Intramolecular Interactions Leading to Quasicubane Cages. Crystal Structure of $[Mo_2(NO)_2(CO)_4\{\mu\text{-}\kappa^2;\kappa^1\text{-}S_2C(H)PCy_3\}_2]$

Daniel Miguel,*[†,‡] Víctor Riera,[†] Mei Wang,[†,§] Claudette Bois,[||] and Sabine Halut[||]

Departamento de Química Orgánica e Inorgánica/
IUQOEM-Unidad Asociada del CSIC,
Universidad de Oviedo, E-33071 Oviedo, Spain, and
Laboratoire de Chimie des Métaux de Transition,
UA-CNRS 419, Université Pierre et Marie Curie,
4 Place Jussieu, 75252 Paris Cedex 05, France

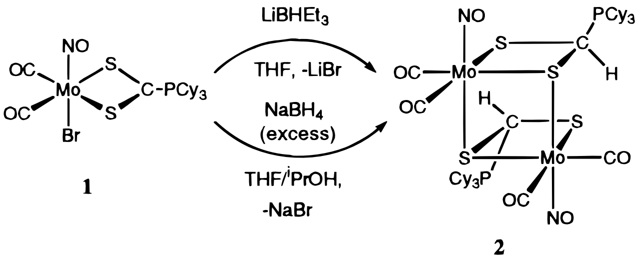
Received October 28, 1997

Introduction

Hydrogen interactions are of primary importance in the fields of molecular recognition and the self-assembly of molecules to form extended supramolecular structures.[1] Although difficult to quantify, the existence of this type of interaction is evidenced in an increasing number of molecular systems, from complex biological molecules such as proteins, to much simpler species such as the well-known inorganic and organic compounds containing hydroxyl groups. This type of interaction seemed to be present only with very electronegative atoms, such as F, O, or N. However, some examples have appeared in which hydrogen interacts with less electronegative atoms, like S, resulting in a supramolecular arrangement in the solid state.[2] As a continuation of our previous studies on the reactivity of transition metal carbonyl complexes containing S_2CPR_3 ligands,[3] we present here the structure of $[Mo_2(NO)_2(CO)_4\{\mu\text{-}\kappa^2;\kappa^1\text{-}S_2C(H)PCy_3\}_2]$, in which the adoption of an open cubane structure can be attributed to the existence of C−H···S interactions.

Zwitterionic trialkylphosphonium dithioformate ligands, S_2CPR_3, display a versatile coordinative behavior toward transition metals, being able to act variably as 2e-κ^1(S), 4e-κ^2(S,S′), and 4e-κ^3(S,C,S′) ligands in mononuclear complexes or as 4e-κ^1(S);κ^1(S′), 4e-κ^1(S);κ^2(S′,C), 6e-κ^1(S);κ^3(S,C,S′), and 8e-κ^2(S,S′);κ^3(S,C,S′) bridging ligands in binuclear complexes.[4] The chemical reactivity of the coordinated S_2CPR_3 ligands depends on the coordination mode. For instance, chelated S_2CPR_3 ligands are susceptible to attack at the central carbon both by nucleophiles, such as H^-, Me^-, and Ph^-,[5−9] and by electrophiles, such as H^+ and Me^+.[10−12]

Scheme 1



The hydride addition to the carbon atom of the κ^2-coordinated S_2CPR_3 ligand in the recently obtained nitrosyl molybdenum complex, $[MoBr(NO)(CO)_2(\kappa^2\text{-}S_2CPCy_3)]$ (**1**),[13] leads to the isolation of the dinuclear complex, $[Mo_2(NO)_2(CO)_4\{\mu\text{-}S_2C(H)PCy_3\}_2]$ (**2**), which, according to X-ray determination, contains two $S_2C(H)PCy_3^-$ ligands acting as 5e-κ^1(S);κ^2(S,S′) bridges. This type of five-electron coordination mode of the phosphoniomethanedithiolate ligand is very scarce, being confined to a few examples of Rh, Mn, and Re. To our knowledge, only two other complexes of this type have been structurally characterized: $[Rh(TeB_{10}H_{10})\{\mu\text{-}S_2C(H)PPh_3\}]_2$[14] and $[Mn_2(CO)_6\{\mu\text{-}S_2C(H)PCy_3\}_2]$.[3]

