

Gold, Silver and Palladium Complexes with the 2,2'-Dipyridylamine Ligand

Mercedes Burgos,^[a] Olga Crespo,^[a] M. Concepción Gimeno,^[a] Peter G. Jones,^[b] and Antonio Laguna^{*[a]}**Keywords:** Gold / N Ligands / Palladium / Silver

Reaction of the 2,2'-dipyridylamine (Py₂NH) ligand with various gold and silver starting products leads to three- or four-coordinate complexes. The structure of compound [Ag(NHPy₂)(PPh₃)]OTf shows weak interactions which produce bands of molecules parallel to the *z* axis. Other hydrogen bonds of the type C–H...O serve to link the ribbons. The derivative PPN[Au(Py₂N)₂] has also been obtained using

PPN[Au(acac)₂] [PPN = bis(triphenylphosphanyl)iminio, acac = acetylacetonate] as starting product to deprotonate the ligand. The palladium complex [PdCl₂(Py₂NH)₂] is also reported.

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Introduction

A search of the CSD affords more than two hundred structures of coordination complexes containing the 2,2'-dipyridylamine ligand (dpa). In most of them, the ligand shows a bidentate coordination mode,^[1] but coordination as a bridging ligand^[2] is not unusual, and monodentate coordination has been found in [M(dpa)₂(CO)₃]^[3] (M = Mo, W, one chelate and other monodentate dpa) and also in the more recently reported [W(dpa)(CO)₅].^[4] The copper complexes of this ligand have been the most widely studied, at first as models for copper-containing plant hormone binding sites,^[1d,5] and also because of their interesting electrochemical behavior.^[6] The blue-light emission of organoaluminium(III) and Zn^{II} complexes with dpa is well known. The chelating effect of dpa in these complexes seems to be the origin of the enhancement and shift from UV to blue of the intraligand $\pi \rightarrow \pi^*$ transition of dpa upon coordination.^[7–10] Nevertheless, the thermal instability or the low emission quantum yields in the solid state make the use of these complexes for practical applications impossible. Recent investigations in this area have involved polymeric or polynuclear complexes.^[1c] Interesting trinuclear complexes in which the dpa acts as a bridging ligand have been described. They show variable-temperature magnetic susceptibility, which ranges from strong antiferromagnetic coupling (tricopper, trinickel)^[11–13] to spin crossover (tricobalt),^[14,15] via Curie law behavior (trichromium).^[2e,16] The coordination to coinage metals other than copper remains

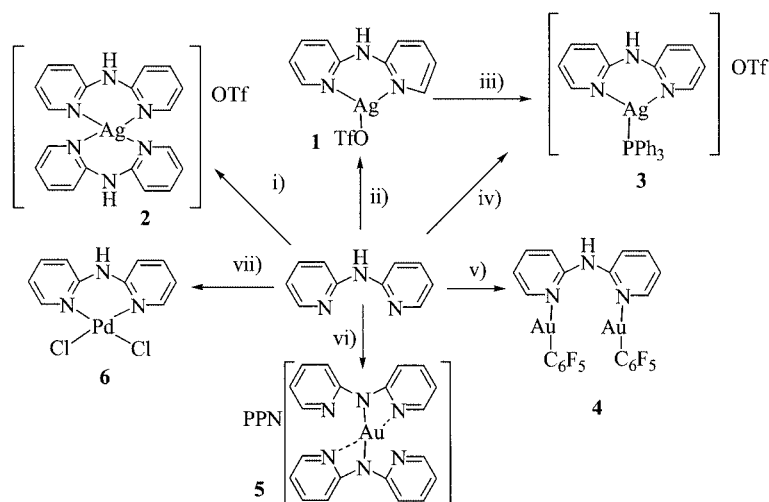
uninvestigated, as far as we know. The silver derivatives may be especially interesting due to the possibility of the formation of supramolecular structures. These structures may be derived from building blocks linked by coordinate covalent^[17] or hydrogen bonds.^[18] Such structures are an active field of research, and many of them are afforded by using *N,N'*-bidentate spacers.^[19] Herein we report the synthesis of some gold and silver complexes with the dpa ligand, and also the palladium derivative [PdCl₂(dpa)]. The structure of compound [Ag(NHPy₂)(PPh₃)]OTf shows weak interactions which produce bands of molecules parallel to the *z* axis. Other hydrogen bonds of the type C–H...O serve to link the ribbons.

