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Carbon−Carbon Coupling via Nucleophilic Addition of a Gold(I) Methanide Complex to Heterocumulenes

Manuel Bardají,[†] M. Concepción Gimeno,[†] Peter G. Jones,[‡] Antonio Laguna,[†]
Mariano Laguna,*[,†] Francisco Merchán,[†] and Inocencio Romeo[†]

*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain, and Institut für
Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329,
D-38023 Braunschweig, Germany*

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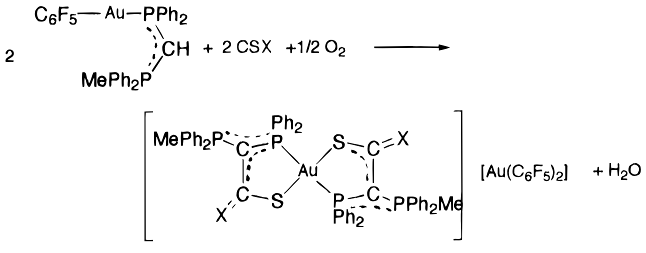
*Summary: The methanide carbon of [Au(C_6F_5)(PPh_2-$CHPPh_2Me$)] acts as a nucleophilic center toward reagents such as carbon disulfide and isothiocyanates, affording [Au^{III}{$PPh_2C(PPh_2Me)C(X)S$}$_2$][Au^I(C_6F_5)$_2$] (X = S (**1**), 4-ClC_6H_4N (**2**), PhN (**3**)) through a carbon−carbon coupling reaction. The X-ray structure of **1** shows the ligand $PPh_2C(PPh_2Me)C(X)S$ acting as a bidentate P,S-chelate.*

Introduction

Insertion reactions of carbon disulfide into an M−X bond (X = H, C, N, P, S, Cl) have been extensively studied,[1] and some examples related to gold chemistry have been reported in Au−C,[2] Au−Cl,[3] and Au−S[4] bonds. However, carbon−carbon coupling reactions of carbon disulfide with ligands coordinated to a metal center are less well-known; only a few have been reported.[5] Bis(diphenylphosphino)methanide complexes have been commonly employed to synthesize polynuclear complexes in which the methanide acts as a tridentate ligand.[6] The reactivity of the electron-rich carbon atom with nonmetallic electrophilic reagents has scarcely been studied, and only some C-alkylated, C-acylated, and C-halogenated diphenylphosphino derivatives (M = Cr, Fe, Mn, Mo, W, Pd, Pt) have been described.[7] Recently, the activation of cyanogen by a manganese methanide compound, to give a tridentate (P,P,N) diphosphine, has been reported.[8] Moreover, as far as we know, there are no examples of coupling reactions between methanide derivatives and heterocumulenes such as carbon disulfide and isothiocyanates; analogous reactions are known for carbodiphosphoranes ($R_3P{=}C{=}PR_3$).[9]

Scheme 1



X = S (**1**), 4- ClC_6H_4N (**2**), C_6H_5 N (**3**)

Now we report on the reactivity of the gold(I) methanide complex[10] [Au(C_6F_5)(PPh_2CHPPh_2Me)] toward heterocumulenes such as CS_2 and RNCS, leading to gold(III) derivatives containing [$PPh_2C(PPh_2Me)C(X)S$]$^-$ (X = S, NR) ligands stabilized by metal coordination. To the best of our knowledge these are the first complexes in which this type of ligand is present.

Results and Discussion

Treatment of an acetone solution of [Au(C_6F_5)(PPh_2-$CHPPh_2Me$)] with an excess of CS_2 led to an orange solution from which the orange solid [Au^{III}{$PPh_2C(PPh_2$-$Me)C(S)S$}$_2$][Au^I(C_6F_5)$_2$] (**1**) was obtained (Scheme 1). Complex **1** was completely characterized by spectroscopic and analytical methods. The main features are: lack of a $C_{methanide}$−H signal in the ^1H NMR, a set of two pseudotriplets (AA′XX′ spin system) in the $^{31}P\{H\}$ NMR, three signals of equivalent C_6F_5 groups bonded to gold(I) in the ^{19}F NMR, and the presence of the parent ion in mass spectra (LSIMS$^+$) at *m*/*z* 1143 (38%).