Results and Discussion

The reaction of the nitrosyl molybdenum complex, $[MoBr(NO)(CO)_2(\kappa^2\text{-}S_2CPCy_3)]$ (**1**),[13] with an equimolar amount of $LiBHEt_3$ in THF, or with an excess of $NaBH_4$ in a mixture of THF and 2-propanol, gave a novel dinuclear complex, $[Mo_2(NO)_2(CO)_4\{\mu\text{-}S_2C(H)PCy_3\}_2]$ (**2**), as orange, air-stable crystals in moderate yields (Scheme 1). In pure THF, the reaction of **1** with $NaBH_4$ went very slowly (more than 2 days at room temperature), due probably to the low solubility of the reactants in THF. When the reaction of **1** with $NaBH_4$ was carried out in THF/methanol, a mixture of three products was obtained, from which complex **2** could be separated in low yield by chromatography.

The other two products were obtained together as a yellow-orange crystalline mixture which resisted our attempt of separation. The IR and NMR data suggest that these complexes are isomers, each containing two methoxide groups. Thus, two singlets attributable to OCH_3 are found for each complex in the ^1H NMR spectrum ($CDCl_3$): δ 4.09 and 3.84; and 4.23 and 3.83 ppm. Surprisingly, they were not obtained in the reaction

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* Corresponding author. E-mail: dmsj@sauron.quimica.uniovi.es.

[†] Universidad de Oviedo.

[‡] Present address: Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain.

[§] Present address: Department of Chemistry, Dalian University of Technology, China.

[||] Université Pierre et Marie Curie.

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10.1021/ic9713590 CCC: $15.00

of **1** with $NaBH_4$ in pure methanol. The structures of these complexes are still not clear and need some further studies. In contrast, the reaction of the related allyl molybdenum complex, $[MoBr(CO)_2(\eta^3\text{-}C_3H_5)(\kappa^2\text{-}S_2CPCy_3)]$, with hydride reagents, $LiBHEt_3$ or $NaBH_4$, gave only decomposition products. Presumably, the hydride ion may attack to the allyl ligand instead of the central carbon atom of the S_2CPR_3 ligand, leading to loss of the allyl ligand and resulting in decomposition of the remaining fragment.

The nitrosyl dinuclear complex **2** has been characterized by IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy and elemental analysis (see Experimental Section). The IR spectrum of **2**, in THF, displays four ν(CO) bands at 2006 m, 1993 s, 1925 s, and 1904 s cm^{-1} and one ν(NO) band at 1627 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet for phosphorus of the $S_2C(H)PCy_3^-$ ligand at δ 29.1 ppm (in $CDCl_3$). In addition to the signals for cyclohexyl groups, the ^1H NMR spectrum of **2** shows the signal of the hydrogen atom of the $S_2C(H)PCy_3^-$ ligand at δ 8.98 ppm with a small coupling constant [$^2J(P-H) = 2$ Hz]. This resonance region seems to be characteristic for the hydrogen atom of the $S_2C(H)PR_3^-$ ligands coordinated as bridges in dimer complexes. The corresponding signals reported for the only other complexes containing phosphoniomethanedithiolato bridges, appear in the range δ 9.2−10.5 ppm for $[Rh(EB_{10}H_{10})\{\mu\text{-}S_2C(H)PPh_3\}]_2$ (E = Se, Te)[14] and $[M_2(CO)_6\{\mu\text{-}S_2C(H)PR_3\}_2]$ (M = Mn, Re; R = Cy, ^{i}Pr).[3] In contrast, the signals for the hydrogen atoms of the $S_2C(H)PR_3^-$ ligands acting as chelates in mononuclear complexes appear in the range of δ 5.2−6.3 ppm.[5,6,10,11,15,16] In our previous study of the crystal structure of $[Mn_2(CO)_6\{\mu\text{-}S_2C(H)PCy_3\}_2]$,[3] we found that the hydrogen atoms of the bridged $S_2C(H)PCy_3^-$ ligands situated within short distances from the sulfur atoms of the opposite chelate ring and it was proposed that such interactions could be responsible for the considerable shifts of the signals of the hydrogens in the ^1H NMR spectra. The same interaction, which results in the downfield shift of the resonance for the central hydrogen atoms, may exist in the dimolybdenum complex **2**, thus suggesting that **2** has a cisoid structure, similar to that found for the dimer $[Mn_2(CO)_6\{\mu\text{-}S_2C(H)PCy_3\}_2]$.[3] In the $^{13}C\{^1H\}$ NMR spectrum of **2**, the signal assigned to the central carbon atoms of the $S_2C(H)PCy_3^-$ ligands appears at δ 50.2 [d, $^1J(P-C) = 28$ Hz], which shifts downfield by ca. 13−15 ppm from those for the dimers $[M_2(CO)_6\{\mu\text{-}S_2C(H)PCy_3\}_2]$ (M = Mn, Re).[3] Only two signals are found in the carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum, suggesting that the four carbonyls appear in two sets: two in the equatorial C(2) and C(4), and two in the axial C(1) and C(3) positions, with respect to the Mo_2S_2 ring.

