Units Linked by a Triphosphine Ligand

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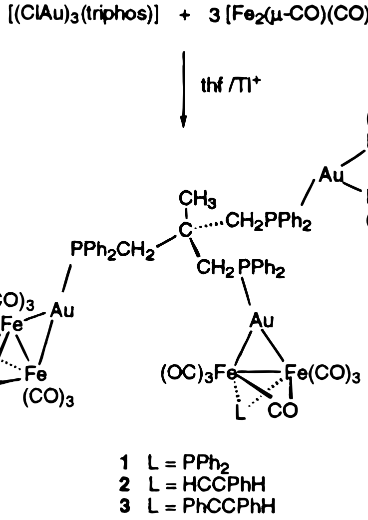
*Summary: Treatment of [(ClAu)$_3$(triphos)] with 3 equiv of the iron anions [Fe$_2$(μ-CO)(CO)$_6$(μ-L)]$^{n-}$ (L = PPh$_2$, HC═CHPh, PhC═CHPh, CO) gives the compounds [{Fe$_2$(μ-CO)(CO)$_6$(μ-L)Au}$_3$(triphos)] (L = PPh$_2$ (**1**), HC═CPhH (**2**), PhC═CPhH (**3**)) and [PPh$_4$]$_3$[{Fe$_2$(μ-CO)$_2$(CO)$_6$Au}$_3$(triphos)] (**4**). The crystal structure of complex **2** reveals three Fe$_2$Au cluster units linked by the three-legged propeller-like structure of the triphos ligand.*

Introduction

Although the triphos ligand, 1,1,1-tris(diphenylphosphinomethyl)ethane, has been used less often as a building block in the synthesis of metal complexes than the closely related more sterically demanding tripod ligand, tris(diphenylphosphino)methane, several monometallic complexes in which the triphos acts as an η^3 or η^2 chelating agent have been reported.[1] Interestingly, however, only two examples are known in which the triphos ligand bridges three metal atoms simultaneously: in [(μ-H)$_3$Ru$_3$(μ_3-COCH$_3$)(CO)$_6${μ_3-(PPh$_2$CH$_2$)$_3$-CCH$_3$}][2] the three ruthenium atoms are metal−metal bonded, but in [(ClAu)$_3$(triphos)][3] the AuCl fragments appears as “almost” independent units which makes this complex an attractive precursor for high-nuclearity gold transition metal complexes. We report here the first structurally characterized tricluster complex containing the triphos ligand in an μ_3-bridging mode, [{Fe$_2$(CO)$_7$-(μ-HC═CPhH)Au}$_3$(triphos)], and other analogous derivatives.

Results and Discussion

The reaction of [(ClAu)$_3$(triphos)] with different molar ratios of [Fe$_2$(μ-CO)(CO)$_6$(μ-L)]$^-$ (L = PPh$_2$, HC═CPhH, and PhC═CPhH) in tetrahydrofuran (THF) at room temperature in the presence of thalium(I) salts gave complicated mixtures of iron/gold clusters of the formula [{Fe$_2$(μ-CO)(CO)$_6$(μ-L)Au}$_{3-x}$(AuCl)$_x$(triphos)]. However, for a 1 Au$_3$:3 Fe$_2$ molar ratio, the only product isolated was in all cases [{Fe$_2$(μ-CO)(CO)$_6$(μ-L)Au}$_3$-(triphos)] (eq 1).



(1)

2 is the compound first structurally characterized in which three independent metal clusters appear to be linked by a triphos ligand. A view of the molecule [{Fe$_2$-(μ-CO)(CO)$_6$(μ-HC═CPhH)Au}$_3$(triphos)] (**2**) with the atom numbering is shown in Figure 1, while selected bond lengths and angles are listed in Table 1. Each of the three legs of the triphosphine ligand is bonded to a [Fe$_2$(μ-CO)(CO)$_6$(μ-HC═CPhH)Au] fragment through the gold atom. Interestingly, the gold atoms are placed at the corners of an almost equilateral triangle which is parallel to the C2AC2BC2C plane and the distances among them are greater than 6.3 Å, far too large for an aurophilic interaction to be considered. Curiously, the carbon of the methyl group of the triphosphine ligand lies approximately at the center of the Au$_3$ triangle.

