The First Cyclometallated (1-Ferrocenylethanone thiosemicarbazone)palladium(II) Compounds − Crystal and Molecular Structure of [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)NHMe}(PPh_3)]

José M. Vila,*[a] Eduardo Gayoso,[a] M. Teresa Pereira,[a] Juan M. Ortigueira,[a] Gemma Alberdi,[a] Marta Mariño,[a] Reyes Alvarez,[a] and Alberto Fernández[b]

Keywords: C−H activation / Ferrocene / Thiosemicarbazone / Palladium / X-ray diffraction

Treatment of the 1-ferrocenylethanone thiosemicarbazone ligands (η^5-C_5H_5)Fe(η^5-C_5H_4)C(Me)=NN(H)C(=S)NHR [R = H (**a**), Me (**b**)] with $K_2[PdCl_4]$ gave the novel heterometallic octanuclear palladium(II) compounds [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)NHR}]$_4$ [R = H (**1a**), Me (**1b**)] as tetramers, after deprotonation of the NH group, with the ligands acting as terdentate donors through the [C,N,S] atoms. Treatment with nucleophiles cleaves the tetrameric clusters giving compounds in which splitting only of the Pd–$S_{bridging}$ bonds has occurred. The strength of the Pd–$S_{chelating}$ bond hinders its cleavage. Thus, treatment of **1a** or **1b** with $Ph_2P(CH_2)_nPPh_2$ [n = 2 (dppe), 3 (dppp), 4 (dppb)] in a 1:2 molar ratio gave the tetranuclear species **2a**–**4a** and **2b**–**4b**, respectively, and treatment with PPh_2R gave the dinuclear compounds **5a**–**7a** and **5b**–**6b** [R = Ph (**5a**, **5b**), Et (**6a**, **6b**), Me (**7a**)]. The complexes described are the first fully characterized cyclometallated palladium(II) complexes with 1-ferrocenylethanone thiosemicarbazone ligands. The crystal and molecular structure of compound **5b** have been determined by X-ray crystallography.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

The synthesis, isolation and characterization of ferrocene[1] marked an important milestone in the evolution of modern organometallic chemistry. One of the developments in this area over the last two decades has been the cyclometallation of ferrocene derivatives. The cyclometallation reaction has been widely investigated in view of the growing chemistry[2] and the novel and outstanding applications which the resultant compounds present. To name but a few examples: the synthesis of new organometallic and organic compounds, many of which can be obtained by insertion reactions of unsaturated species to the metal−carbon bond,[3] the design of complexes with specific antitumor activity towards some forms of cancer[4] or their promising properties as liquid crystals,[5] and their use in the isolation of enantiomerically pure chiral compounds[6] or as efficient catalytic materials.[7]

In the past years, great efforts have been made in order to achieve the isolation and characterization of palladacycles derived from [C,N,X] terdentate ligands (C = phenyl C; X = N,[8] P,[9] O,[10] S[11]), mainly due to the potential hemilability of the Pd−X bond in these systems, which plays an important role in homogeneous catalysis.[12] The reported examples of those complexes containing terdentate [$C_{ferrocene}$,N,X] ligands are scarce, and only compounds with X = N have been described.[13] In some instances potentially terdentate [C,N,N] ferrocenyl ligands do not undergo cyclometallation reactions and only complexes with *N*,*N*-coordination could be isolated.[14] More recently, insertion of alkynes into the $C_{ferrocene}$−Pd bond has given new insights into the chemistry of cyclometallated ferrocene compounds such as the influence of the binding mode of the ferrocenyl ligand.[15]

As a continuation of our studies related to cyclometallated compounds with terdentate [C,N,S] ligands, we have extended our work in this area aimed at incorporating the −C(Me)=NN(H)C(=S)NHR system into the ferrocene ring, to give (η^5-C_5H_5)Fe(η^5-C_5H_4)C(Me)=NN(H)C(=S)NHR (R = H, Me), with the purpose of producing the hitherto unknown cyclometallated 1-ferrocenylethanone thiosemicarbazone complexes by treatment with an appropriate palladium(II) salt. These compounds turned out to be octanuclear species, and we wished to further explore their reactivity with tertiary mono- and diphosphane ligands which affords the corresponding dinuclear and tetranuclear complexes, respectively. Our report includes a description of the first known crystal structure of this kind of compounds.

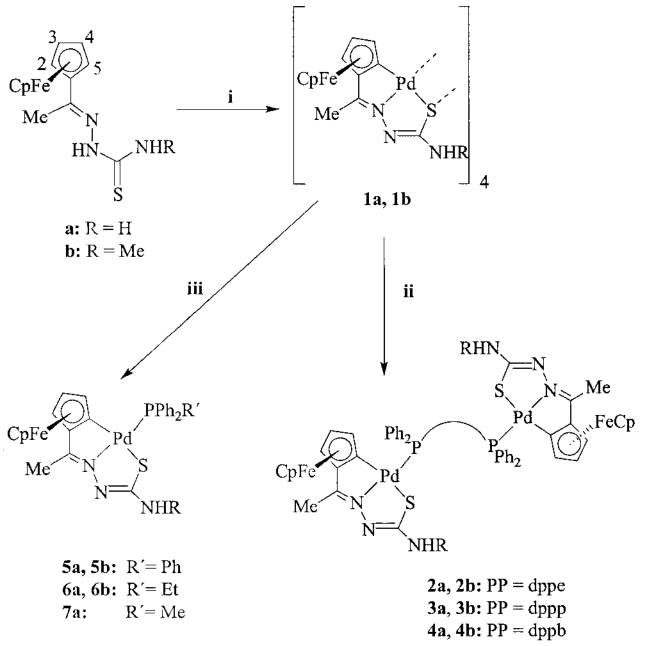
---

[a] Departamento de Química Inorgánica, Universidad de Santiago de Compostela,
15782 Santiago de Compostela, Spain
Fax: (internat.) + 34-981-595012
E-mail: qideport@usc.es
[b] Departamento de Química Fundamental, Universidad de A Coruña,
15071 A Coruña, Spain

DOI: 10.1002/ejic.200300709 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Results and Discussion

For convenience, the compounds and reactions are shown in Scheme 1. The compounds described in this paper were characterized by elemental analyses (C, H, N, S), mass spectrometry (in part), IR spectroscopy, and ^{1}H and ^{31}P{^{1}H} NMR spectroscopy (data in the Exp. Sect.).



