A General Route for the Synthesis of Triazacyclononane Functionalised with Pendant Phosphane Arms − Crystal Structures of $[NiL^1Cl(HOEt)][ClO_4]$ and $[NiL^1(NCS)_2]$ with L^1 = *N*-(Diphenylphosphanylpropyl)-1,4,7-triazacyclononane

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Keywords: Macrocyclic ligands / Phosphanes / Nickel / Zinc

We present a general route for the synthesis of triazacyclononane functionalised with one, two or three pendant phosphane arms, by the free radical addition of PPh_2H to the appropriate alkene precursor *N*-[3-(diphenylphosphanyl)-propyl]-1,4,7-triazacyclononane (L^1). L^1 forms structurally characterised complexes with Zn^{II} and Ni^{II}. $[Zn_2L^1{}_2Cl_3][ClO_4]$ has a dinuclear structure in which a bridging chloride ion allows both zinc centres to be formally six-coordinate, while $NiL^1Cl(HOEt)][ClO_4]$ achieves pseudo-octahedral geometry around the nickel centre by coordinating an ethanol molecule. The ethanol molecule and the chloride ion bound to $[NiL^1Cl(HOEt)][ClO_4]$ are both labile and can be replaced by $[NCS]^-$ to give $[NiL^1(NCS)_2]$.

Introduction

The small, facially coordinating, three-nitrogen macrocycle 1,4,7-triaza-cyclononane (9[ane]N_3) has been *N*-functionalised with a wide variety of pendant arms ending in hard donor groups (−COOH, −OH, $-NH_2$, pyridyl, polypyridyl etc).[1]−[3] There are a few recent examples of functionalisation by soft donor arms, for example 4-mercaptobenzoyl,[4] $-CH_2CH_2$ SH[5] and 2-mercaptobenzyl,[6] but so far 9[ane]N_3 has not been functionalised with pendant arms ending in a phosphane group.[7]

When this work was started there were only two published examples of nitrogen macrocycles with pendant phosphane arms: 1,4,8,11-tetrakis[(diphenylphosphanyl)methyl]-1,4,8,11-tetraazacyclotetradecane which is prepared by a "one-pot" synthesis[8] which cannot be generalised, and a series of N_2O_2, N_2S_2 and NO_3 macrocycles with 2-phosphanylethyl arms.[9] Although the synthetic method used to prepare the latter series of ligands should be applicable to all nitrogen macrocycles we have not found it to be suitable in practice for 9[ane]N_3, possibly because of the high basicity of the nitrogen atoms in this ligand. Since our original communication[10] two papers have appeared reporting the synthesis of 9[ane]N_3[11] and cyclam[12] with pendant [*o*-(diphenylphosphanyl)benzyl]alkyl arms.

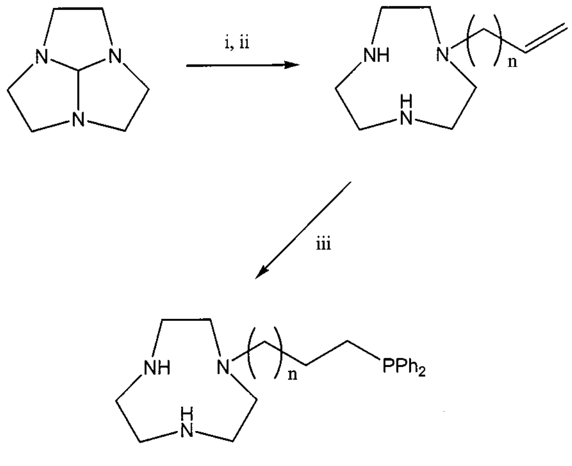
In view of the ubiquitous use of phosphane ligands in organometallic and coordination chemistry, and in particular the predominance of phosphane ligands in homogeneous catalysis, we have embarked upon a program designed to prepare ligands based on nitrogen macrocycles (hard ligands) bearing pendant phosphane arms. Of particular interest is the combination of three nitrogen atoms and one phosphane group giving a ligand which contains both hard and soft ligands and which is capable of forming coordinatively unsaturated complexes.

We report a general method for the preparation of phosphane pendant-arm macrocycles in which 9[ane]N_3 is functionalised with one, two or three arms. This is accomplished by free radical addition of PPh_2H to the appropriate alkene precursor. The only restriction on the method is that the arms must contain a minimum of three carbon atoms. The method is also applicable to larger nitrogen macrocycles e.g. cyclam or cyclen. A preliminary communication[10] has been published in which the crystal structure of $[Zn_2L^1{}_2Cl_3][ClO_4]$ (**3**) is described.