Results and Discussion

The reaction of [Py₂NH] with AgOTf in a 1:1 or 2:1 molar ratio affords the three coordinate [Ag(OTf)(Py₂NH)] (1) or four coordinate [Ag(Py₂NH)₂](OTf) (2) species (Scheme 1). Their IR spectra show the vibrations corresponding to N–H deformation and C=N, C=C stretching modes of the pyridine rings at 1586, 1540 cm^{−1} (1) or 1601, 1524 cm^{−1} (2) and the band corresponding to the N–H stretching vibration at 3320 (1) or 3340 (2).^[1c,20,21] Those bands corresponding to covalent (1, 1240 and 1119 cm^{−1}) or anionic (2, 1272 and 1154 cm^{−1}) trifluoromethanesulfonate anion are also present.^[22] The conductivity of compound 1 in acetone solution shows a higher value than expected for a non-electrolyte. This can be explained by taking into account the lability of the trifluoromethanesulfonate anion, which, in solution, is probably highly dissociated. In the ¹H NMR spectra the pyridine protons appear as four signals in the range δ = 7.16–8.20 (1) and 6.88–8.11 ppm (2). In 1, one signal at δ = 11.30 ppm (br. s)

[a] Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

[b] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany



Scheme 1. i) 1/2 AgOTf, ii) AgOTf, iii) PPh₃, iv) [AgOTf(PPh₃)], v) 2 [Au(C₆F₅)(tht)], vi) PPN[Au(acac)₂], vii) [PdCl₂(PhCN)₂]

corresponds to the NH hydrogen atom, whereas in **2** it is overlapped with the resonances of the pyridinic protons. In the LSIMS (+) mass spectra the cationic molecular peaks appear at $m/z = 428$ (6%) for **1** and $m/z = 450$ (9%) for **2**. The displacement of the OTf ligand by PPh₃ in **1**, or the reaction of NHPy₂ with [Ag(OTf)(PPh₃)] in a 1:1 molar ratio, affords the derivative [Ag(NHPy₂)(PPh₃)]OTf (**3**). The characteristic vibrations of the dpa ligand appear in the IR spectrum at 1640, 1581 and 3330 cm⁻¹; those corresponding to the OTf anion appear at 1283 and 1097 cm⁻¹. The ¹H NMR spectrum displays a broad resonance at $\delta = 9.64$ ppm, which corresponds to the NH hydrogen atom. Three signals are observed in the $\delta = 5.5$ –8 ppm region, one of which involves the phenyl group and two the pyridinic protons. A broad signal at $\delta = 14.46$ ppm is observed in the ³¹P{¹H} NMR spectrum at room temperature. When the spectrum is recorded at -50 °C, the signal is split into two doublets, centered at $\delta = 17.6$ ppm, due to the coupling of the phosphorus atom with the two silver isotopomers ($J^{109}_{\text{AgP}} = 773.2$, $J^{107}_{\text{AgP}} = 678.4$ Hz). The LSIMS (+) mass spectrum shows the cationic molecular peak at $m/z = 541$ (53%).

The molecular structure of **3** has been determined by X-ray diffraction studies. The geometry at the silver atom is distorted trigonal (Figure 1, Table 1). The major distortion comes from the restricted bite angle of the bidentate ligand [N11–Ag–N21 82.82(9)°], with concomitantly wide values for the other two angles [N11–Ag–P 139.80(7)°; N21–Ag–P 131.22(7)°]. The Ag–N distances [Ag–N11 2.264(2), Ag–N21 2.283(3) Å] are in the range of those observed in [Au₂Ag₂{ μ -(PPh₂)₂N}(OCIO₃)(PPh₃)₂]^[23] [2.239(4) Å], in which the silver centers show trigonal geometries. Longer distances have been found in other silver complexes in which the silver atom is three-coordinate, such as [Ag{1,2-(C₅H₄NS)₂-1,2-C₂B₁₀H₁₀}(PPh₃)₂][OTf] [2.345(2), 2.350(2) Å].^[24] The Ag–P distance of 2.3414(8) Å is similar to that found in [Ag{1,2-(C₅H₄NS)₂-1,2-C₂B₁₀H₁₀}(PPh₃)₂][OTf] (2.33832(7) Å) or to the shortest