Scheme 1. i) K_2PdCl_4, ethanol/water; ii) $Ph_2P(CH_2)_nPPh_2$ (n = 2, 3, 4), 1:2 ratio, acetone; iii) PPh_2R' (R′ = Me, Et, Ph), 1:4 ratio, acetone

The 1-ferrocenylethanone thiosemicarbazones[16] **a** and **b** were prepared by treatment of thiosemicarbazide or 4-methylthiosemicarbazide, respectively, with acetylferrocene in water in the presence of a few drops of hydrochloric acid, and obtained as air-stable solids, which were fully characterized (see Exp. Sect.). In particular, the IR spectra showed the typical ν(C=N) and ν(C=S) stretches,[17] and the ^{1}H NMR spectra revealed the NH resonances at δ = 7.38 (**a**) and 6.20 (**b**) ppm.

Cyclopalladated compounds derived from ferrocenyl ligands may be prepared by cyclomercuration and ulterior transmetallation reactions or by direct treatment with a palladium salt. The additional presence of a base such as NaOAc may be necessary.[13f] In the latter case, M_2PdCl_4 (M = Li, Na, K) proved to be a convenient reagent, as well as in the synthesis of cyclopalladated compounds derived from thiosemicarbazone ligands. Thus, treatment of a suspension of potassium tetrachloropalladate in ethanol/water with the corresponding 1-ferrocenylethanone thiosemicarbazone ligand yielded complexes **1a** and **1b** as brown air-stable solids, with the ligand in an (*E*,*Z*) configuration and the sulfur atom of each cyclometallated moiety displaying two different coordination modes: chelating, as part of the Pd*N*NC(NHR)*S* coordination ring, and bridging, linking two cyclometallated moieties through the metal atoms. We tentatively assigned a tetrameric structure for these species in accordance with the results reported by us[18] and others[19] in related complexes derived from terdentate [C,N,S] ligands, as shown by the spectroscopic data. Hence **1a** and **1b** should be considered as novel octanuclear cyclometalled palladium(II) compounds.

The IR spectra showed, as the main difference from the starting material, the disappearance of the ν(N−H) bands due to the −NH group[20] and the ν(C=S) band at 900−800 cm^{-1}, which indicated deprotonation and loss of the C=S double bond character, respectively. The position of the NH_2 and NH bands showed that the former group was not coordinated. The displacement of the ν(C=N) band towards lower wavenumbers upon complex formation[21] is in contrast with other thiosemicarbazone complexes in which the shift is towards higher wavenumbers, probably due to the presence of the five-membered metallacycle in compounds **1a** and **1b**.[22] No ν(Pd−Cl) band was found in the IR spectra of the compounds, indicating the absence of a chloride ligand in the coordination sphere of the metal center. The FAB mass spectra of **1a** and **1b** showed clusters of peaks, centered at 1622 and 1678 amu, which both correspond to $[M]^+$.[23] The ^{1}H NMR spectra showed only one set of signals, although the activation of the $C_{\text{ferrocene}}$−H bond promotes planar chirality (R_s or R_p) in the ferrocenyl moiety.[24] This issue has been dealt with elsewhere.[25] In the ^{1}H NMR spectra, the absence of the −NH proton resonance confirms deprotonation as observed in other coordination and organometallic compounds with similar ligands.[26] Broad signals at δ ≈ 6.60 ppm were assigned to the NH_2 (**1a**) and N*H*Me (**1b**) proton resonances, shifted upfield with respect to their positions in the free ligands. A group of three signals at δ ≈ 4.50−4.10 ppm, integrating for one proton each, and a singlet at δ = 4.22 ppm assigned to the C_5H_5 group in each case were consistent with 1,2-disubstituted ferrocenes.[27] These facts provided evidence of metallation of the ligand. Variable-temperature NMR experiments did not produce any significant changes in the spectra.

Treatment of **1a** or **1b** with $Ph_2P(CH_2)_nPPh_2$ [n = 2 (dppe), 3 (dppp), 4 (dppb)] in a 1:2 molar ratio gave the tetranuclear species **2a**−**4a** and **2b**−**4b**, respectively (see Scheme 1). These reactions confirm the different reactivities of the chelating and bridging Pd−S bonds, the former being retained in the final products, even when a large excess of diphosphane was used, whilst the latter was cleaved in all instances, in agreement with the tendency observed in other cyclometallated Pd_4 cluster complexes derived from thiosemicarbazone ligands, indicating once again the greater strength of the $Pd{-}S_{\text{chelating}}$ bond.[18] All compounds were fully characterized by elemental analyses, and by IR and NMR spectroscopy. The ^{1}H NMR spectra showed only one set of signals in each case. The metallated cyclopentadienyl ring protons appeared as three signals at δ ≈ 4.67−3.48 ppm, with the 4-H proton resonance experiencing an upfield shift and appearing at lower frequency values than the C_5H_5 signal (see Exp. Sect.), due to the shielding effect of the phosphane phenyl rings, consistent with a P

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

trans to N arrangement within the terms of the "transphobic effect".[28] Unfortunately, the coupling constants to the phosphorus nuclei could not be assigned, in contrast with related complexes with diphosphane ligands.[29] The $^{31}P\{^1H\}$ NMR spectra showed singlets for the two equivalent phosphorus nuclei, shifted to higher frequency compared with those in the spectrum of the free phosphane, in agreement with the phosphorus atom coordinating to the metal center.[30] Based on the ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data we propose a centrosymmetric arrangement for the compounds (see Scheme 1). Variable-temperature NMR experiments failed to show any noteworthy changes in the spectra. Also, the ^1H NMR spectra for compounds **2a**−**4a** and **2b**−**4b** were recorded in the presence of an NMR shift reagent {tris[3-heptafluoropropylhydroxymethylene-*d*-camphorato]europium(III), [Eu(hfc)$_3$]} and the appearance of the resultant spectra in terms of the positions of the signals and the presence of new signals remained unchanged upon varying the quantity of the chiral ligand.