The structure of complex **1** has been confirmed by an X-ray crystallographic study (Figure 1). Single crystals of **1** were grown by slow diffusion of a 1:1 mixture of *n*-hexane/diethyl ether into a dichloromethane solution at −20 °C. The molecule consists of an [Au^{III}{PPh_2C-$(PPh_2Me)C(S)S$}$_2$]$^+$ cation and an [Au^I(C_6F_5)$_2$]$_2$$^-$ anion, both with the gold atom lying on a symmetry center.

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* To whom correspondence should be addressed. E-mail: mariano.laguna@msf.unizar.es.

[†] Universidad de Zaragoza-CSIC.

[‡] Technische Universität Braunschweig.

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(1) For a leading reference see: Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37.

(2) Werner, H.; Otto, H. *Chem Ber.* **1987**, *120*, 97.

(3) Jentsch, D.; Jones, P. G.; Thoene, C.; Schwarzmann, E. *J. Chem. Soc., Chem. Commun.* **1989**, 1495.

(4) Vicente, J.; Chicote M.-T.; Gonzalez-Herrero, P.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1995**, 745.

(5) (a) Raubenheimer, H. G.; Kruger, G. J.; Viljoen, H. W. *J. Chem. Soc., Dalton Trans.* **1985**, 1963. (b) Raubenheimer, H. G.; Kruger, G.; Lombard, A. *J. Organomet. Chem.* **1982**, *240,* C11. (c) Raubenheimer, H. G.; Lotz, S.; Kruger, G. J.; Lomard, A. A.; Viljoen, J. C. *J. Organomet. Chem.* **1987**, *336,* 349. (d) Grötsch, G.; Malish, W. *J. Organomet. Chem.* **1984**, *262,* C38.

(6) See for instance: (a) Laguna, A.; Laguna, M. *J. Organomet. Chem.* **1990**, *394,* 743 and references therein. (b) Ruiz, J.; Araúz, R.; Riera, V.; Vivanco, M.; García-Granda, S.; Pérez-Carreño, E. *J. Chem. Soc., Chem. Commun.* **1993**, 740. (c) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; López-de-Luzuriaga, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33,* 87. (d) Gimeno, M. C.; Jiménez, J.; Jones, P. G.; Laguna, A.; Laguna, M. *Organometallics* **1994**, *13*, 2508.

(7) (a) Ruiz, J.; Araúz, R.; Riera, V.; Vivanco, M.; García-Granda, S.; Menéndez-Velázquez, A. *Organometallics* **1994**, *13*, 4162. (b) Falvello, L. R.; Forniés, J.; Navarro, R.; Rueda, A.; Urriolabeitia, E. P. *Organometallics* **1996**, *15*, 309 and references therein.

(8) Ruiz, J.; Riera, V.; Vivanco, M.; García-Granda, S.; Salvadó, M. A. *Organometallics* **1996**, *15*, 1079.

(9) Ramirez, F.; Pilot, J. F.; Desai, N. B.; Smith, C. P.; Hansen, B.; McKelvie, N. J. *J. Am. Chem. Soc.* **1967**, *89*, 6273.

(10) Usón, R.; Laguna, A.; Laguna, M.; Lázaro, I.; Morata, A.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 669.

S0276-7333(96)00893-X CCC: $14.00

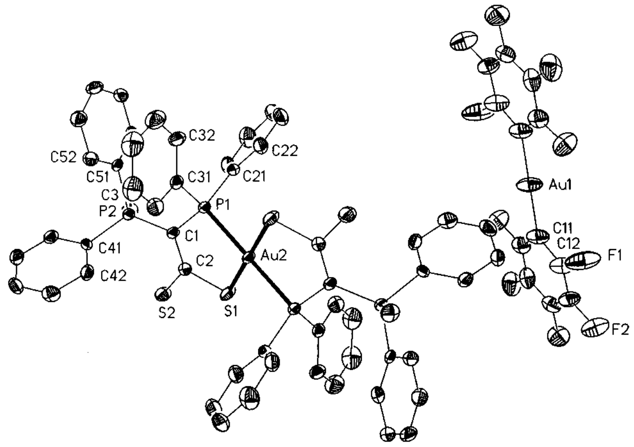

Figure 1. Structure of the complex $[Au\{PPh_2C(PPh_2Me)CS_2\}][Au(C_6F_5)_2]$ in the crystal state showing the atom-numbering scheme. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1[a]