Results and Discussion

Preparation of the Phosphane Ligands

The pendant-arm phosphane ligands were prepared by free-radical addition of diphenylphosphane across the alkene double bond of their corresponding alkene pendant-arm derivatives (Scheme 1). The only restriction to this



Scheme 1. Reagents and conditions: L^1 (n = 1): i: allyl bromide, THF; ii: NaOH/H_2O; iii: PPh_2H, hν; L^2 (n = 2): i: 4-bromobut-1-ene; ii: NaOH/H_2O; iii: PPh_2H, hν

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method is that the pendant arm must contain a minimum of three carbon atoms. The free-radical additions were accomplished in essentially quantitative yields by photolysis under strictly anaerobic conditions using a mercury lamp. The reactants were irradiated as neat liquids; *the use of solvents increased the amount of phosphane oxides in the product and was found to severely hinder the reaction rate.* Excess diphenylphosphane was removed from the reaction mixture by washing with petroleum ether (boiling range 40−60 °C) or by distillation under reduced pressure.

Free radicals are electron-deficient species and their stability decreases in the order tertiary > secondary > primary. The addition is therefore strictly *anti*-Markovnikov, since the formation of a secondary radical is preferred over the formation of a primary radical. It was originally believed that the free amine functions in L^1 and L^2 would quench the radical addition but it was soon realised that this was not the case. It was anticipated that branched alkene ligands would undergo free-radical addition with diphenylphosphane to produce racemic phosphane pendant-arm macrocycles; however, the addition reaction was extremely slow and the alkene macrocycle degraded under the photolytic conditions before any significant amount of addition was achieved. No addition products were observed for, for example, *N*-(2-methylbut-2-en-1-yl)triazacyclononane even when radical initiators such as AIBN were added.

The synthetic method is exemplified by the preparation of L^1 and L^2 and has also been used to prepare *N,N′,N′′*-tris[3-(diphenylphosphanyl)propyl]-1,4,7-triazacyclononane from *N,N′,N′′*-triallyl-1,4,7-triazacyclononane and *N*-methyl-*N′,N′′*-bis[3-(diphenylphosphanyl)propyl]-1,4,7-triazacyclononane from *N,N′*-diallyl-*N′′*-methyl-1,4,7-triazacyclononane.