Treatment of **1a** and **1b** with PPh$_2$R gave the dinuclear air-stable solids **5a**−**7a**, **5b**−**6b** [R = Ph (**5a**, **5b**), Et (**6a**, **6b**), Me (**7a**)] (see Scheme 1). Characteristic microanalytical, IR and NMR spectroscopic data are given in the Exp. Sect. Important spectroscopic features include the absence of the ν(NH) and ν(C=S) bands in the IR spectra (vide supra), the shift of the 4-H signal in the ^1H NMR spectra, which appears to high field of the non-substituted C$_5$H$_5$ resonance, and the chemical shift value of the ^{31}P singlets in the $^{31}P\{^1H\}$ NMR spectra, the latter two being consistent with a P *trans* to N geometry (vide supra). The molecular structure of compound **5b** has been determined by a single-crystal X-ray diffraction analysis.

Molecular Structure of Complex 5b

Suitable crystals of **5b** were grown by slowly concentrating a chloroform solution. The crystal structure has been determined (Figure 1) and confirms the geometry predicted from spectroscopic studies. Selected bond lengths and angles are listed in Table 1. The structure is comprised of a molecule of **5b** per asymmetric unit, with discrete molecules separated by van der Waals distances. Chirality is introduced in the complex due to activation of the C(sp^2)−H bond. The centrosymmetric space group of the crystal structure, however, indicates that both enantiomers are present in the solid state. The palladium atom Pd(1) is in an approximately square-planar coordination environment (r.m.s. = 0.0845 Å, plane 1) bonded to a terdentate 1-ferrocenylethanone thiosemicarbazone ligand through the ferrocene carbon atom C(1), the nitrogen atom N(1) of the C=N moiety, and the thioamide sulfur atom S(1), all of which pertain to the thiosemicarbazone ligand, with the remaining site occupied by the phosphorus atom P(1) of the triphenylphosphane group. Each molecule contains a [5,5,5] tricyclic system which includes the three fused ferrocenyl, cyclometallated and chelate rings, with the *C,N*-metallacycle and the *N,S*-chelate rings sharing the Pd(1) atom. The cyclometallated [Pd(1),C(1),C(5),C(11),N(1), plane 2], coordination [Pd(1),N(1),N(2),C(12),S(1), plane 3] and metallated ferrocenyl [C(1)−C(5), plane 4] rings are also planar (r.m.s. = 0.0208, 0.0076 and 0.0039 Å, respectively) and coplanar with the palladium coordination plane (angles between planes: 1/2 = 6.2°, 1/3 = 5.5°, 2/3 = 1.2°, 1/4 = 9.5°, 2/4 = 3.8°, 3/4 = 5.0°). The angles between adjacent atoms in the coordination geometry of the metal atom are close to the expected value of 90°, with the most noticeable distortion in the P(1)−Pd(1)−S(1), C(1)−Pd(1)−N(1) and N(1)−Pd(1)−S(1) angles of 103.47(8), 81.0(3) and 81.3(2)°, respectively. The sum of the angles around the palladium atom is approximately 360°. All bond lengths are within the expected ranges, allowing for the strong *trans* influence of the phosphorus donor ligand,[18] which is reflected in the Pd(1)−N(1) distance of 2.067(6)Å (cf. sum of the covalent radii for palladium and nitrogen, 2.01 Å[31]). The Pd(1)−C(1) bond of 2.001(8) Å is shorter than the expected value of 2.081 Å based on the sum of the covalent radii of carbon (sp^2) and palladium, 0.771 and 1.31 Å, respectively,[31] but similar to values reported for other cyclometallated complexes.[25,32] The Pd(1)−P(1) distance, 2.245(2) Å, is also shorter than the expected value of 2.41 Å.[31] The S(1)−C(12) bond length of 1.764(8) Å, and the N(2)−C(12) length of 1.305(9) Å, are consistent with increased single- and double-bond character, respectively, resulting from deprotonation of the ligand. The two C$_5$H$_5$ rings are parallel with a tilt angle of 0.8°. They are also nearly eclipsed, being skewed 8.9° form an eclipsed conformation.

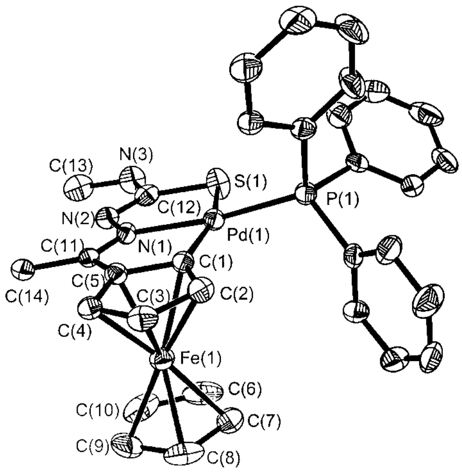


Figure 1. Molecular structure of [Pd{(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$)C(Me)=NN=C(S)NHMe}(PPh$_3$)] (**5b**) with labeling scheme; hydrogen atoms have been omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for **5b**