Au(1)−C(11)	2.054(7)	Au(2)−S(1)	2.314(2)
Au(2)−P(1)	2.339(2)	P(1)−C(1)	1.771(6)
P(1)−C(31)	1.811(6)	P(1)−C(21)	1.820(7)
P(2)−C(1)	1.768(5)	P(2)−C(41)	1.800(6)
P(2)−C(3)	1.805(7)	P(2)−C(51)	1.808(6)
S(1)−C(2)	1.767(6)	S(2)−C(2)	1.671(6)
C(1)−C(2)	1.393(8)		
C(11)#1−Au(1)−C(11)	180.0	C(16)−C(11)−Au(1)	124.0(5)
C(12)−C(11)−Au(1)	122.0(5)	S(1)#2−Au(2)−S(1)	180.0
S(1)#2−Au(2)−P(1)	94.29(6)	S(1)−Au(2)−P(1)	85.71(5)
P(1)−Au(2)−P(1)#2	180.0	C(1)−P(1)−C(31)	113.8(3)
C(1)−P(1)−C(21)	111.2(3)	C(31−P(1)−C(21)	107.6(3)
C(1)−P(1)−Au(2)	105.2(2)	C(31)−P(1)−Au(2)	109.6(2)
C(21)−P(1)−Au(2)	109.4(2)	C(1)−P(2)−C(41)	111.6(3)
C(1)−P(2)−C(3)	113.6(3)	C(41)−P(2)−C(3)	108.0(3)
C(1)−P(2)−C(51)	112.2(3)	C(41)−P(2)−C(51)	105.7(3)
C(3)−P(2)−C(51)	105.2(3)	C(2)−S(1)−Au(2)	105.0(2)
C(2)−C(1)−P(2)	116.8(4)	C(2)−C(1)−P(1)	118.4(4)
P(2)−C(1)−P(1)	124.8(3)	C(1)−C(2)−S(2)	126.0(4)
C(1)−C(2)−S(1)	121.6(5)	S(2)−C(2)−S(1)	112.3(4)
C(26)−C(21)−P(1)	119.6(5)	C(22)−C(21)−P(1)	120.0(5)
C(36)−C(31)−P(1)	118.3(5)	C(32)−C(31)−P(1)	122.0(5)
C(42)−C(41)−P(2)	122.0(4)	C(46)−C(41)−P(2)	117.9(5)
C(52)−C(51)−P(2)	119.9(5)	C(56)−C(51)−P(2)	119.5(5)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x, -y, -z$; (#2) $-x + 1, -y + 1, -z + 1$.

Table 1 collects the selected bond lengths and angles. The cation of **1** shows the gold atom in the square-planar geometry expected for gold(III) derivatives. The chelate ring shows an envelope conformation, with the gold atom lying 0.54 Å out of the plane of P1,C1,C2,S1 (mean deviation 0.02 Å). The bite angle P(1)−Au(2)−S(1) is 85.71(5)°, slightly narrower than in the complexes $[Au(C_6F_5)_2(PPh_2CHPPh_2S)]$ (89.6(1)°)[11] and $[Au(PPh_2C_6H_4S)_2]^+$ (86.4(1) and 87.2(1)°),[12] which also contain a gold(III) center chelated by a heterofunctional P,S ligand. The Au(2)−P(1) and Au(2)−S(1) distances, 2.339(2) and 2.314(2) Å, are similar to those found in the complex $[Au(PPh_2C_6H_4S)_2]^+$ (2.325(4) and 2.332(4) Å (Au−P), 2.333(4) and 2.312(4) Å (Au−S)). The S−C bond lengths are very dissimilar, S(1)−C(2) = 1.767(6) Å and S(2)−C(2)= 1.671(6) Å, typical values for a dithiocarbamate ligand coordinated through one of the sulfur atoms as in the complex $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(S_2CNMe_2)_2]$ (1.753(6) and 1.682(6) Å)[13] and indicating some multiple-bond character for C2−S2. Extensive electron delocalization in the ligand is underlined by the C(1)−C(2) distance of 1.398(8) Å and by the P(1)−C(1) and P(2)−C(1) bond distances of 1.771(6) and 1.768(5) Å, which are shorter than in gold−phosphine derivatives such as $[Au(C_6F_5)_2\{(PPh_2)_2CH_2\}]^+$ (1.845(9) Å),[14] whereby the difference may be considered to arise from a degree of multiple P−C bonding in the methanide ligand. The angles at C(1) and C(2) are close to 120°. The anion $[Au(C_6F_5)_2]^-$ is very similar to the recently reported[15] $NBu_4[Au(C_6F_5)_2]$, and the Au(1)−C(11) bond length is 2.054(7) Å.