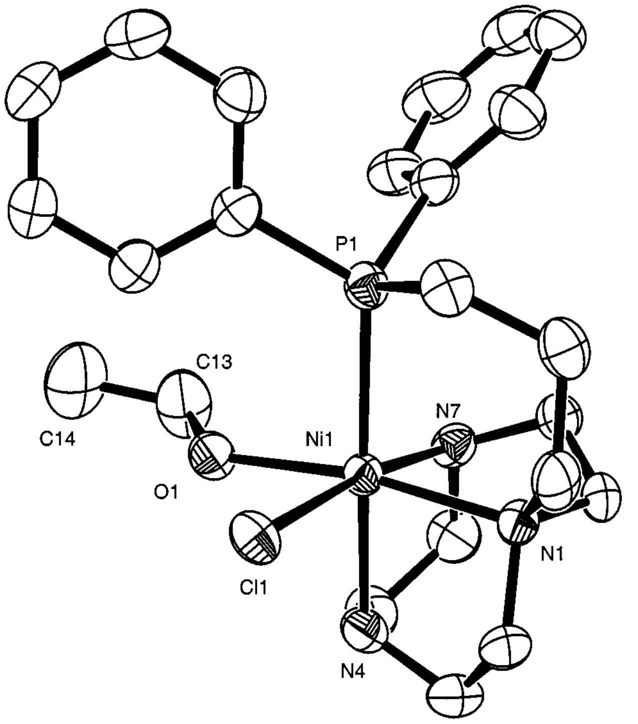

Figure 1. ORTEP for Windows[21] plot of the cation of **1** (thermal ellipsoids are drawn at 50% probability); selected bond lengths [Å] and angles [°]: Ni(1)−N(4) 2.093(3), Ni(1)−N(7) 2.094(3), Ni(1)−N(1) 2.137(3), Ni(1)−O(1) 2.171(2), Ni(1)−Cl(1) 2.438(1), Ni(1)−P(1) 2.454(1); N(4)−Ni(1)−N(7) 81.9(1), N(4)−Ni(1)−N(1) 83.7(1), N(7)−Ni(1)−N(1) 83.5(1), N(4)−Ni(1)−O(1) 86.9(1), N(7)−Ni(1)−O(1) 96.5(1), N(1)−Ni(1)−O(1) 170.6(1), N(4)−Ni(1)−Cl(1) 91.42(8), N(7)−Ni(1)−Cl(1) 172.67(8), N(1)−Ni(1)−Cl(1) 92.59(8), O(1)−Ni(1)−Cl(1) 86.18(7), N(4)−Ni(1)−P(1) 178.43(8), N(7)−Ni(1)−P(1) 97.98(8), N(1)−Ni(1)−P(1) 94.72(8), O(1)−Ni(1)−P(1) 94.56(7), Cl(1)−Ni(1)−P(1) 88.54(3), C(13)−O(1)−Ni(1) 133.8(2)

Metal Complexes

The only crystals of metal complexes which were suitable for crystallographic studies were obtained with L^1 using the perchlorate counteranion. Numerous attempts were made to form complexes of the other ligands with a variety of transition metal ions. In most cases spectroscopic evidence (UV/Vis, ^{31}P NMR) indicated that reaction had occurred.

Nickel Complexes

[NiL^{1}Cl(EtOH)][ClO$_4$] (1)

Reaction of L^1 with NiCl$_2$·6H$_2$O in ethanol followed by the addition of excess LiClO$_4$ produced [NiL^{1}Cl(EtOH)]-[ClO$_4$]·H$_2$O (**1**) (Figure 1). The nickel atom is coordinated to the three amine functions and the phosphane pendant arm of L^1. An ethanol molecule and chloride ion complete the coordination sphere around the nickel centre to give a pseudo-octahedral geometry. The bonding trends in the complex are similar to those observed in the zinc dimer.[10] The longest Ni−N bond is to the nitrogen atom bearing the pendant arm and the shortest Ni−N bond is to the nitrogen atom *trans* to the phosphane group. The Ni−P bond is much longer than the average of Ni−PPh$_3$ bond lengths (2.321 Å) and well above the upper quartile (2.331 Å).[13]

[NiL^1(NCS)$_2$] (2)

The addition of KSCN to [NiL^{1}Cl(EtOH)]$^+$ displaced the coordinated chloride ion and ethanol molecule to give a new nickel(II) complex containing two coordinated thiocyanate groups (Figure 2). The thiocyanate ion coordinates to the nickel(II) centre via the nitrogen function of the ligand. The Ni−N bonds of the macrocycle follow the same trends observed in [NiL^{1}Cl(EtOH)]$^+$, but the bond lengths are slightly longer in the thiocyanate complex. The Ni−P bond length in [NiL^1(NCS)$_2$] is slightly shorter to that observed in [NiL^{1}Cl(EtOH)]$^+$, but is still very much longer than those observed for Ni−PPh$_3$. The closest reported structure related to [NiL^1(NCS)$_2$] is the *trans*-phosphane complex [Ni(NCS)$_4${P(CH$_2$CH$_2$CN)$_3$}$_2$]$^{2-}$ [14] in which the Ni−P bond length is 2.420Å and is only slightly longer than that in [NiL(NCS)$_2$]. The Ni−NCS bond lengths are also very similar at 2.072 and 2.068Å.