Pd(1)−C(1)	2.001(8)	C(1)−C(5)	1.438(9)
Pd(1)−N(1)	2.067(6)	C(5)−C(11)	1.441(9)
Pd(1)−P(1)	2.245(2)	C(11)−N(1)	1.285(8)
Pd(1)−S(1)	2.343(2)	N(2)−C(12)	1.305(9)
C(12)−S(1)	1.764(8)		
C(1)−Pd(1)−N(1)	81.0(3)	C(1)−Pd(1)−S(1)	162.1(2)
C(1)−Pd(1)−P(1)	94.4(2)	N(1)−Pd(1)−S(1)	81.3(2)
N(1)−Pd(1)−P(1)	170.0(2)	P(1)−Pd(1)−S(1)	103.47(8)

© 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Experimental Section

General Remarks: All solvents were distilled prior to use from appropriate drying agents.[33] Chemicals were used as supplied from commercial sources. Elemental analyses (C, H, N, S) were carried out at the Servicio de Análisis Elemental at the University of Santiago de Compostela using a Carlo−Erba Elemental Analyzer, model 1108. IR spectra were recorded as KBr discs or Nujol mulls with a Perkin−Elmer 1330 spectrophotometer. NMR spectra were recorded with a Bruker WM250 or AMX-300 spectrometer in $CDCl_3$ and were referenced to $SiMe_4$ (^1H) or 85% H_3PO_4 ($^{31}P\{^1H\}$). The FAB mass spectra were recorded with a Fisons Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

Synthesis of (η^5-C_5H_5)Fe(η^5-C_5H_4)C(Me)=NN(H)C(=S)NH_2 (a): A suspension of thiosemicarbazide (0.19 g, 2.19 mmol) and hydrochloric acid (0.1 mL) in water (40 mL) was stirred at room temperature. Acetylferrocene (0.5 g, 2.19 mmol) was added and the mixture stirred for 4 h, filtered and the resultant orange solid dried in vacuo. Yield 603.8 mg, 91.2%. $C_{13}H_{15}FeN_3S$ (301.2): calcd. C 51.8, H 5.0, N 13.9, S 10.7; found C 52.2, H 4.9, N 13.6, S 10.5. IR: $\tilde{\nu}$ = 3406 s, 3221 s [ν(N−H)], 1590 s [ν(C=N)], 819 m [ν(C=S)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.54 (br., 1 H, NH), 7.38 (br., 1 H, NH_2), 6.20 (br., 1 H, NH_2), 4.57 [d, ^3J(HH) = 1.6 Hz, 2 H, 2-H, 5-H], 4.39 (br., 2 H, 3-H, 4-H), 4.16 (s, 5 H, C_5H_5), 2.18 (s, 3 H, Me).

Synthesis of (η^5-C_5H_5)Fe(η^5-C_5H_4)C(Me)=NN(H)C(=S)NHMe (b): Thiosemicarbazone **b** was synthesized as an orange solid in a similar fashion. Yield 673 mg, 97.4%. $C_{14}H_{17}FeN_3S$ (315.2): calcd. C 53.3, H 5.4, N 13.3, S 10.2; found C 53.2, H 5.3, N 12.9, S 9.9. IR: $\tilde{\nu}$ = 3361 s, 3235 m [ν(N−H)], 1663 w [ν(C=N)], 897 m [ν(C=S)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.23 (br., 1 H, NH), 7.64 (br., 1 H, N*H*Me), 4.55 (br., 2 H, 2-H, 5-H), 4.37 (br., 2 H, 3-H, 4-H), 4.14 (s, 5 H, C_5H_5), 3.34 [d, ^3J(HH) = 3.9 Hz, 3 H, NH*Me*], 2.26 (s, 3 H, Me).

Preparation of [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)-NH_2}]$_4$ (1a): To a stirred solution of potassium tetrachloropalladate (0.2 g, 0.61 mmol) in water (6 mL) were added ethanol (40 mL) and ligand **a** (0.2 g, 0.67 mmol) and the mixture was stirred at room temperature for 24 h. The dark brown precipitate was filtered, washed with cold ethanol and dried in vacuo. Yield 581.3 mg, 58.7%. $C_{52}H_{52}Fe_4N_{12}Pd_4S_4$ (1622.4): calcd. C 38.5, H 3.2, N 10.4, S 7.9; found C 38.3, H 3.1, N 10.2, S 7.7. IR: $\tilde{\nu}$ = 3434 s [ν(N−H)], 1569 w [ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 6.50 (br., 2 H, NH_2), 4.45 (br., 1 H, 2-H), 4.32 (br., 1 H, 3-H), 4.22 (s, 5 H, C_5H_5), 4.12 (br., 1 H, 4-H), 2.13 (s, 3 H, Me) ppm. FAB-MS: *m/z* = 1622 $[M]^+$.

Preparation of [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)-NHMe}]$_4$ (1b): Complex **1b** was prepared as a brown solid in a similar manner. Yield 678.2 mg, 66.2%. $C_{56}H_{60}Fe_4N_{12}Pd_4S_4$ (1678.5): calcd. C 40.1, H 3.6, N 10.0, S 7.6; found C 40.0, H 3.4, N 9.8, S 7.8. IR: $\tilde{\nu}$ = 3402 m [ν(N−H)], 1588 s [ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 6.78 (br., 1 H, N*H*Me), 4.45 [d, ^3J(HH) = 1.1 Hz, 1 H, 2-H], 4.33 (br., 1 H, 3-H), 4.22 (s, 5 H, C_5H_5), 4.11 (br., 1 H, 4-H), 2.73 [d, ^3J(H,H) = 4.6 Hz, 3 H, NH*Me*], 2.16 (s, 3 H, Me) ppm. FAB-MS: *m/z* = 1678 $[M]^+$.