The electrochemical behavior of complex **1** has been studied by cyclic voltammetry. The cyclic voltammogram shows a quasi-reversible reduction wave (i_{ox}/i_{red} = 0.80−0.83 in the scan rate range 20−300 mV s^{-1}) centered at −0.83 V (versus SCE), similar to that found in $[Au(PPh_2C_6H_4S)_2]^{+}$ [12] or in $[Au(MNT)_2]^{-}$ [16] (MNT = maleonitriledithiolate) for the couple Au^{III}/Au^{II}.

In order to establish the nature of some intermediate species, the reaction was monitored by ^1H and $^{31}P\{H\}$ NMR: it was observed in the ^1H NMR spectra that the C methanide proton signal became broad and disappeared quickly, while the $^{31}P\{^1H\}$ NMR spectra always showed only starting material and final product. It is noteworthy that the same reaction carried out in diethyl ether gave a slightly orange solution, from which only the starting methanide was isolated. A similar result is observed if thoroughly deoxygenated acetone is used as solvent, whereas bubbling pure O_2 accelerated the process only in acetone; the presence of this element is essential in the reaction pathway. It is not possible to deduce an exact mechanism from these data, although the initial step could be the interaction between the carbon disulfide molecule and the sp^2 methanide carbon; then a symmetrization reaction to give $[AuL_2][Au(C_6F_5)_2]$ (a reaction type already observed[17]) and finally a partial oxidation of gold and bidentate coordination of the ligand should stabilize the complex **1**. The subproduct of the oxygen reduction should be water, because no other products except H_2O and acetone were detected in the reaction mixture.

The same procedure, but with RNCS (R = $4\text{-}ClC_6H_4$, Ph) instead of CS_2, afforded the derivatives $[Au^{III}\{PPh_2C(PPh_2Me)C(NR)S\}][Au^{I}(C_6F_5)_2]$ (R = $4\text{-}ClC_6H_4$ (**2**), Ph (**3**)). Complexes **2**−**3** were fully characterized by spectroscopic and analytical methods, confirming their similarity to complex **1** (Scheme 1).

Further attempted reactions with CO_2 and RNCNR were unsuccessful, which can be explained by the stabilizing driving force of the metallacycle with the ligand acting as a bidentate P,S donor.

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(11) Usón, R.; Laguna, A.; Laguna, M.; Fraile, M. N.; Jones, P. G.; Erdbrügger, C. F. *J. Chem. Soc., Dalton Trans.* **1989**, 73.

(12) Dilworth, J. R.; Hutson, A. J.; Zubieta, J.; Chen, Q. *Transition Met. Chem.* **1994**, *19*, 61.

(13) Bardají, M.; Blasco, A.; Jimenez, J.; Jones, P. G.; Laguna, A.; Laguna, M.; Merchan, F. *Inorg. Chim. Acta* **1994**, *223*, 55.

(14) Usón, R.; Laguna, A.; Laguna, M.; Fernández, E.; Villacampa, M. D.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1679.

(15) Jones, P. G. *Z. Kristallogr.* **1993**, *208*, 347.

(16) (a) Waters, J. H.; Gray, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3543. (b) Waters, J. H.; Bergendhal, T. L.; Lewis, D. R. *J. Chem. Soc., Chem. Commun.* **1971**, 334.

(17) See for instance: (a) Usón, R.; Laguna, A.; Vicente, J.; García, J.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, 655. (b) Usón, R.; Laguna, A.; Laguna, M.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, 366.