found in [Ag(dppf)(PPh₃)]OTf [dppf = 1,1'-bis(diphenylphosphanyl)ferrocene]^[25] [2.4244–2.4802(12) Å]. The silver center lies 0.30 Å out of the plane formed by the N11, N21 and P atoms, associated with a contact to a triflate oxygen, Ag–O3 2.725(3) Å. This value is somewhat longer than the 2.601(4) Å in [Ag₄{ μ -SC₂B₁₀H₁₀}₂(μ -O₃SCF₃)₂(PPh₃)₄]^[26] but both values can be considered to lie in a typical range for triflate-silver contacts. The same oxygen atom acts as an acceptor for a hydrogen bond from the NH group [N–O 3.021(4), H–O 2.20(2) Å] (Table 2). The overall effect of the two weaker interactions is to produce bands of molecules parallel to the *z* axis (Figure 2). Other “weak” hydrogen bonds of the type C–H...O play a role in the crystal packing; two H...O distances from *para*-H atoms of the phosphane phenyl rings are particularly short (2.31, 2.32 Å), and these H bonds serve to link the ribbons.

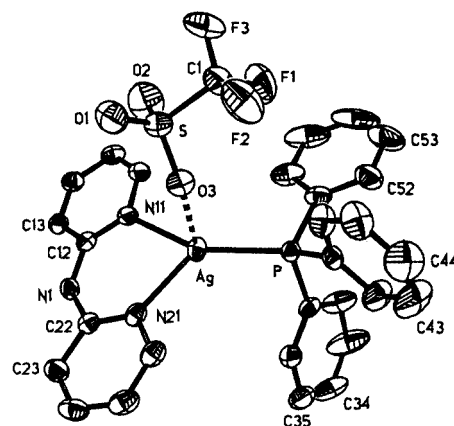


Figure 1. Structure of compound **3**; thermal ellipsoids are drawn with surfaces at the 50% probability level; hydrogens and solvent have been omitted for clarity

Gold(I) complexes have also been obtained by the reaction of Py₂NH with very different starting products (Scheme 1). Thus, the reaction of the ligand with

Table 1. Selected bond lengths [Å] and angles [°] for **3**

| | | | |
|----------------|------------|-------------------|------------|
| Ag–N(11) | 2.264(2) | N(1)–C(22) | 1.377(4) |
| Ag–N(21) | 2.283(3) | N(1)–C(12) | 1.393(4) |
| Ag–P | 2.3414(8) | N(11)–C(12) | 1.335(4) |
| Ag–O(3) | 2.725(3) | N(11)–C(16) | 1.349(4) |
| P–C(51) | 1.811(3) | N(21)–C(22) | 1.333(4) |
| P–C(41) | 1.820(3) | N(21)–C(26) | 1.357(4) |
| P–C(31) | 1.825(3) | | |
| | | | |
| N(11)–Ag–N(21) | 82.82(9) | C(41)–P–Ag | 116.19(10) |
| N(11)–Ag–P | 139.80(7) | C(31)–P–Ag | 110.36(11) |
| N(21)–Ag–P | 131.22(7) | C(22)–N(1)–C(12) | 135.1(3) |
| N(11)–Ag–O(3) | 94.01(8) | C(12)–N(11)–C(16) | 117.2(3) |
| N(21)–Ag–O(3) | 95.48(8) | C(12)–N(11)–Ag | 126.8(2) |
| P–Ag–O(3) | 101.64(6) | C(16)–N(11)–Ag | 113.2(2) |
| C(51)–P–C(41) | 104.46(16) | C(22)–N(21)–C(26) | 117.4(3) |
| C(51)–P–C(31) | 104.61(15) | C(22)–N(21)–Ag | 127.3(2) |
| C(41)–P–C(31) | 104.35(14) | C(26)–N(21)–Ag | 114.8(2) |
| C(51)–P–Ag | 115.66(12) | S–O(3)–Ag | 130.65(1) |