The disposition of the CH$_3$C(CH$_2$PPh$_2$Au)$_3$ fragment differs from both free phosphine[4] and the trigold derivative,[3] [(ClAu)$_3$(triphos)], the local symmetry being approximately C_3 and displaying a propeller-like arrange-

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

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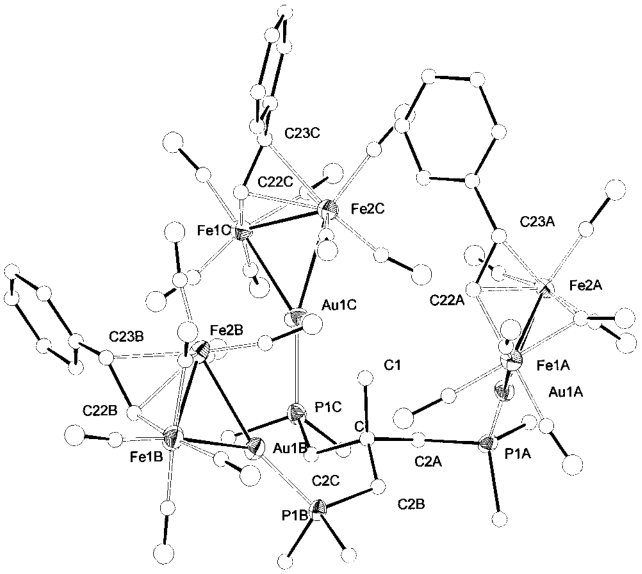


Figure 1. ORTEP view of the structure of the complex **2** together with the atom numbering scheme. Only the carbon atoms (excepting those attached to the P atoms) of the phenyl rings of triphos have been omitted for clarity. The ellipsoids for the atoms are drawn at the 30% probability level.

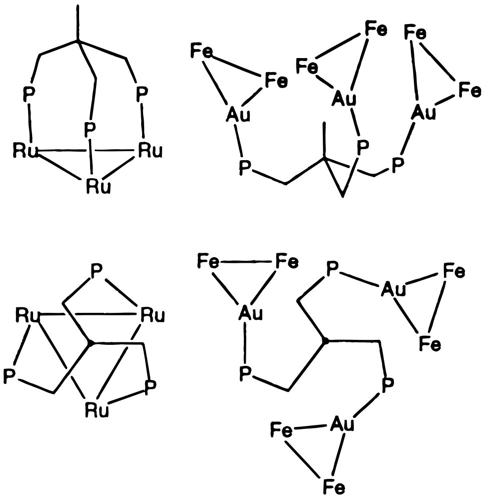
Table 1. Selected Bond Distances (Å) and Angles (deg) for 2

	A	B	C
Au(1)−Fe(1)	2.634(7)	2.703(8)	2.668(6)
Au(1)−Fe(2)	2.728(6)	2.679(6)	2.725(6)
Fe(1)−Fe(2)	2.601(8)	2.618(8)	2.600(9)
Fe(1)−C(22)	1.99(4)	1.92(4)	1.98(5)
Fe(2)−C(22)	2.12(4)	2.14(4)	2.16(4)
Fe(2)−C(23)	2.28(4)	2.25(4)	2.30(4)
C(22)−C(23)	1.45(5)	1.48(6)	1.40(6)
P(1)−Au(1)	2.276(12)	2.292(11)	2.297(10)
C(1)−C−C(2)	109(3)	114(3)	114(3)
C−C(2)−P(1)	115(2)	116(2)	119(2)
C(2)−P(1)−Au	118(1)	123(1)	122(1)
P(1)−Au−Fe(1)	161.1(3)	144.0(3)	142.1(3)
P(1)−Au−Fe(2)	140.9(3)	157.7(3)	160.2(3)
Fe(1)−Au−Fe(2)	58.0(2)	58.2(2)	57.6(2)
Fe(1)−C(21)−Fe(2)	84(2)	85(2)	83(2)
Fe(1)−C(22)−Fe(2)	78(1)	80(2)	78(2)
C(22)−C(23)−C(24)	121(3)	116(3)	124(3)
Fe(2)−C(23)−C(24)	118(2)	118(3)	118(2)
Fe(2)−C(23)−C(22)	65(2)	66(3)	66(2)
Fe(2)−C(22)−C(23)	77(2)	75(2)	77(2)
Fe(1)−C(22)−C(23)	119(3)	119(3)	117(3)