Experimental Section

The starting material $[Au(C_6F_5)(PPh_2CHPPh_2Me)]$ was prepared as described previously.[10] All other reagents were commercially available.

The C, H, N, and S analyses were carried out in a Perkin-Elmer Model 2400 microanalyzer. The infrared spectra were recorded (4000−200 cm^{-1}) on a Perkin-Elmer 883 spectrometer using Nujol mulls between polyethylene sheets. The ^1H, ^{31}P, and ^{19}F NMR spectra were recorded on Varian Unity 300 and Bruker ARX 300 spectrometers, in $(CD_3)_2CO$. Chemical shifts are cited relative to $SiMe$ (^1H), 85% H_3PO_4 (external, ^{31}P), and $CFCl_3$ (external, ^{19}F). Mass spectra were recorded on a VG Autospec with the LSIMS technique (with Cs gun) using 3-nitrobenzyl alcohol as matrix.

$[Au^{III}\{PPh_2C(PPh_2Me)C(S)S\}_2][Au^I(C_6F_5)_2]$ (1). To an acetone solution (25 mL) of $[Au(C_6F_5)(PPh_2CHPPh_2Me)]$ (0.1 g, 0.13 mmol) was added an excess of CS_2 (0.5 mL) at room temperature. The colorless solution became orange, was stirred for 6 h, and then concentrated to *ca.* 5 mL, whereupon addition of diethyl ether (15 mL) gave **1** as an orange solid, which was washed with diethyl ether (3 × 5 mL). Yield: 80%. Data for **1** are as follows. Anal. Calcd for $C_{66}H_{46}F_{10}P_4S_4Au_2$: C, 47.3; H, 2.7; S, 7.6. Found: C, 46.8; H, 2.8; S, 7.2. ^1H NMR: δ 7.7−7.1 (m, 40H, Ph), 2.5 (d, 3H, Me, $J = 13.07$ Hz) ppm. $^{31}P\{^1H\}$ NMR: δ 33.1 (“t”, $J_{XX'} = 0$ and $J_{AA'} = J_{AX} = J_{A'X'} = 18.7$ Hz), 16.5 (“t”) ppm. $^{19}F\{^1H\}$ NMR: δ −114.7 (m, *o*-F), −163.4 (t, *p*-F, $J = 20.7$ Hz), −164.4 (m, *m*-F) ppm. IR: 955 cm^{-1} due to $Au-C_6F_5$. LSIMS$^+$: *m*/*z* (% abundance) 1143 (38, $[Au\{PPh_2C(PPh_2Me)C(S)S\}_2]^+$). LSIMS$^-$: *m*/*z* (% abundance) 531 (100) $[Au(C_6F_5)_2]^-$.