Preparation of [{Pd[(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)-NH_2]}$_2${μ-$Ph_2P(CH_2)_2PPh_2$}] (2a): 1,2-Bis(diphenylphosphanyl)ethane (14.7 mg, 0.037 mmol) was added to a suspension of **1a** (30.0 mg, 0.0185 mmol) in acetone (8 mL). The mixture was stirred for 24 h and the resultant orange solid filtered and dried. Yield 28.7 mg, 64.2%. $C_{52}H_{50}Fe_2N_6P_2Pd_2S_2$ (1209.6): calcd. C 51.6, H 4.2, N 6.9, S 5.3; found C 51.5, H 4.2, N 6.9, S 5.5. IR: $\tilde{\nu}$ = 3428 s [ν(N−H)], 1572 sh [ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 5.78 (br., 2 H, NH_2), 4.54 [d, ^3J(HH) = 1.7 Hz, 1 H, 2-H], 4.40 (br., 1 H, 3-H), 4.14 (s, 5 H, C_5H_5), 4.01 (br., 1 H, 4-H), 2.01 (s, 3 H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ = 58.7 (s).

Preparation of [{Pd[(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)-NH_2]}$_2${μ-$Ph_2P(CH_2)_3PPh_2$}] (3a), [{Pd[(η^5-C_5H_5)Fe(η^5-C_5H_3)-C(Me)=NN=C(S)NH_2]}$_2${μ-$Ph_2P(CH_2)_4PPh_2$}] (4a), [{Pd[(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)NHMe]}$_2${μ-$Ph_2P(CH_2)_2$-PPh_2}] (2b) [{Pd[(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)NH-Me]}$_2${μ-$Ph_2P(CH_2)_3PPh_2$}] (3b), [{Pd[(η^5-C_5H_5)Fe(η^5-C_5H_3)C-(Me)=NN=C(S)NHMe]}$_2${μ-$Ph_2P(CH_2)_4PPh_2$}] (4b): Compounds **3a**, **4a** and **2b**−**4b** were synthesized as air-stable orange solids according to a similar procedure for the preparation of **1a**, but using the appropriate diphosphane ligand. In the case of **3a** and **3b** no solid precipitated and so the solvent was removed at reduced pressure from the resultant solution and the residue recrystallized from dichloromethane/hexane.

3a: Yield 30.8 mg, 68.0%. $C_{53}H_{52}Fe_2N_6P_2Pd_2S_2$ (1223.6): calcd. C 52.0, H 4.3, N 6.9, S 5.2; found C 51.9, H 4.0, N 6.7, S 5.3. IR: $\tilde{\nu}$ = 3443 s [ν(N−H)],] 1570 sh [ν(C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 5.81 (br., 2 H, NH_2), 4.46 [d, ^3J(HH) = 0.9 Hz, 1 H, 2-H], 4.35 (br., 1 H, 3-H), 4.12 (s, 5 H, C_5H_5), 3.83 (m, 1 H, 4-H), 2.29 (s, 3 H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ = 5.8 s.

4a: Yield 36.1 mg, 78.9%. $C_{54}H_{54}Fe_2N_6P_2Pd_2S_2$ (1237.7): calcd. C 52.4, H 4.4, N 6.8, S 5.2; found C 52.3, H 4.3, N 6.5, S 5.1. IR: $\tilde{\nu}$ = 3439 m [ν(N−H)], 1570 m [ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.82 (br., 2 H, NH_2), 4.25 [d, ^3J(HH) = 2.3 Hz, 1 H, 2-H], 4.12 (br., 1 H, 3-H), 3.81 (s, 5 H, C_5H_5), 3.49 [d, ^4J(PH) = 1.9 Hz, 1 H, 4-H], 2.20 (s, 3 H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ = 27.0 (s).

2b: Yield 41.2 mg, 93.2%. $C_{54}H_{54}Fe_2N_6P_2Pd_2S_2$ (1237.7): calcd. C 52.4, H 4.4, N 6.8, S 5.2; found C 52.6, H 4.3, N 6.7, S 5.1. IR: $\tilde{\nu}$ = 3376 m [ν(N−H)], 1628 sh [ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 5.81 (br., 1 H, N*H*Me), 4.61 [d, ^3J(HH) = 3.2 Hz, 1 H, 2-H], 4.13 (br., 1 H, 3-H), 4.06 (s, 5 H, C_5H_5), 3.99 (br., 1 H, 4-H), 2.87 [d, ^3J(HH) = 4.5 Hz, 3 H, NH*Me*], 2.37 (s, 3 H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ = 62.9 (s).

3b: Yield 32.3 mg, 72.2%. $C_{55}H_{56}Fe_2N_6P_2Pd_2S_2$ (1251.7): calcd. C 52.8, H 4.5, N 6.7, S 5.1; found C 52.6, H 4.4, N 6.5, S 5.0. IR: $\tilde{\nu}$ = 3418 m [ν(N−H)], 1626 w [ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 6.01 (br., 1 H, N*H*Me), 4.67 [d, 1 H, 2-H, ^3J(HH) = 3.6 Hz], 4.31 (br., 1 H, 3-H), 4.17 (s, 5 H, C_5H_5), 3.81 (br., 1 H, 4-H), 2.99 [d, ^3J(HH) = 4.6 Hz, 3 H, NH*Me*], 2.16 (s, 3 H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ = 3.71 (s).

4b: Yield 36.8 mg, 81.3%. $C_{56}H_{58}Fe_2N_6P_2Pd_2S_2$ (1265.7): calcd. C 53.1, H 4.6, N 6.6, S 5.1; found C 53.0, H 4.5, N 6.4, S 5.1. IR: ν(N−H) 3434 s, ν(C=N) 1629 w cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.67 (br., 1 H, N*H*Me), 4.25 (br., 1 H, 2-H), 4.10 (br., 1 H, 3-H), 3.82 (s, 5 H, C_5H_5), 3.48 (m, 1 H, 4-H), 2.97 [d, 3 H, NH*Me*, ^3J(HH) = 4.9 Hz], 2.24 (s, 3 H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ = 24.7 (s).