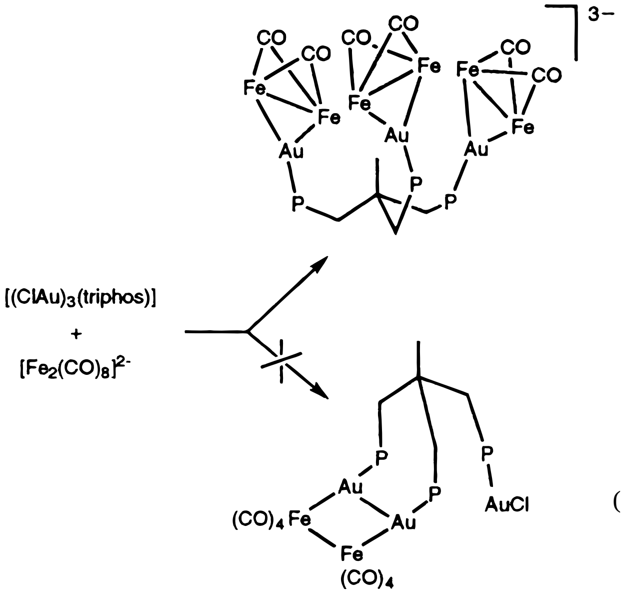
ment. A related disposition can be found in the compound [(μ-H)$_3$Ru$_3$(μ_3-COCH$_3$)(CO)$_6$(triphos)],[2] but due to steric demands in the latter, the methyl group is located on the opposite side of the cluster (methyl-out isomer) in contrast with the compound described here (methyl-in isomer) (Scheme 1). The three [Fe$_2$(CO)$_7$(μ-HC=CPhH)] units attached to the gold atoms are disarranged relative to the local 3-fold axis, which could be attributable to the different configurations of the three cluster units.

The bond parameters for the cluster fragments are comparable, and the basic skeleton consists of an Fe$_2$Au triangle where the Fe−Fe bond is bridged by a carbonyl ligand and a σ,π-phenylethenyl group. The organic bridge is σ-bonded to Fe1 with an average Fe1−C22 distance of 1.96(4) Å and is unsymmetrically π-bonded to Fe2 with average Fe2−C22 and Fe2−C23 distances of 2.14(4) and 2.28(4) Å; moreover, the hydrogen atoms are in a trans configuration. It is noteworthy that the configurations at the C22 and C23 atoms in the three legs are not the same; in the enantiomer represented in Figure 1, they are *R,S* in the legs A and B and *S,R* in the leg C; in the last leg, the coordination around the cluster is the mirror image of the other two. The Au−Fe distances are similar to those observed in the related compound [{Fe$_2$(μ-CO)(CO)$_6$(μ-PhC=CPhH)-(μ-AuPPh$_3$)].[5]

Scheme 1



In the reaction of [(ClAu)$_3$(triphos)] with the [Fe$_2$(CO)$_8$]$^{2-}$ anion, it was anticipated that both the negative charge and the doubly coordinatively unsaturated character of the dianion could promote the simultaneous attachment of both iron atoms to give a cluster containing a planar Fe$_2$Au$_2$ skeleton close to that reported for [Fe$_2$Au$_2$(CO)$_8$(dppm)] (dppm = bis(diphenylphosphino)methane), eq 2.[6]



(2)

However, the only cluster formed independent of the molar ratio was the highly unstable [{Fe$_2$(μ-CO)$_2$(CO)$_6$-

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Au}$_3$(triphos)]$^{3-}$ (**4**), which showed only one signal in the ^{31}P NMR spectrum as well as a band in the IR spectrum at about 1750 cm^{-1}, consistent with the presence of bridging carbonyl ligands, typical of an Fe$_2$-Au triangular skeleton. Probably, the large bite angle and flexibility of the triphos ligand precludes the simultaneous bonding of both iron atoms and, as a result, the formation of the Fe$_2$Au$_2$ planar arrangement.

