Notes

Synthesis of a Triosmium Carbonyl Cluster Complex with a Side-On-Coordinated Imine Ligand

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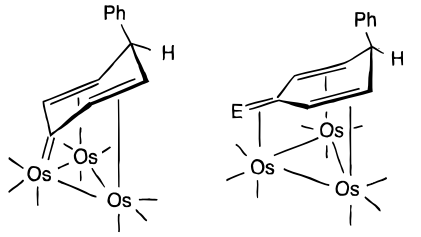
Summary: A triosmium cluster with a novel side-on coordinated imine ligand has been synthesized by the reaction between a triosmium carbene complex and ammonia. In the first step of the reaction, an anionic amino complex is formed which reacts upon treatment with $[Ph_3C]^+$ *to abstract a hydride from the amino group to form the imine complex, the molecular structure of which has been determined.*

Introduction

Arene ligands which adopt a face-capping coordination mode,[1] *e.g.* in the complex $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\ \eta^2\text{-}C_6H_6)]$ **1**,[2] can be considered as model compounds for the coordination of arenes on metal surfaces.[3] We synthesized the triosmium carbene complex **2** during our investigations of the reactivity of the benzene ligand in cluster complex **1**. The organic ligand in complex **2**



2 **3a,** E = O
3b, E = S
4, E = CH_2

is coordinated in an unusual manner with the carbene carbon bound to one osmium atom and the ring bound to the two other osmium atoms through formal carbon−carbon double bonds.[4] Complex **2** can be converted into a cyclohexadienone complex **3a** in air and in the presence of a Lewis base such as NEt_3.[4] The homologous thioketone complex **3b** can also be synthesized,[5] and in the reaction with methylidene triphenylphosphorane a C═C double bond is formed, resulting in a complex with a methylene cyclohexadiene ligand **4**.[6]

After the observed formation of element−carbon double bonds between the carbene carbon and group 14 (**4**) and group 16 (**3a**, **3b**) elements, an attempt was made to synthesize the isoelectronic imine complex bearing a side-on-coordinated C═N double bond, and the results of this study are reported here.

Results and Discussion

Gaseous ammonia, which can act as a Lewis base, was chosen as the source of nitrogen for the reaction with the carbene complex **2**. The reaction proceeded rapidly at room temperature in dichloromethane with an immediate color change from orange to yellow. The IR spectrum of this solution revealed a shift of the carbonyl bands to lower wavenumbers, which is consistent with the formation of an anionic amino-substituted cyclohexadienyl complex. The shape and position of the absorption bands are similar to those observed in the case of other anionic cyclohexadienyltriosmium complexes.[5,7] After evaporation of the solvent under vacuum, the original carbene complex **2** is regenerated. We consider that the ammonium ion which is formed as a counterion protonates the amino group and shifts the equilibrium back to the left-hand side (Scheme 1).

However, upon addition of DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene), as a stronger base, and $[N(PPh_3)_2]$-Cl, it is possible to isolate the amino-substituted anionic cyclohexadienyl complex **5**. The ^1H NMR spectrum of **5** is similar to that of the thiol-substituted $[N(PPh_3)_2]$-$[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\ \eta^1\text{:}\ \eta^2\text{-}HSC_6H_5Ph)]$ salt[5] or the unsubstituted cyclohexadienyltriosmium complexes.[7] Treatment of a solution of **5** in dichloromethane with $H[BF_4]$ also results in a back-reaction to the carbene complex **2**.

An attempt was made to remove a hydride from the amino group in **5** using triphenylcarbenium tetrafluoroborate as a hydride abstracting reagent. The reaction was carried out in dichloromethane at −78 °C. After purification on TLC plates, three products were isolated.

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(1) Wadepohl, H. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 247−366. Braga, D.; Dyson, P. J.; Grepioni, F.; Johnson, B. F. G. *Chem. Rev.* **1994**, *94*, 1585−1620.
(2) Gomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wright, A. H *J. Chem. Soc., Chem. Commun.* **1985**, 1682−1684.
(3) Somorjai, G. A. *J. Phys. Chem.* **1990**, *94*, 1013−1023. Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; Wiley: New York, 1994.
(4) Edwards, A. J.; Gallop, M. A.; Johnson, B. F. G.; Köhler, J. U.; Lewis, J.; Raithby, P. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1093−1094.
(5) Köhler, J. U.; Lewis, J.; Raithby, P. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 993−995.
(6) Edwards, A. J.; Köhler, J. U.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1995**, 3251−3252.
(7) (a) Gallop, M. A.; Johnson, B. F. G.; Lewis, J.; Wright, A. H. *J. Chem. Soc., Dalton Trans.* **1989**, 481−487. (b) Gallop, M. A. Ph.D. Thesis, University of Cambridge, Cambridge, U.K., 1988.