$[Au^{III}\{PPh_2C(PPh_2Me)C(NR)S\}_2][Au^I(C_6F_5)_2]$ (R = 4-ClC_6H_4 (2), Ph (3)). To an acetone solution (25 mL) of $[Au(C_6F_5)(PPh_2CHPPh_2Me)]$ (39 mg, 0.05 mmol) was added 4-ClC_6H_4NCS (8 mg, 0.05 mmol) at room temperature. The colorless solution turned orange slowly and was stirred for 1 day. The solvent was then evaporated to *ca.* 5 mL, and addition of hexane (20 mL) gave **2** as a orange oil, which became a pink solid after cooling. Then it was filtered and washed with hexane (3 × 5 mL). Yield: 13%. For R = Ph we proceed in a similar manner, but using 0.1 g of the complex and a excess of the isothiocyanate (0.2 mL). The resulting orange oil was recrystallized from dichloromethane−diethyl ether. Yield: 24%. Data for **2** are as follows. Anal. Calcd for $C_{78}H_{54}F_{10}P_4S_2N_2Cl_2Au_2$: C, 50.3; H, 2.9; N, 1.5; S, 3.4. Found: C, 50.5; H, 2.9; N, 1.3; S, 3.2. ^1H NMR: δ 8.0−7.2 (m, 40H, Ph), 7.0 (d, 2H, half of 4-ClC_6H_4NCS, $J = 8.6$ Hz), 6.4 (d, 2H, half of 4-ClC_6H_4NCS), 2.8 (d, 3H, $J = 13.0$ Hz) ppm. $^{31}P\{^1H\}$ NMR: δ 24.6 (“t”, $J_{XX'} = 0$ and $J_{AA'} = J_{AX} = J_{A'X'} = 14.1$ Hz), 18.2 (“t”) ppm. $^{19}F\{^1H\}$ NMR: δ −114.7 (m, *o*-F), −163.6 (t, *p*-F, $J = 19.7$ Hz), −164.4 (m, *m*-F) ppm. LSIMS$^+$: *m*/*z* (%) 1329 (51, $[Au\{PPh_2C(PPh_2Me)C(4\text{-}ClC_6H_4N)S\}_2]^+$), LSIMS$^-$: *m*/*z* (%) 531 (100) $[Au(C_6F_5)_2]^-$. Data for **3** as follows. Anal. Calcd for $C_{78}H_{56}F_{10}P_4S_2N_2Au_2$: C, 52.2; H, 3.1; N, 1.6; S, 3.6. Found: C, 52.7; H, 2.8; N, 1.4; S, 3.2. ^1H NMR: δ 8.0−7.3 (m, 40H, Ph), 2.7 (d, 3H, $J = 13.0$ Hz) ppm. $^{31}P\{^1H\}$ NMR: δ 26.8 (“t”, $J_{XX'} = 0$ and $J_{AA'} = J_{AX} = J_{A'X'} = 14.4$ Hz), 15.64 (“‘t”) ppm. $^{19}F\{^1H\}$ NMR: δ −114.6 (m, *o*-F), −163.6 (t, *p*-F, $J = 20.4$ Hz), −164.3 (m, *m*-F) ppm. LSIMS$^+$: *m*/*z* (%) 1261 (70, $[Au\{PPh_2C(PPh_2Me)C(C_6H_5N)S\}_2]^+$). LSIMS$^-$: *m*/*z* (%) 531 (100, $[Au(C_6F_5)_2]^-$.

Crystal Structure Determination of Compound 1. Crystal data: $\mathbf{1}\cdot 3CH_2Cl_2$, $C_{69}H_{52}Au_2Cl_6F_{10}P_4S_4$, $M_r = 1929.86$, triclinic, space group $P\bar{1}$, $a = 9.0780(14)$ Å, $b = 11.9585(14)$ Å, $c = 17.011(2)$ Å, $\alpha = 97.402(6)°$, $\beta = 92.120(10)°$, $\gamma = 102.888(10)°$, $V = 1781.1(4)$ Å^3, $Z = 1$, $D_c = 1.799$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.710 73 Å, $\mu = 4.614$ mm^{-1}, $F(000) = 940$, $T = -100$ °C.

Data Collection and Reduction. An orange plate (0.65 × 0.35 × 0.05 mm) was used to record 9294 intensities to $2\theta_{max} = 50°$ (Siemens P4 diffractometer), of which 6205 were unique ($R_{int} = 0.052$). An absorption correction was applied on the basis of Ψ-scans, with transmission factors of 0.237−1.0. Cell constants were refined fron setting angles of 65 reflections in the range $2\theta = 9-25°$.

Structure Solution and Refinement. The structure was solved by the heavy-atom method and subjected to full-matrix least-squares refinement on F^2 (SHELXL-93);[18] all non-H atoms were refined anisotropically, and H atoms were included using a riding model or rigid methyls. Refinement proceeded to $R_w(F^2) = 0.109$ for 6190 reflections, 436 parameters, and 341 restraints (to local ring geometry and light atom displacement parameters), conventional $R(F) = 0.040$, $S(F^2) = 1.010$, maximum $\Delta\rho = 2.18$ e Å^{-3}. The structure contains two disordered dichloromethane molecules. One lies across an inversion center; the other has three chlorine positions, which were assigned occupancies of $^2/_3$. The solvent H atoms were not included.

Acknowledgment. We thank the Spanish DGICYT (Project PB95-0140) and the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: Tables giving crystal data, atomic coordinates and *U* values, anisotropic thermal parameters, and interatomic distances and angles for **1** (7 pages). Ordering information is given on any current masthead page.

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[18] Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.