Table 2. Crystallographic Data for $2 \cdot {}^1/_2CH_2Cl_2$

formula	$C_{86}H_{60}Au_3Fe_6O_{21}P_3 \cdot {}^1/_2CH_2Cl_2$	γ, deg	83.76(2)
mol wt	2490.78	V, Å^3	4566(2)
cryst syst	triclinic	Z	2
space group	$P\bar{1}$	D_{calcd}, g cm^{-3}	1.812
a, Å	14.632(4)	F(000)	2406
b, Å	14.768(4)	μ(Mo Kα), cm^{-1}	58.73
c, Å	21.750(6)	GOF^a	1.172
α, deg	88.71(2)	$R(F_o)^b$	0.0540
β, deg	77.75(2)	$R(F_o)^c$	0.0640

^{a} GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{var})]^{1/2}$. ^{b} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{c} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

Experimental Section

All manipulations were performed under an atmosphere of prepurified N$_2$ with the use of standard Schlenk techniques, and all solvents were distilled from appropriate drying agents. Elemental C and H analyses were carried out at the Institut de Bio-Orgànica de Barcelona. Infrared spectra were recorded in toluene solutions on an FT-IR 520 Nicolet spectrophotometer. ^{31}P{^{1}H} NMR (δ(85% H$_3$PO$_4$) = 0.0 ppm), ^{1}H NMR, and ^{13}C NMR (δ(TMS) = 0.0 ppm) were obtained on either a Bruker DXR 250 or a Varian Unity-300 spectrometer. The compounds [PPh$_4$][HFe(CO)$_4$],[7] [PPh$_4$]$_2$[Fe$_2$(CO)$_8$],[8] [PPh$_4$][Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)],[9] and [PPh$_4$][Fe$_2$(μ-CO)(CO)$_6$(μ-PhC=CPhH)][10] were prepared as described previously. The complex [(ClAu)$_3$(triphos)] was synthesized and isolated as a solid from a [AuCl(tht)] solution by adding the appropriate amount of triphos.

Preparation of [PPh$_4$][Fe$_2$(μ-CO)(CO)$_6$(μ-HC=CPhH)]. A mixture of Fe$_2$(CO)$_9$ (1.0 g, 2.75 mmol), [PPh$_4$][HFe(CO)$_4$] (1.0 g, 1.96 mmol), and HCCPh (0.2 mL, 2 mmol) in THF (30 mL) was refluxed for 1 h. After the reaction mixture was cooled to room temperature, the suspension was filtered through Celite and evaporated to dryness. The residual solid was dissolved in a mixture of 4 mL of dichloromethane and 5 mL of methanol. Cooling this solution to −30 °C overnight resulted in the deposition of dark red-brown microcrystals. Yield: 600 mg, 41%, based on [PPh$_4$][HFe(CO)$_4$]. IR (CH$_2$Cl$_2$, cm^{-1}), ν(CO): 2026 (m), 1976 (vs), 1933 (s), 1758 (w). ^{1}H NMR (25 °C, CDCl$_3$): 8.50 (d, 1H, *H*C=CPhH, ^3J(H−H) = 11.6 Hz), 7.88−6.80 (m, Ph), 3.6 (d, 1H, HC=CPh*H*). Anal. Calcd for C$_{39}$H$_{27}$Fe$_2$O$_7$P: C, 62.40; H, 3.60. Found: C, 62.58; H, 3.49.