All analytical and spectroscopic data of **2** support the dimeric structure proposed in Scheme 1. To know the structure in detail, an X-ray crystal determination was carried out for **2**. A perspective view of **2** is shown in Figure 1. Relevant crystallographic data are given in Table 1, and selected interatomic distances and angles are in Table 2.

The structure of **2** consists of two equal fragments, "$Mo(NO)(CO)_2\{\kappa^2\text{-}S_2C(H)PCy_3\}$", which are held together by two sulfur bridges, each $S_2C(H)PCy_3^-$ ligand contributing one sulfur, to form a distorted square core of $[Mo_2S_2]$. As in the structure of the dimanganese compound mentioned above,[3] the Mo_2S_2 ring in **2** is not planar, being folded by 32.89 (5)° with respect to the Mo(1)···Mo(2) line.

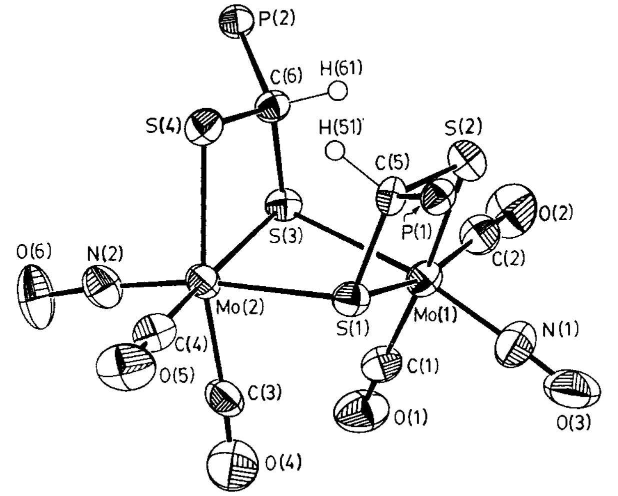

Figure 1. Perspective view (CAMERON)[23] of **2**, showing the atom numbering. Cyclohexyl rings of the phosphine groups have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table 1. Relevant Crystal Data and Refinement Details for $[Mo_2(NO)_2(CO)_4\{\mu\text{-}\eta^2;\eta^1\text{-}S_2C(H)PCy_3\}_2]$(**2**)

empirical formula	$C_{42}H_{68}Mo_2N_2O_6P_2S_4$
fw	1079.08
cryst syst	monoclinic
space group	$P2_1/c$, No. 14
a, Å	16.170(5)
b, Å	12.878(3)
c, Å	23.391(6)
β, deg	90.95(2)
V, Å^3	4870(4)
Z	4
T, °C	21
ρ_{calcd}, g cm^{-3}	1.47
λ (Mo Kα), Å	0.710 69
μ, cm^{-1}	7.76
residuals R, R$_w$[a]	0.037, 0.045

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = \{\Sigma(w(|F_o| - |F_c|)^2)/\Sigma w|F_o|^2\}^{1/2}$.