Table 2. Hydrogen bonds [Å and °] for **3**

| D–H...A ^[a] | d(D–H) | d(H...A) | d(D...A) | <(DHA) |
|------------------------|-----------|----------|----------|--------|
| N(1)–H(01)...O(3)#1 | 0.841(18) | 2.20(2) | 3.021(4) | 166(3) |
| C(34)–H(34)...O(1)#2 | 0.95 | 2.32 | 3.262(5) | 169.9 |
| C(54)–H(54)...O(2)#3 | 0.95 | 2.31 | 3.224(5) | 162.1 |
| C(46)–H(46)...O(3) | 0.95 | 2.58 | 3.400(5) | 144.5 |
| C(99)–H(99A)...O(1) | 0.99 | 2.65 | 3.554(8) | 152.5 |
| C(23)–H(23)...O(3)#1 | 0.95 | 2.68 | 3.446(4) | 138.2 |

^[a] Symmetry transformations used to generate equivalent atoms: #1 $x, -y + 1/2, z + 1/2$; #2 $x + 1, y, z + 1$; #3 $-x + 1, -y, -z + 1$.

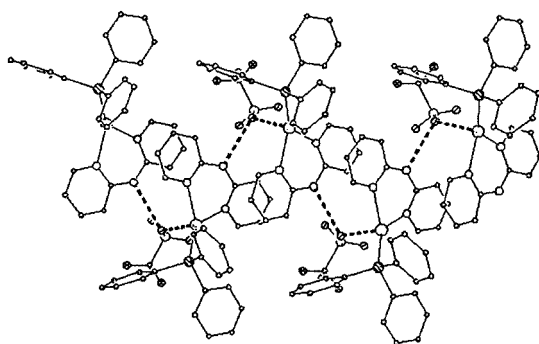


Figure 2. Crystal structure of **3**; hydrogens have been omitted for clarity; secondary interactions Ag...O and N...O are indicated by dashed lines

[Au(C₆F₅)(tbt)] in a 1:2 molar ratio affords the dinuclear complex [Au₂(C₆F₅)₂(μ-Py₂NH)] (**4**). Apart from the characteristic bands of dpa at 1610, 1532 and 3296 cm^{−1}, the IR spectrum of **4** shows the vibrations of the pentafluorophenyl ring bonded to gold(I) at 1507 and 961 cm^{−1}. In the ¹H NMR spectrum, three of the signals come from the pyridinic protons, one of which integrates for double the value of the others. The NH hydrogen atom resonance

appears at δ = 8.57 ppm. The ¹⁹F NMR spectrum shows three signals, which correspond to the *ortho*, *meta* and *para* fluorine atoms. In the LSIMS (+) mass spectrum the molecular peak appears at m/z = 899 (68%).

When the reaction is carried out with PPN[Au(acac)₂] in a 2:1 molar ratio, the ligand is deprotonated and the homoleptic derivative PPN[Au(Py₂N)₂] (**5**) obtained. The IR and ¹H NMR spectra confirm the deprotonation of the coordinated ligands. In the ¹H NMR spectrum, once again, one of the signals belonging to the pyridinic protons is overlapped, in this particular case with the broad signal from the phenyl groups of the PPN cation. The anionic molecular peak at m/z = 537 (35%) is present in the LSIMS(−) mass spectrum. No crystal suitable for X-ray analyses has been obtained. Tentatively we propose three- or four-coordination at gold, involving coordination to the deprotonated nitrogen atoms and one or two of the pyridinic nitrogen atoms (see Scheme 1).

We have also obtained the palladium complex [PdCl₂(Py₂NH)₂] by displacement of the PhCN ligands in [PdCl₂(PhCN)₂] by Py₂NH. In the IR spectrum the characteristic vibrations of dpa appear at 3490, 1634 and 1587 cm^{−1}. Four resonances for the pyridinic hydrogen atoms, and the signal corresponding to the NH proton at δ = 9.50 ppm, appear in the ¹H NMR spectrum. The LSIMS (+) mass spectrum shows the molecular peak at m/z = 348 (11%).

Experimental Section

General Remarks: AgOTf, Py₂NH, PPh₃ and [PdCl₂(PhCN)₂] were purchased from Aldrich and used as received. The starting products [Au(C₆F₅)(tbt)],^[27] PPN[Au(acac)₂]^[28] and [Ag(OTf)(PPh₃)]^[29] were synthesized according to literature methods.