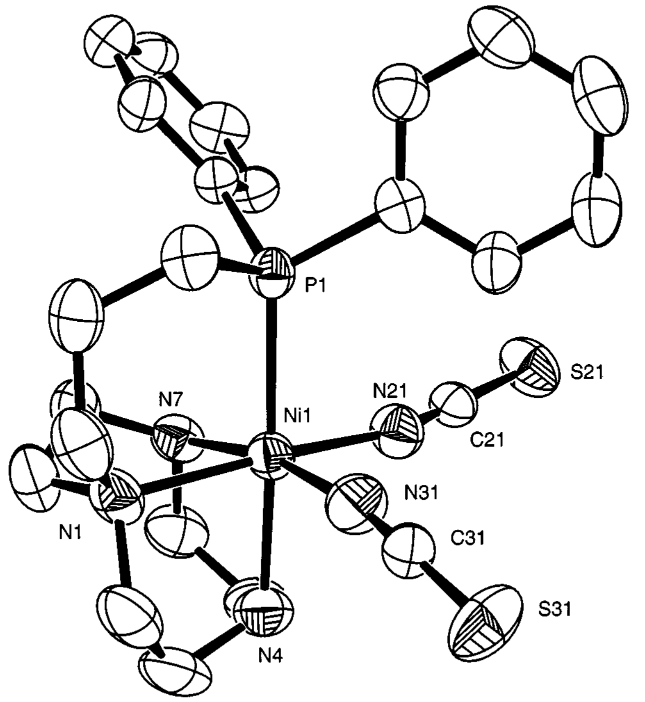

Figure 2. ORTEP for Windows[21] plot of **2** (thermal ellipsoids are drawn at 50% probability); selected bond lengths [Å] and angles [°]: Ni(1)−N(31) 2.056(3), Ni(1)−N(21) 2.066(3), Ni(1)−N(4) 2.109(3), Ni(1)−N(7) 2.128(2), Ni(1)−N(1) 2.186(3), Ni(1)−P(1) 2.4165(9); N(31)−Ni(1)−N(21) 95.19(11), N(31)−Ni(1)−N(4) 89.76(11), N(21)−Ni(1)−N(4) 90.71(11), N(31)−Ni(1)−N(7) 169.03(11), N(21)−Ni(1)−N(7) 90.25(10), N(4)−Ni(1)−N(7) 80.64(10), N(31)−Ni(1)−N(1) 91.93(11), N(21)−Ni(1)−N(1) 70.32(11), N(4)−Ni(1)−N(1) 82.76(11), N(7)−Ni(1)−N(1) 81.67(10), N(31)−Ni(1)−P(1) 89.20(9), N(21)−Ni(1)−P(1) 92.61(8), N(4)−Ni(1)−P(1) 176.60(8), N(7)−Ni(1)−P(1) 100.09(7), N(1)−Ni(1)−P(1) 94.04(8), C(21)−N(21)−Ni(1) 167.2(3), C(31)−N(31)−Ni(1) 168.3(3)

Zinc Complex

$[\text{ZnL}^1\text{Cl}(\mu\text{-Cl})\text{ZnL}^1\text{Cl}][\text{ClO}_4]$ (3)

Reaction of L^1 with anhydrous ZnCl_2 in ethanol followed by the addition of excess LiClO_4 precipitated $[\text{ZnL}^1\text{Cl}(\mu\text{-Cl})\text{ZnL}^1\text{Cl}]\text{ClO}_4$ which was recrystallised from acetonitrile. The crystal structure of the complex has been described previously.[10] It consists of a asymmetric cation in which both zinc atoms are coordinated by the three amine functions and the pendant phosphane arm of L^1. Both the zinc atoms achieve pseudo-octahedral geometry via a terminal and a bridging chloride ion.

Conclusion

We have described a general method for preparing N-macrocycles with pendant phosphane arms. The method is illustrated with the synthesis of mono-substituted L^1 and L^2 but can be used to prepare pendant-arm macrocycles in which all, or any number of, N atoms are "armed" by selective alkylation.

Experimental Section

Triazacyclononane was synthesised by the Richmond−Atkins method,[15] detosylation being effected by heating in concentrated H_2SO_4 at 115−120 °C for 36−48 h. 1,4,7-triazatricyclo-[5.2.1.0^{4,10}]decane[16] and *N*-allyltriazacyclononane[17] were prepared by published routes.

Caution: Perchlorates are potentially dangerous. Caution is advised and the handling of only small quantities is recommended.