The long intermetallic distance of 3.378(1) Å, shows that no direct Mo−Mo bond exists in the dimer **2**. The two $S_2C(H)PCy_3^-$ ligands in **2** are coordinated as κ^2(S,S′) chelate of 3e toward one molybdenum atom and as κ^1(S) monodentate of 2e toward the other. The Mo−S distances are in the range 2.522(2)−2.634(2) Å, similar to those found in complexes containing $\kappa^2(S,S')\text{-}S_2CPR_3$ chelates: *i.e.* 2.488(2) and 2.531(2) Å for $[Mo(CO)_2\{S_2P(OEt)_2\}(S_2CPCy_3)(SnPhCl_2)]$.[17] In contrast, the distances C−S, ranging from 1.833(6) to 1.839(6) Å in **2**, are significantly longer than those of the S_2CPR_3 ligand in the mononuclear molybdenum compound, 1.669(7) and 1.684(7) Å.[17]

As it can be seen in Scheme 2, the two chelate MoS_2C rings in **2** present a cisoid disposition with respect to the central Mo_2S_2 square, the same arrangement found in the two reported structures of complexes containing $S_2C(H)PR_3^-$ bridges, $[Rh(TeB_{10}H_{10})\{\mu\text{-}S_2C(H)PPh_3\}]_2$[14] and $[Mn_2(CO)_6\{\mu\text{-}S_2C(H)PCy_3\}_2]$.[3]

As a result of the cisoid disposition of the two $S_2C(H)PCy_3^-$ ligands, the central part of the molecule can be described as a quasicubane cage formed by two Mo, four S, and two C. As it can be expected from the different sizes of the atoms situated at the corners, the resulting cube is severely distorted: the two

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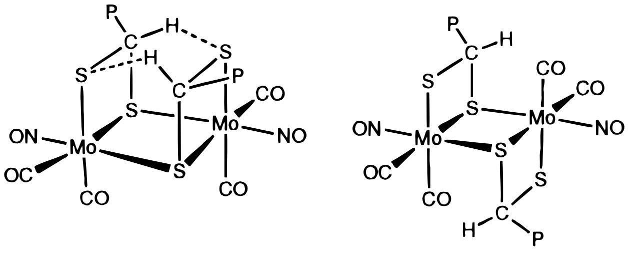
Table 2. Selected Interatomic Distances (Å) and Angles (deg) in $[Mo_2(NO)_2(CO)_4\{\mu\text{-}\eta^2;\eta^1\text{-}S_2C(H)PCy_3\}_2]$ (**2**)

Mo(1)−S(1)	2.585(2)	Mo(1)−S(2)	2.522(2)
Mo(1)−S(3)	2.634(2)	Mo(1)−N(1)	1.844(6)
Mo(1)−C(1)	1.955(7)	Mo(1)−C(2)	1.982(7)
Mo(2)−S(1)	2.619(2)	Mo(2)−S(3)	2.544(2)
Mo(2)−S(4)	2.537(2)	Mo(2)−N(2)	1.805(6)
Mo(2)−C(3)	1.994(7)	Mo(2)−C(4)	2.008(7)
S(1)−C(5)	1.835(6)	S(2)−C(5)	1.833(6)
S(3)−C(6)	1.839(6)	S(4)−C(6)	1.839(6)
P(1)−C(5)	1.821(6)	P(2)−C(6)	1.819(6)
C(5)−H(51)	1.06	C(6)−H61	0.95
S(2)···H(61)	2.676(6)	S(4)···H(51)	2.465(6)
S(1)−Mo(1)−S(2)	71.65(5)	S(1)−Mo(1)−S(3)	82.88(5)
S(2)−Mo(1)−S(3)	92.30(5)	S(3)−Mo(1)−N(1)	171.6(2)
S(2)−Mo(1)−C(1)	174.8(2)	S(1)−Mo(1)−C(2)	166.3(2)
S(1)−Mo(2)−S(3)	83.99(5)	S(1)−Mo(2)−S(4)	90.75(5)
S(3)−Mo(2)−S(4)	71.52(5)	S(1)−Mo(2)−N(2)	171.1(2)
S(4)−Mo(2)−C(3)	168.6(2)	S(3)−Mo(2)−C(4)	170.2(2)
Mo(1)−S(1)−Mo(2)	91.86(5)	Mo(1)−S(1)−C(5)	88.0(2)
Mo(2)−S(1)−C(5)	109.6(2)	Mo(1)−S(3)−Mo(2)	92.41(5)
Mo(1)−S(3)−C(6)	110.5(2)	Mo(2)−S(3)−C(6)	90.1(2)
Mo(1)−N(1)−O(3)	176.9(6)	Mo(2)−N(2)−O(6)	174.6(5)
S(1)−C(5)−S(2)	109.2(3)	S(1)−C(5)−P(1)	113.0(3)
S(2)−C(5)−P(1)	110.3(3)	S(3)−C(6)−S(4)	107.7(3)
S(3)−C(6)−P(2)	110.9(3)	S(4)−C(6)−P(2)	114.3(3)