Infrared spectra were recorded in the range 4000–200 cm^{−1} on a Perkin–Elmer FT-IR Spectrum 1000 spectrophotometer as Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5 × 10^{−4} M acetone solutions with a Jenway 4010 conductimeter. C, H, N, S analysis was carried out with a Perkin–Elmer 240C microanalyser. Mass spectra were recorded on a VG Autospec using the LSIMS techniques and nitrobenzyl alcohol as matrix and on a HP59987 A ELECTROSPRAY. ¹H, ¹⁹F and ³¹P NMR spectra were recorded on a Bruker ARX 300 in CDCl₃ solutions. Chemical shifts are quoted relative to SiMe₄ (¹H, external), CFC₃ (¹⁹F, external) and H₃PO₄ (85%) (³¹P, external).

Synthesis of [Ag(OTf)(Py₂NH)] (1**):** Py₂NH (0.1 mmol, 0.017 g) was added to a diethyl ether solution (20 mL) of Ag(OTf) (0.1 mmol, 0.025 g). The solution was stirred for 30 min. Upon concentration to ca. 5 mL compound **1** precipitated as a white solid (31 mg, yield 76%). C₁₁H₉AgF₃N₃O₃S (428.1): calcd. C 30.85, H 2.10, N 9.8, S 7.45; found C 30.85, H 2.10, N 9.8, S 7.60. Λ_M 107 Ω^{−1}cm²mol^{−1}. ¹H NMR: δ = 7.16 (dd, $J_{H,H}$ = 6.53, 6.51 Hz, 2H-Py), 7.52 (d, $J_{H,H}$ = 8.74 Hz, 2H-Py), 7.90 (dd, $J_{H,H}$ = 7.94, 7.20 Hz, 2H-Py), 8.20 (br. m, 2H-Py), 11.30 (br. s, 1H-NH) ppm.

Synthesis of [Ag(Py₂NH)₂]OTf (2**):** Py₂NH (0.2 mmol, 0.034 g) was added to a diethyl ether solution (20 mL) of Ag(OTf) (0.1 mmol, 0.025 g). The solution was stirred for 30 min. Upon concentration to ca. 5 mL compound **2** precipitated as a white solid (45 mg, yield

76%). $C_{21}H_{18}AgF_3N_6O_3S$ (599.3): calcd. C 42.05, H 3.0, N 14.0, S 5.35; found C 41.65, H 2.7, N 14.1, S 5.15. Λ_M 119 $\Omega^{-1}cm^2mol^{-1}$. 1H NMR: δ = 6.88 (br. m, 4H-Py), 7.3 (br. m, 4H-Py), 7.64 (br. m, 4H-Py), 8.11 (br. m, 4H-Py) ppm.

Synthesis of $[Ag(Py_2NH)(PPh_3)]\cdot OTf$ (3). **Method (a):** Py_2NH (0.1 mmol, 0.017 g) was added to a dichloromethane solution (20 mL) of $[Ag(OTf)(PPh_3)]$ (0.1 mmol, 0.052 g). After stirring for 30 min, the solution was concentrated to ca. 5 mL. Addition of diethyl ether afforded **3** as a white solid. **Method (b):** PPh_3 (0.1 mmol, 0.026 g) was added to a dichloromethane solution (20 mL) of $[Ag(OTf)(Py_2NH)]$ (0.1 mmol, 0.043 g). After stirring for 30 min, the solution was concentrated to ca. 5 mL. Addition of diethyl ether afforded **3** as a white solid (64 mg, yield 94%). $C_{29}H_{24}AgF_3N_3O_3PS$ (690.4): calcd. C 50.45, H 3.5, N 6.0, S 4.65; found C 50.2, H 3.2, N 6.25, S 4.7. Λ_M 102 $\Omega^{-1}cm^2mol^{-1}$. 1H NMR: δ = 6.82 (br. m, 2H-Py), 7.38–7.54 (br. m, 2H-Py + 15H-Ph), 7.63 (br. m, 2H-Py), 7.93 (br. m, 2H-Py), 9.64 (br. s, 1H-NH) ppm.