Preparation of [{Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)Au}$_3$(triphos)] (1). Solid [(ClAu)$_3$(triphos)] (0.16 g, 0.12 mmol) and TlBF$_4$ (0.11 g, 0.36 mmol) were added to a THF solution (40 mL) of [PPh$_4$][Fe$_2$(μ-CO)(CO)$_6$(μ-PPh$_2$)] (0.30 g, 0.36 mmol) at room temperature. The solution turned deep violet immediately. After 30 min of stirring, the mixture was filtered and taken to dryness. The remaining solid was extracted with toluene (3 × 5 mL), filtered via cannula, and concentrated to dryness. The residue was dissolved in a dichloromethane/diethyl ether (1:10) mixture, and violet crystals were formed on cooling overnight. Yield: 240 mg, 70%. IR (toluene, cm^{-1}), ν(CO): 2043 (m), 2012 (vs), 1971 (s, br), 1779 (m). ^{31}P{^{1}H} NMR (25 °C, CDCl$_3$): δ 131.1 (d, Fe$_2$*P*Ph$_2$, ^3J(P−P) = 24 Hz), 36.8 (d, Au*P*Ph$_2$). ^{1}H NMR (25 °C, CDCl$_3$): δ 7.36−7.05 (m, Ph), 2.72 (d, 6H, C*H*$_2$P, ^2J(H−P) = 10.7 Hz), 2.03 (s, 3H, C*H*$_3$). ^{13}C NMR (25 °C, CDCl$_3$): δ 138.8−128.0 (m, Ph), 44.9 (dt, *C*H$_2$P, ^1J(C−P) = 21, ^3J(C−P) = 8 Hz), 38.2 (s, br, CH$_3$*C*), 28.9 (q, *C*H$_3$, ^3J(C−P) = 5 Hz). Anal. Calcd for C$_{98}$H$_{69}$Au$_3$Fe$_6$O$_{21}$P$_6$·2C$_4$H$_{10}$O: C, 44.79; H, 3.15. Found: C, 44.21; H, 3.26.

Preparation of [{Fe$_2$(μ-CO)(CO)$_6$(μ-RC=CPhH)Au}$_3$(triphos)] (R = H (2), Ph (3)). Solid [(ClAu)$_3$(triphos)] (0.17 g, 0.13 mmol) and TlBF$_4$ (0.11 g, 0.36 mmol) were added to a THF solution (40 mL) of [PPh$_4$][Fe$_2$(μ-CO)(CO)$_6$(μ-HC=CPhH)] (0.27 g, 0.36 mmol) at room temperature. The solution turned deep green immediately. After 30 min of stirring, the mixture was filtered and taken to dryness. The remaining solid was extracted with toluene (3 × 5 mL), filtered via cannula, and taken once more to dryness. After the residue was dissolved in 10 mL of dichloromethane, the addition of 50 mL of methanol and cooling overnight afforded dark green microcrystals of **2**. Yield: 220 mg, 68%. IR (toluene, cm^{-1}), ν(CO): 2049 (w), 2018 (vs), 1981 (s, br), 1951 (m, sh), 1719 (m). ^{31}P{^{1}H} NMR (25 °C, CD$_2$Cl$_2$): δ 33.5. ^{1}H NMR (25 °C, CD$_2$Cl$_2$): δ 8.04 (d, 3H, *H*C=CPhH, ^3J(H−H) = 13.4 Hz), 7.43−7.02 (m, Ph), 4.75 (d, 3H, HC=CPh*H*), 2.68 (d, 6H, C*H*$_2$P, ^2J(H−P) = 10.8 Hz), 2.30 (s, 3H, C*H*$_3$). ^{13}C NMR (25 °C, CD$_2$Cl$_2$): δ 137.7−126.9 (m, Ph), 140.5 (s, H*C*=CPhH), 99.5 (s, HC=*C*PhH), 46.3 (m, *C*H$_2$P), 39.3 (s, CH$_3$*C*), 28.9 (s, *C*H$_3$). Anal. Calcd for C$_{86}$H$_{60}$Au$_3$Fe$_6$O$_{21}$P$_3$·0.5CH$_2$Cl$_2$: C, 41.71; H, 2.47. Found: C, 41.47; H, 2.55.