Scheme 2



cisoid

transoid

Mo−S−C−S chelate rings, which form two opposite faces of the distorted cubane, are not parallel, forming instead an angle of 26.92(5)°, this being the most important deviation for the ideal cubic geometry. The hydrogen atoms bonded to the central carbon of the ligands are positioned midway and above the two open edges of the distorted cube. As it can be seen in Scheme 2, there are short contacts between the H atoms and the opposite sulfur atoms: H(51)···S(4), 2.465(6) Å, and H(61)···S(2), 2.676(6) Å, which compare well to those found in the solid state arrangement of $(SPMe_2)_2NH$, 2.513(5) Å;[2a] $(SPMe_2)(SPPh_2)NH$, 2.43(9) Å;[2b] and $(SPPh_2)_2NH$, 2.638(25) Å.[2c] In some sense, these S···H interactions help to close the cubane cage, thus conferring additional stability to the dimer, and this leads to the formation of the cisoid instead of the transoid structure.

All previously reported reactions of nucleophilic attack by hydride ions to the central carbon atoms of the chelated S_2CPR_3 ligands in mononuclear complexes can be divided into two types: displacement of the phosphine group on the central carbon by hydride ion,[18,19] or addition of hydride ion to the central carbon of the S_2CPR_3 ligand with retention of phosphine group.[5,9] The obtained products, either with S_2CH^- or $S_2C(H)PR_3^-$ ligand, are usually mononuclear complexes. However, dimerization occurs spontaneously in the reaction of $[MoBr(NO)(CO)_2(\kappa^2\text{-}S_2CPCy_3)]$ with hydride reagents (see Scheme 1). No signal attributable to a mononuclear intermediate can be observed by IR monitoring, which suggests that the dimerization is a fast step in the reaction. The only examples previously known for this type of dimerization, concurring with hydride addition to the central carbon of the chelated S_2CPR_3 ligand, are the reactions of $[M(CO)_3X(\kappa^2\text{-}S_2CPCy_3)]^{n+}$ (M = Mn, Re; X = $OClO_3$, $n = 0$; X = PPh_3, CO, $n = 1$) with $NaBH_4$.[3] On the other hand, the $S_2C(H)PR_3^-$ ligands on the above-mentioned Rh complex are produced by addition of PR_3 to a chelating dithioformate S_2CH^-, which is analogously followed by spontaneous dimerization.[14]

It is interesting to notice that in related dinuclear complexes containing bridging thiocarbamate, dithiocarbamate, or dithiophosphinate ligands, both types of geometry, cisoid and transoid (see Scheme 2) have been observed, and the factors that could favor either of these two steric isomers are still a matter of discussion and investigation.[20] Remarkably, all examples reported so far, of dimers with $S_2C(H)PR_3^-$ bridges, adopt a cisoid geometry, displaying the same type of intramolecular C−H···S interactions, which have been confirmed by structure determinations and, indirectly, by ^1H NMR spectroscopy. There is therefore a strong suggestion that these S···H interactions could be the determinant factor in the formation of the quasicubane cage.

Experimental Section

General Procedures. Reactions and manipulations were carried out under nitrogen atmosphere by using Schlenk techniques. Solvents were freshly distilled under nitrogen with standard methods before use. $NaBH_4$, $LiBHEt_3$, and other reagents were purchased and used without further purification. The starting complex $[MoBr(NO)(CO)_2(\kappa^2\text{-}S_2CPCy_3)]$ (**1**) was prepared from $Mo(CO)_6$, $NOBF_4$, and S_2CPCy_3 in three steps.[3] Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker AC-300 instrument. The ^1H and ^{13}C spectra are referenced to internal TMS and the ^{31}P spectra to external 85% H_3PO_4. Elemental analysis was performed on a Perkin-Elmer 240B microanalyzer.