***N*-[3-(Diphenylphosphanyl)propyl]-1,4,7-triazacyclononane (L^1):** A Schlenk tube was equipped with a magnetic stirring bar, attached to a Schlenk line and charged with *N*-allyl-1,4,7-triazacyclononane (1 g, 5.92 mmol), dissolved in dry degassed dichloromethane (5 mL). The Schlenk tube was evacuated and purged with nitrogen and diphenylphosphane (1.29 g, 1.2 mL, 6.93 mmol) was transferred to the Schlenk tube using a syringe under a strong flow of nitrogen. The contents of the flask were mixed and the dichloromethane was removed under reduced pressure. The flask was then irradiated with a 125-W Hanovia medium-pressure mercury lamp with stirring under nitrogen for 72 h. Excess diphenylphosphane was removed by washing with dry degassed petroleum ether (boiling range 40−60 °C) (2 × 5 mL). The remaining viscous oil was then left under vacuum overnight to remove any solvent and volatiles. The product was obtained in essentially quantitative yield as a very viscous yellow oil. − ^{1}H NMR (200 MHz, CDCl_3): δ = 1.51 (m, 2 H, $-\text{CH}_2-\textit{CH}_2-\text{P}$), 1.98 (m, 2 H, $-\textit{CH}_2-\text{CH}_2-\text{P}$), 2.45−2.78 (m, 14 H, $\text{N}-\textit{CH}_2-$), 7.21−7.39 (m, 10 H, Ar−*H*). − ^{13}C NMR (51 MHz, CDCl_3): δ = 24.25 (d, J_{PC} = 16 Hz, $\text{N}-\text{CH}_2\text{CH}_2\textit{CH}_2-\text{P}$), 25.69 (d, J_{PC} = 11.5 Hz, $\text{N}-\text{CH}_2\textit{CH}_2\text{CH}_2-\text{P}$), 46.73, 46.82, 53.06 ($\text{N}-\textit{CH}_2-$, ring), 58.73 (d, J_{PC} = 13 Hz, $\text{N}-\textit{CH}_2\text{CH}_2\text{CH}_2-\text{P}$), 128.36, 132.68, 133.95, 138.94 (all d, aromatic). − ^{31}P NMR (81 MHz, CDCl_3): δ = −16.2.

***N*-[3-(Diphenylphosphanyl)butyl]-1,4,7-triazacyclononane (L^2):** The same procedure was used as described for *N*-[3-(diphenylphosphanyl)propyl]-1,4,7-triazacyclononane. Quantities used were 1.5 g (8.2 mmol) of *N*-(but-3-en-1-yl)-1,4,7-triazacyclononane, 1.68 g (1.56 mL, 9.1 mmol) of diphenylphosphane and an irradiation time of 96 h. Yield 3 g (quant.). − ^{1}H NMR (200 MHz, CDCl_3): δ = 1.52 (m, 4 H, $\text{N}-\text{CH}_2\text{CH}_2\textit{CH}_2\textit{CH}_2-\text{P}$), 2.05 (m, 2 H, $\text{N}-\text{CH}_2\textit{CH}_2\text{CH}_2\text{CH}_2-\text{P}$), 2.47−2.70 (m, 14 H, $\text{N}-\textit{CH}_2-$), 2.85 (b, 2 H, N−H), 7.25−7.55 (m, 10 H, Ar−*H*). − ^{13}C NMR (51 MHz, CDCl_3): δ = 23.63 (d, $\text{P}-\textit{CH}_2-$, J_{PC} = 16.3 Hz), 27.83 (d, $\text{N}-\text{CH}_2\text{CH}_2\textit{CH}_2\text{CH}_2-\text{P}$, J_{PC} = 11.6 Hz), 28.86 (d, $\text{N}-\text{CH}_2\textit{CH}_2\text{CH}_2\text{CH}_2-\text{P}$, J_{PC} = 12.1 Hz), 43.83, 45.14, 50.67 ($\text{N}-\textit{CH}_2-$, ring), 56.42 ($\text{N}-\textit{CH}_2-$, arm), 128.47, 132.63, 133.85, 138.51 (all d, aromatic). − ^{31}P NMR (81 MHz, CDCl_3): δ = −16.43.

$[\text{NiL}^1\text{Cl(EtOH)}][\text{ClO}_4]\cdot\text{H}_2\text{O}$ (1): $\text{NiCl}_2\cdot6\text{H}_2\text{O}$ (107 mg, 0.45 mmol) and LiClO_4 (240 mg, 2.25 mmol) were dissolved in degassed ethanol (20 mL) and a solution of L^1 (200 mg, 0.56 mmol) in degassed ethanol (2 mL) was added. An initial red precipitate formed which turned blue on stirring overnight. This was filtered off and recrystallised from acetonitrile/nitromethane to yield 50 mg (18%) of **1**. − $\text{C}_{23}\text{H}_{38}\text{Cl}_2\text{N}_3\text{NiO}_6\text{P}$ (613.14): calcd. C 45.1, H 6.25, N 6.85; found C 45.1, H 6.2; N 6.85.

$[\text{NiL}^1(\text{NCS})_2]\cdot\text{CH}_3\text{NO}_2$ (2): A solution of KNCS (20 mg, 0.21 mmol) in acetonitrile was added to a solution of **1** (27 mg, 0.045 mmol) also in acetonitrile. The resulting purple solution was left to crystallise. Crystals of **2** suitable for crystallography were obtained from nitromethane. − $\text{C}_{24}\text{H}_{33}\text{N}_6\text{NiO}_2\text{PS}_2$ (591.36): calcd. C 48.8, H 5.6, N 14.2; found C 48.7, H 5.85, N 14.9.