A similar procedure was used to prepare derivative **3**. Yield: 210 mg, 63%. IR (toluene, cm^{-1}), ν(CO): 2047 (m), 2018 (vs), 1977 (s), 1945 (m, sh), 1785 (m). ^{31}P{^{1}H} NMR (25 °C, acetone-d_6): δ 35.9. ^{1}H NMR (25 °C, acetone-d_6): δ 7.67−7.00 (m, Ph), 4.63 (s, 3H, PhC=CPh*H*), 3.01 (d, 6H, C*H*$_2$P, ^2J(H−P) = 11.4 Hz), 2.71 (s, 3H, C*H*$_3$). ^{13}C NMR (25 °C, acetone-d_6): δ 133.1−126.4 (m, Ph), 138.8 (s, Ph*C*=CPhH), 91.6 (s, PhC=*C*PhH), 46.3 (m, *C*H$_2$P), 40.3 (s, CH$_3$*C*).

Preparation of [PPh$_4$]$_3$[{Fe$_2$(μ-CO)$_2$(CO)$_6$Au}$_3$(triphos)] (4). Solid [(ClAu)$_3$(triphos)] (0.13 g, 0.1 mmol) was added to a suspension of [PPh$_4$]$_2$[Fe$_2$(CO)$_8$] (0.30 g, 0.3 mmol) in THF at room temperature. After 30 min of stirring, the resulting orange reaction mixture was filtered and evaporated to dryness. The residual solid was extracted with 5 mL of CH$_2$Cl$_2$. After the addition of 10 mL of MeOH, an orange-brown precipitate was obtained, which was filtered off and dried in vacuo. Yield: 130 mg, 40%. IR (THF, cm^{-1}), ν(CO): 2007 (w), 1961 (s), 1915 (vs), 1750 (w). ^{31}P{^{1}H} NMR (25 °C, THF): δ 34.8 (Au*P*Ph$_2$), 22.8 (*P*Ph$_4^+$).

X-ray Data Collection, Structure Determination, and Refinement for $2 \cdot {}^1/_2CH_2Cl_2$. All crystals were of poor quality and diffracted weakly. Three sets of data were collected from different crystals, those of the third crystal (of dimensions 0.20 × 0.25 × 0.30 mm) were the best and were used in the analysis. Crystallographic data are summarized in Table 2. The intensities were collected on a Philips PW 1100 diffractometer using graphite-monochromated Mo Kα radiation and the θ−2θ scan technique. There were 8477 unique reflections measured with θ in the range 3−20°; 2906 of them, having $I > 2\sigma(I)$, were used in the refinement. One standard reflection was monitored every 100 measurements; no significant decay was noticed over the time of data collection. Intensities were corrected for Lorentz and polarization effects. An empirical correction for absorption was applied (maximum and minimum values for the transmission factors were 1.0 and 0.5527).[11]

The structure was solved by direct and Fourier methods and refined by full-matrix least-squares procedures with isotropic thermal parameters; a dichloromethane molecule of solvation was also found. In the last cycles, only the Au, Fe, and P atoms were refined anisotropically and the nine phenyl rings were treated as rigid groups in order to decrease the number of variables. The hydrogen atoms were not introduced in the geometrically calculated positions in the final structure factor

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calculations (the ethenyl hydrogens surely deviate remarkably from the theoretical positions). The final cycles of refinement were carried out on the basis of 441 variables; after the last cycles, no parameters shifted by more than 0.25 esd. The highest remaining peak in the final difference map (close to the gold atom) was equivalent to about 0.96 e/Å^3. In the final cycles of refinement, a weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence, the K and g values were 0.526 and 0.0022, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 12. All calculations were carried out on the GOULD POWERNODE 6040 and ENCORE 91 computers of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma, using the SHELX-76 and SHELXS-86 crystallographic computer programs.[13]

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Supporting Information Available: Tables of final values of atomic coordinates for the non-hydrogen atoms, anisotropic thermal parameters, and a complete list of bond distances and angles (10 pages). Ordering information is given on any current masthead page.

OM970078X

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