Synthesis of $[Au_2(C_6F_5)_2(\mu-Py_2NH)]$ (4): Py_2NH (0.1 mmol, 0.017 g) was added to a solution of $[Au(C_6F_5)(tht)]$ (0.2 mmol, 0.091 g) in dichloromethane (20 mL). The solution was stirred for 30 min. Concentration to ca. 5 mL and addition of diethyl ether afforded **4** as a white solid (59 mg, yield 66%). $C_{22}H_9Au_2F_{10}N_3$ (899.2): calcd. C 29.35, H 1.0, N 4.65; found C 29.4, H 1.45, N 5.15. Λ_M 22 $\Omega^{-1}cm^2mol^{-1}$. 1H NMR: δ = 7.0 (br. m, 2H-Py), 7.77 (br. m, 4H-Py), 8.29 (br. m, 2H-Py), 8.57 (br. s, 1H-NH) ppm. ^{19}F NMR: δ = -117 (m, 4F, *o*-F), -159.3 (t, 2F, *p*-F, $^3J(FF)$ 19.64 Hz), -163.1 (m, 4F, *m*-F) ppm.

Synthesis of $PPN[Au(Py_2N)_2]$ (5): Py_2NH (0.1 mmol, 0.017 g) was added to a solution of $PPN[Au(acac)_2]$ (0.05 mmol, 0.047 g) in dichloromethane (20 mL). The solution was stirred for 30 min and then concentrated to ca. 5 mL. Addition of hexane afforded **5** as a white solid (33 mg, yield 31%). $C_{56}H_{46}AuN_7P_2$ (1075.9): calcd. C 62.5, H 4.3, N 9.1; found C 62.7, H 4.1, N 9.45. Λ_M 73 $\Omega^{-1}cm^2mol^{-1}$. 1H NMR: δ = 6.84 (br. m, 2H-Py), 7.41–7.6 (br. m, 2H-Py + 30H-Ph), 7.67 (br. m, 2H-Py), 8.26 (br. m, 2H-Py) ppm.

Synthesis of $[PdCl_2(Py_2NH)]$ (6): Py_2NH (0.1 mmol, 0.017 g) was added to a solution of $[PdCl_2(PhCN)_2]$ (0.1 mmol, 0.035 g) in dichloromethane (20 mL). The solution was stirred for 30 min and then concentrated to ca. 5 mL. Addition of diethyl ether afforded **6** as a yellow-orange solid (49 mg, yield 95%). $C_{10}H_9Cl_2N_3Pd$ (348.5): calcd. C 34.45, H 2.6, N 12.05; found C 34.15, H 2.65, N 11.80. 1H NMR: δ = 6.92 (br. m, 2H-Py), 7.33 (br. m, 2H-Py), 7.62 (br. m, 2H-Py), 8.65 (br. m, 2H-Py), 9.50 (br. m, 1H-NH) ppm.

X-ray Crystallographic Study of Compound $3\cdot CH_2Cl_2$: Colorless prism; $0.23 \times 0.11 \times 0.09$ mm. Crystal data: $C_{30}H_{26}AgCl_2F_3N_3O_3PS$, $M = 775.34$, monoclinic, space group $P2_1/c$, $a = 12.0173(14)$, $b = 28.699(3)$, $c = 9.6308(9)$ Å, $\beta = 102.311(3)^\circ$, $V = 3245.1(6)$ Å³, $T = -130$ °C, $Z = 4$, $\mu = 0.953$ mm⁻¹, 32407 reflections (Bruker SMART 1000-CCD, Mo- K_α radiation, $2\theta_{max}$ 56.6°, ω - and ϕ -scans), 7985 unique. The program SADABS, based on multiple scans, was used for the absorption correction (transmission max., min.: 0.928, 0.732). Solution by direct methods. Refinement on F^2 ; program system SHELXL-97³⁰. Hydrogen atoms riding except for the aminic hydrogen, which was refined freely with an N–H distance restraint. Final $R1 = 0.0428$, $wR2 = 0.1060$, for 401 parameters; $S(F^2)$ 0.930; max. $\Delta\rho$ 0.792 e·Å⁻³.

CCDC-199151 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge

CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the Dirección General de Investigación (D.G.I) (n° BQU2001-2409-C02-01), the Fonds der Chemischen Industrie, and the Caja de Ahorros de la Inmaculada for financial support.

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Received December 5, 2002