Table 1. Crystallographic data for **1** and **2**; $R = \Sigma(|F_o| - |F_c|)/\Sigma(F_o)$; $wR = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/4}$

	1	**2**
Empirical formula	$C_{23}H_{38}Cl_2N_3NiO_6P$	$C_{24}H_{33}N_6NiO_2PS_2$
M	613.14	591.36
Crystal system	triclinic	monoclinic
Space group	$P-1$	$C2/c$
a [Å]	9.8208(15)	33.195(4)
b [Å]	11.2858(16)	10.6180(10)
c [Å]	14.2217(12)	17.1470(10)
α [°]	107.142(9)	90
β [°]	105.117(9)	111.450(10)
γ [°]	102.798(12)	90
V [Å^3]	1376.0(3)	5625.1(9)
Z	2	8
D_c [gcm^{-3}]	1.480	1.397
$F(000)$	644	2480
μ(Mo-K_α) [cm^{-1}]	10.0	9.28
T [K]	292	292
No. of independent reflections	5650	9340
n in $I > n\sigma(I)$	4842	8119
No. used in refinement	4842	8119
No. of refined parameters	307	302
$R[I > 2\sigma(I)]$	0.0414	0.0508
$wR[I > 2\sigma(I)]$	0.1004	0.1129
Largest remaining feature in electron density map [e Å^{-3}]	+0.635 −0.296	+0.485 −0.445

[ZnL^{1}Cl(μ-Cl)ZnL^{1}Cl][ClO$_4$] (3): L^1 (203 mg, 0.57 mmol) was added to a solution of $ZnCl_2$. (68 mg, 0.5 mmol) in ethanol (20 mL) containing $LiClO_4$ (270 mg). The white precipitate was filtered, washed with ethanol and dried under vacuum. Recrystallisation from MeCN produced 111 mg (42%) of white crystals which, although of poor quality, were suitable for X-ray crystallography. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.77−7.37 (m, 20 H, phenyl−*H*), 2.97−1.92 (m, 40 H, C*H*$_2$ and N*H*). − ^{31}P NMR (81 MHz, CD_3CN): δ (25 °C) = −17.0, −17.3, −17.6, −19.3 (major), −27.2; δ (70 °C) = −17.0. − $C_{42}H_{60}Cl_4N_6O_4P_2Zn_2$ (1042.15): calcd. C 48.16, H 5.77, N 8.02; found C 48.23, H 6.01; N 7.65.

Crystallography: Details of the data collection and analysis of **1** and **2** are given in Table 1. Single crystals of suitable size were attached to a glass fibre using acrylic resin, and mounted on a goniometer head in a general position. Data were collected with an Enraf−Nonius TurboCAD4 diffractometer for **2** and with a Siemens P4 diffractometer for **2**, both using graphite-monochromated X-radiation (λ = 0.71073 Å). Precise unit-cell dimensions were determined by refinement of the setting angles of high-angle reflections which were flagged during data collection. Standard reflections were measured every 2 h during data collection, and a small decay of ca 7% (**1**) and 11% (**2**) was noted, and interpolated corrections were applied to the reflection data. Lorentz-polarization corrections were then applied to the reflection data. ψ-scans for **1** indicated that no absorption correction was necessary, while a semi-empirical correction was applied to **2**. The structures were solved by direct methods (SIR92).[18] All non-H atoms were allowed anisotropic thermal motion. Aliphatic CH hydrogen atoms were included at calculated positions, with C−H = 0.96 Å, while the two NH hydrogen atoms were found from difference Fourier maps and refined using a riding model. Refinement (SHELXL97)[19] was by full-matrix least squares on F^2. The weighting scheme $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$ where $P = [F_o^2/3 + 2F_c^2/3]$ was used, with values of A, B = 0.0610, 0.2733 for **1** and 0.0591, 0.8873 for **2**. Counting statistics were used to estimate $\sigma(F_o)^2$. Neutral atom scattering factors, coefficients of anomalous dispersion and absorption coefficients were obtained from ref.[20].

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-132772 (**1**) and -132773 (**2**). 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].

Acknowledgments

We thank the EPSRC for financial support for D. E. (GR/J81150), and for funds towards the purchase of a diffractometer.

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Received August 11, 1999
[I99301]