Preparation of [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)NH_2}-(PPh_3)] (5a): Triphenylphosphane (19.4 mg, 0.0739 mmol) was added to a suspension of **1a** (30.0 mg, 0.0185 mmol) in acetone (8 mL). The mixture was stirred for 24 h and the resultant orange solid filtered and dried. The residue was recrystallized from dichloromethane/hexane. Yield 35.7 mg, 72.3%. $C_{31}H_{28}FeN_3PPdS$ (667.9): calcd. C 55.8, H 4.2, N 6.3, S 4.8; found C 55.5, H 4.1, N

6.2, S 4.8. IR: $\tilde{\nu}$ = 3346 s [ν(N−H)], 1594 m [ν(C=N)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.05 (br., 2 H, NH_2), 4.29 (br., 1 H, 2-H), 4.11 (m, 1 H, 3-H), 3.90 (s, 5 H, C_5H_5), 3.30 [d, ^{3}J(HH) = 2.2 Hz, 1 H, 4-H], 2.25 (s, 3 H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ = 30.6 (s).

Preparation of [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)NH_2}-($PEtPh_2$)] (6a), [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)-NH_2}($PMePh_2$)] (7a), [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)NHMe}(PPh_3)] (5b), [Pd{(η^5-C_5H_5)Fe(η^5-C_5H_3)C(Me)=NN=C(S)NHMe}($PEtPh_2$)] (6b): Compounds **5a**−**7a**, **5b** and **6b** were obtained as air-stable orange solids according to a similar procedure for the synthesis of **1a**, but using the appropriate phosphane ligand. In the case of **6a** no solid precipitated so the solvent was removed at reduced pressure from the resultant solution and the residue recrystallized from dichloromethane/hexane.

6a: Yield 29.5 mg, 64.3%. $C_{27}H_{28}FeN_3PPdS$ (619.8): calcd. C 52.3, H 4.5, N 6.8, S 5.2; found C 52. 3, H 4.2, N 6.7, S 5.1. IR: $\tilde{\nu}$ = 3367 m [ν(N−H)], 1579 m [ν(C=N)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 4.58 (br., 1 H, 2-H), 4.38 (br., 1 H, 3-H), 4.15 (s, 5 H, C_5H_5), 3.86 (br., 1 H, 4-H), 2.37 (s, 3 H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ = 33.6 (s).

7a: Yield 30.8 mg, 68.7%. $C_{26}H_{26}FeN_3PPdS$ (605.8): calcd. C 51.6, H 4.3, N 6.9, S 5.3; found C 51.4, H 4.1, N 6.8, S 5.2. IR: $\tilde{\nu}$ = 3409 m [ν(N−H)], 1564 m [ν(C=N)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 4.83 (br., 2 H, NH_2), 4.28 [d, ^{3}J(HH) = 1.9 Hz, 1 H, 2-H], 4.13 (m, 1 H, 3-H), 3.97 (s, 5 H, C_5H_5), 3.51 [d, ^{3}J(HH) = 2.1 Hz, 1 H, 4-H], 2.32 (s, 3 H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ = 29.3 (s).

5b: Yield 35.7 mg, 73.3%. $C_{32}H_{30}FeN_3PPdS$ (681.9): calcd. C 56.4, H 4.4, N 6.2, S 4.7; found C 56.0, H 4.4, N 6.1, S 4.6. IR: $\tilde{\nu}$ = 3352 m [ν(N−H)], 1625 w [ν(C=N)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 4.63 (br., 1 H, N*H*Me), 4.28 [d, ^{3}J(HH) = 2.1 Hz, 1 H, 2-H], 4.07 [t, ^{3}J(HH) = 2.1 Hz, 1 H, 3-H], 3.89 (s, 5 H, C_5H_5), 3.27 [d, ^{3}J(HH) = 2.1 Hz, 1 H, 4-H], 2.93 [d, ^{3}J(HH) = 4.9 Hz, 3 H, NH*Me*], 2.26 (s, 3 H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ = 30.7 (s).

6b: Yield 30.0 mg, 66.2%. $C_{28}H_{30}FeN_3PPdS$ (633.9): calcd. C 53.1, H 4.8, N 6.6, S 5.1; found C 53.2, H 4.7, N 6.5, S 5.1. IR: $\tilde{\nu}$ = 3345 s [ν(N−H)], 1575 w [ν(C=N)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 4.70 (br., 1 H, N*H*Me), 4.26 (br., 1 H, 2-H), 4.12 (br., 1 H, 3-H), 3.84 (s, 5 H, C_5H_5), 3.52 (br., 1 H, 4-H), 2.98 [d, ^{3}J(HH) = 4.9 Hz, 3 H, NH*Me*], 2.25 (s, 3 H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ = 27.8 (s).

X-ray Crystallographic Study:[34] Three-dimensional, room-temperature X-ray data were collected in the range 2.28° < θ < 25.87° with a Bruker CCD diffractometer using the ω-scan method. Reflections were measured from a hemisphere of data collected in frames each covering 0.3° in ω. The 5968 reflections measured were corrected for Lorentz and polarization effects and for absorption using a semiempirical correction based on symmetry-equivalent and repeated reflections (max/min transmissions: 0.95/0.63). The structure was solved by direct methods and refined by full-matrix least-squares unique data (354 parameters) with allowance for the thermal anisotropy of all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined using the riding mode. The refinement was carried out taking into account the minor components of the disorder. Minimum/maximum final electron density: −1.204/0.564 e·Å^{-3}. The structure solution and refinement were carried out using the SHELX-97 program package.[35] Crystal data are given in Table 2.