Preparation of $[Mo_2(NO)_2(CO)_4\{\mu\text{-}S_2C(H)PCy_3\}_2]$ (2). Method A: To a suspension of $[MoBr(NO)(CO)_2(\kappa^2\text{-}S_2CPCy_3)]$ (**1**) (310 mg, 0.5 mmol) in THF (20 mL) was added a solution of $LiBHEt_3$ (0.5 mL, 0.5 mmol, 1 M in THF). The mixture was stirred for 4 h at room temperature. After the solvent was evaporated in vacuo, the residue was redissolved in CH_2Cl_2 (10 mL) and chromatographed on alumina with a minimum amount of methylene chloride as eluent. The collected orange solution was concentrated in vacuo to ca. 5 mL, and then 10 mL of hexane was added. Slow diffusion for 1 day at room temperature afforded prismatic orange crystals of **2**. Yield: 150 mg, 56%. Anal. Calcd for $C_{42}H_{68}N_2O_6S_4P_2Mo_2$: C, 46.75; H, 6.35; N, 2.60. Found: C, 46.79; H, 6.41; N, 2.47%.

Method B: A mixture of **1** (310 mg, 0.5 mmol) and $NaBH_4$ (38 mg, 1 mmol) in THF/2-propanol (1:1) was stirred for 2 h at room temperature. The workup was as described above to obtain **2** as orange crystals. Yield: 180 mg, 67%. Anal. Calcd for $C_{42}H_{68}N_2O_6S_4P_2Mo_2$: C, 46.75; H, 6.35; N, 2.60. Found: C, 46.44; H, 6.36; N, 2.80.

Spectroscopic Data for 2. IR(THF): ν(CO) 2006 m, 1993 s, 1925 s, 1904 s; ν(NO) 1627 s cm^{-1}. ^1H NMR($CDCl_3$): δ 8.98 [d, $^2J(P-H) = 2$ Hz, 2H, $S_2C(H)PCy_3$], 2.80 [m, 6H, C*H* of Cy], 2.18−1.37 [m, 60H, CH_2 of Cy]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.1 s. $^{13}C\{^1H\}$ NMR

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(CDCl$_3$): δ 223.0 [s, 2*C*O], 219.5 [s, 2*C*O], 50.2 [d, ^1J(P−C) = 28 Hz, S*C*(H)PCy$_3$], 30.7 [d, ^1J(P−C) = 39 Hz, C^1 of Cy], 27.8−27.1 [m, C^2, C^3, C^5, and C^6 of Cy], 25.7 [s, C^4 of Cy].

X-ray Difraction Study of [Mo$_2$(NO)$_2$(CO)$_4${μ-S$_2$C(H)PCy$_3$}$_2$] (2). Relevant crystallographic details are given in Table 1. Unit cell parameters were determined from the least squares refinement of a set of 25 centered reflections in the range $14 \leq \theta \leq 16°$. Three reflections were measured every 2 h as orientation and intensity control. Significant decay was not observed. Corrections were made for Lorentz and polarization effects. Extinction correction was applied. Computations were performed with CRYSTALS.[21] The structure was solved by direct methods with SHELX86[22] and subsequent Fourier maps. All non-hydrogen atoms were refined anisotropically. H(51) and H(61), involved in S···H interactions, were found on difference maps and refined as riding atoms attached to C(5) and C(6), respectively. The remaining hydrogen atoms were geometrically positioned, and they were given an overall isotropic thermal parameter. Drawing in Figure 1 was made with CAMERON.[23]

Acknowledgment. We are grateful to the Spanish Ministerio de Educación for financial support (DGICYT PB94-1332), and for the award of a grant to M.W. The authors thank Dr. Julio A. Pérez-Martínez for many helpful discussions.

Supporting Information Available: X-ray crystallographic file, in CIF format, for the structure determination of **2** is available on the Internet only. Access information is given on any current masthead page.

IC9713590

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