Table 2. Crystal data and structure refinement data for compound **5b**

Empirical formula	$C_{32}H_{30}N_3Cl_2PSFePd$
Formula mass	681.87
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell	a = 11.134(2) Å
	b = 11.807(3) Å
	c = 12.418(4) Å
	α = 75.781(19)°
	β = 75.92(2)°
	γ = 70.355(19)°
Volume	1467.1(7) Å^3
Z	2
Density (calculated)	1.544 Mg cm^{-3}
Absorption coefficient	1.259 mm^{-1}
F(000)	692
Crystal size	0.40 × 0.12 × 0.04 mm
θ range for data collection	2.28−25.87°
hkl	−13/0, −14/13, −15/14.
Number of reflections collected	5968
Number of independent reflections	5660 [R(int) = 0.0977]
Max/min transmission	0.422/1.0
Completeness to θ = 25.87°	99.4%
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5660/0/354
Goodness-of-fit	0.927
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0511, wR_2 = 0.0888
R indices (all data)	R_1 = 0.2655, wR_2 = 0.1229
Largest difference peak/hole	0.564/−1.203 e/Å^3

Acknowledgments

We thank the DGESIC (Ministerio de Ciencia y Tecnología) Proyecto BQU2002-04533-C02-01 and the Xunta de Galicia, incentive PGIDIT03PXIC20912PN, for financial support. M. M. acknowledges a fellowship from the Xunta de Galicia (Spain). We also thank Dr. Susana López-Estévez for helpful NMR discussions.

---

[1] [1a] T. Kealy, P. L. Pauson, *Nature* **1951**, *168*, 1039−1040. [1b] S. Miller, *J. Chem. Soc.* **1952**, *74*, 632−635. [1c] G. Wilkinson, *J. Am. Chem. Soc.* **1952**, *74*, 2125−2126. [1d] R. Woodward, *J. Am. Chem. Soc.* **1952**, *74*, 3458−3459. [1e] P. Eiland, *J. Am. Chem. Soc.* **1952**, *74*, 4971. [1f] G. Wilkinson, *J. Am. Chem. Soc.* **1952**, *74*, 6148−6149. [1g] E. Fischer, W. Pfab, *Z. Naturforsch., Teil B* **1952**, *7*, 377−379. [1h] J. Dunitz, L. E. Orgel, *Nature* **1953**, *171*, 121−2.

[2] [2a] E. C. Constable, *Polyhedron* **1984**, *3*, 1037−1057. [2b] I. Omae, "Organometallic Intramolecular-Coordination Compounds", in *J Organomet. Chem. Library*, Elsevier, Amsterdam, **1986**. [2c]V. V. Dunina, O. A. Zalewskaya, V. M. Potapov, *Russ. Chem. Rev.* **1988**, *57*, 250−269.

[3] [3a] A. D. Ryabov, *Synthesis* **1985**, *3*, 233−252. [3b] J. Spencer, M. Pfeffer, *Adv. Met.-Org. Chem.* **1994**, *3*, 1−50. [3c] J. Spencer, M. Pfeffer, *Adv. Met.-Org. Chem.* **1998**, *6*, 103−144.

[4] [4a] C. Navarro-Ranninger, I. López-Solera, V. M. González, J. M. Pérez, J. H. Rodríguez, J. L. García-Ruano, P. Raithby, J. R. Masaguer, C. Alonso, *J. Med. Chem.* **1993**, *36*, 3795−3801. [4b] C. Navarro-Ranninger, I. López-Solera, V. M. González, J. M. Perez, A. Alvarez-Valdés, A. Martin, P. Raithby, J. R. Masaguer, C. Alonso, *Inorg. Chem.* **1996**, *35*, 5181−5187.

[5] M. Marcos, *Metallomesogens − Synthesis, Properties and Applications* (Ed. J. L. Serrano), VCH, Weinheim, **1996**.

[6] [6a] W. A. Herrmann, C. Brossmer, K. Ökefe, C. P. Reisinger, T. Priermeier, M. Beller, M. H. Fischer, *Angew. Chem. Int. Ed. Engl.* **1995**, *107*, 1844−1848. [6b] S. B. Wild, *Coord. Chem. Rev.* **1997**, *166*, 291−311.

[7] [7a] J. Dupont, M. Pfeffer, J. Spencer, *Eur. J. Inorg. Chem.* **2001**, 1917−1927. [7b] L. Botella, C. Nájera, *Angew. Chem. Int. Ed.* **2002**, *41*, 179−181.

[8] A. Fernández, P. Uría, J. J. Fernández, M. López-Torres, A. Suárez, D. Vázquez-García, M. T. Pereira, J. M. Vila, *J. Organomet. Chem.* **2001**, *620*, 8−19.

[9] A. G. J. Ligtenbag, E. K. van Beuken, A. Meetsma, N. Veldman, W. J. J. Smeets, A. Spek, B. L. Feringa, B. L, *J. Organomet. Chem.* **1998**, *556*, 21−30.

[10] [10a] C. Cativiela, L. R. Falvello, J. C. Ginés, R. Navarro, E. P. Urriolabeitia, *New. J. Chem.* **2001**, *25*, 344−352. [10b] A. Fernández, D. Vázquez-García, J. J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J. M. Vila, *New. J. Chem.* **2002**, *26*, 398−404.

[11] [11a] X. Riera, C. Lopez, A. Caubet, V. Moreno, X. Solans, M. Font-Bardia, *Eur. J. Inorg. Chem.* **2001**, 2135−2141. [11b] A. Fernández, D. Vazquez-Garcia, J. J. Fernández, M. López-Torres, A. Suarez, S. Castro-Juiz, J. M. Ortigueira, J. M. Vila, *New. J. Chem.* **2002**, *26*, 105−112.

[12] C. S. Stone, D. A. Weinberger, C. A. Mirkin, *Progr. Inorg. Chem.* **1999**, *48*, 233.

[13] [13a] I. R. Butler, *Organometallics* **1992**, *11*, 74−83. [13b] C. J. Isaac, C. Price, B. R. Horrocks, A. Houlton, M. R. J. Ebegood, W. Clegg, *J. Organomet. Chem.* **2000**, *598*, 248−253. [13c] A. Caubet, C. López, J. Sales, X. Solans, M. Font-Bardia, *J. Organomet. Chem.* **1999**, *577*, 292−304. [13d] C. López, A. Caubet, X. Soláns, M. Font-Bardia, *J. Organomet. Chem.* **2000**, *598*, 87−102. [13e] C. López, A. Caubet, S. Pérez, X. Soláns, M. Font-Bardia, *J. Organomet. Chem.* **2002**, *651*, 105−113.

[14] Bosque, A. Caubet, C. López, E. Espinosa, E. Molíns, *J. Organomet. Chem.* **1997**, *544*, 233−241.

[15] S. Pérez, C. López, A. Caubet, A. Pawelczyk, R. Bosque, X. Soláns, M. Font-Bardiá, *Organometallics* **2003**, *22*, 2396−2408.

[16] For earlier reports and reactions of ligands **a** and **b** see for example: [16a] J. Boichard, J-P. Monin, J. Tirouflet, *Bull. Soc. Chim. Fr.* **1963**, 851−856. [16b] J. S. Casas, M. V. Castaño, M. C. Cifuentes, A. Sánchez, J. Sordo, *Polyhedron* **2002**, *21*, 1651−1660. [16c] R. Carballo, J. S. Casas, E. García-Martínez, G. Pereiras-Gabién, A. Sánchez, J. Sordo, E. M. Vázquez-López, J. C. García-Monteagudo, U. Abram, *J. Organomet. Chem.* **2002**, *656*, 1−10.

[17] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley & Sons, New York, **1997**.

[18] [18a] J. M. Vila, M. T. Pereira, J. M. Ortigueira, M. Graña, D. Lata, A. Suárez, A. Fernández, J. J. Fernández, M. López-Torres, H. Adams, *J. Chem. Soc., Dalton Trans.* **1999**, 4193−4201. [18b] A. Amoedo, M. Graña, J. Martínez, T. Pereira, M. López-Torres, A. Fernández, J. J. Fernández, J. M: Vila, *Eur. J. Inorg. Chem.* **2002**, 613−620.

[19] [19a] K. Kawamoto, Y. Nagasawa, H. Kuma, Y. Kushi, *Inorg. Chem.* **1996**, *35*, 2427−2432. [19b] A. G. Quiroga, J. M. Pérez, I. López-Solera, J. R. Masaguer, A. Luque, P. Román, A. Edwards, C. Alonso, M. C. Navarro-Ranninger, *J. Med. Chem.* **1998**, *41*, 1399−1408.

[20] T. S. Lobana, A. Sánchez, J. S. Casas, A. Castiñeiras, J. Sordo, M. S. García-Tasende, E. Vázquez-López, *J. Chem. Soc., Dalton Trans.* **1997**, 4289−4299.

[21] D. X. West, J. S. Ives, G. A. Bain, A. E. Liberta, J. Valdés-Martínez, K. H. Ebert, S. Hernández-Ortega, *Polyhedron* **1997**, *16*, 1895−1905.

[22] H. Onoue, I. Moritani, *J. Organomet. Chem.* **1972**, *43*, 431−436.

[23] Mass electrospray measurements were also performed with an HP Series 1100 MSD instrument, using dichloromethane/formic acid (1%) as the matrix. Alternatively, molecular weight determinations were also carried out with a Knauer osmometer. In both cases analogous results to the FAB data were obtained.

[24] M. Benito, C. López, X. Morván, *Polyhedron* **1999**, *18*, 2583−2595.

[25] [25a] G. Zhao, Q. G. Wang, T. C. W. Mak, *J. Chem. Soc., Dalton Trans.* **1998**, 3785−3789. [25b] R. Bosque, C. Lopez, X. Solans, M. Font-Bardia, *Organometallics* **1999**, *18*, 1267−1274.

[26] [26a] D. Kovala-Demertzi, A. Domopoulou, M. A. Demertzis, C. P. Raptopoulou, A. Terzis, *Polyhedron* **1994**, *13*, 1917−1925. [26b] F. Hueso-Ureña, N. A. Illán-Cabeza, M. Moreno-Carretero, A. M. Peñas-Chamorro, R. Faure, *Inorg. Chem. Commun.* **1999**, *2*, 323−326.

[27] *Gmelin Handbuch der Anorganische Chemie*, "Eisen Organische-Verbindungen − Ferrocen", Springer-Verlag, Heidelberg, Germany, **1977−1986**, part A1−A8.

[28] J. Vicente, J. A. Abad, A. D. Frankland, M. C. Ramirez de Arellano, *Chem. Eur. J.* **1999**, *5*, 3067−3076.

[29] J. M. Vila, E. Gayoso, T. Pereira, M. Mariño, J. Martínez, J. J. Fernández, A. Fernández, M. López-Torres, *J. Organomet. Chem.* **2001**, *637−639*, 577−585.

[30] P. S. Pregosin, R. W. Kuntz, "^{31}P and ^{13}C NMR of Transition Metal Phosphane Complexes", in *NMR 16* (Eds. P. Diehl, E. Fluck, R. Kosfeld), Springer, Berlin, **1979**.

[31] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, New York, **1960**, pp.224.

[32] [32a] C. Lopez, R. Bosque, X. Solans, M. Font-Bardia, *J. Organomet. Chem.* **1997**, *547*, 309−317. [32b] G. Zhao, F. Xue, Z. Y. Zhang, T. C. W. Mak, *Organometallics* **1997**, *16*, 4023−4026. [32c] C. Lopez, R. Bosque, X. Solans, M. Font-Bardia, *New J. Chem.* **1998**, *22*, 977−982.

[33] W. L. F. Armarego, D. D. Perrin, *Purification of Laboratory Chemicals*, 4th ed., Butterworth-Heinemann, Oxford, **1997**.

[34] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-220842. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

[35] G. M. Sheldrick, *SHELX-97, An integrated system for solving and refining crystal structures from diffraction data*, University of Göttingen, Germany, **1997**.

Received October 7, 2003
Early View Article
Published Online May 5, 2004