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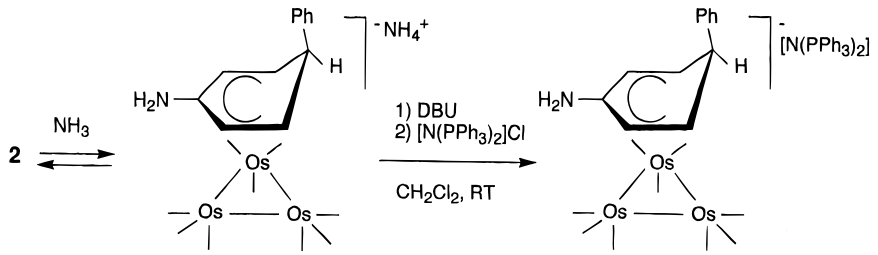
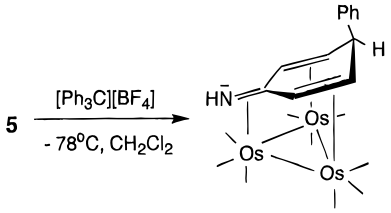
Scheme 1. Preparation of the Amino-Substiuted Cyclohexadienyl Complex 5



5

Scheme 2. Preparation of Imine Complex 6



6

Two side products were identified as carbene complex **2** and cyclohexadienone complex **3a**. The formation of **3a** can be explained by a reaction with oxygen from the air. As discussed previously, the carbene complex **2** reacts in the same way with NEt_3. The isolation of this product confirms the assumption made earlier[4] that the amine attacks first at the carbene carbon before reacting with oxygen. The third product, which was isolated in 27% yield as an orange yellow powder, was the imine complex $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}HN{=}C_6H_5Ph)]$, **6** (Scheme 2). We assume that the mechanism is similar to that proposed for the abstraction of a hydride from the thiol group of $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{: }\eta^1\text{: }\eta^2\text{-}HSC_6H_5Ph)]^-$.[5] However, it should be recalled that the acidity of an amino group differs from that of a thiol group, which is much more acidic. The structure of the imine complex **6** has been confirmed by an X-ray analysis of a single crystal. Crystal data for **6** is given in Table 1, and the structure is shown in Figure 1, which includes selected bond parameters. Complexes of imine ligands coordinated in a side-on mode exist for early transition metals which are described as metallaaziridenes because of the π-donation from the metal (*e.g.*, zirconium) to the coordinated imine ligand.[8] To our knowledge this is the first example of an η^2-coordinated imine complex with a N-H bond, and it can be considered as an isomer of a phenyl-substituted aniline ligand. The C=N bond distance is 1.35(2) Å, which is similar to distances found for π-bound N=C double bonds in triosmium clusters such as $[Os_3H(CO)_9(\mu_3\text{-}\eta^2\text{-}HNCCF_3)]$ (1.40(2) Å).[9]

The ^1H NMR spectrum of complex **6** shows, apart from the signals in the phenyl region, four other peaks, three of them broad, with an integration of 1:2:1:2. The triplet at 5.03 ppm (J = 2.5 Hz) is assigned to the *endo* hydrogen at the sp^3-carbon of the cyclohexadiene ring. The chemical shift and coupling constants are comparable to those of complexes **3a**,[4] **3b**,[5] and **4**.[6] A singlet at 3.62 ppm is assigned to the imine hydrogen. A broad peak at 3.91 ppm splits at −80 °C into a doublet. It is assumed that these signals are from the hydrogen in the β position to the imine group. In the spectra of the isoelectronic complexes **3a**,[4] **3b**,[5] and **4**,[6] a doublet of doublets appears with a similar chemical shift in each case. A broad doublet, at room temperature, at 2.84 ppm separates clearly into two broad doublets (2.78 and 2.56 ppm) at −80 °C. These are assigned to the hydrogens in the α position of the imine group. In this region of the spectrum, a doublet of doublets is found in the case of the previously discussed isoelectronic compounds.

The fluxionality of the spectrum even at −80 °C can be explained by an inversion of the hydrogen bonded to the nitrogen. When the hydrogen atom points in one direction (on the same side of the molecule as C(2) (Figure 1)) and the lone pair of the nitrogen in another (on the same side of the molecule as C(6) (Figure 1)) or *vice versa*, the two hydrogens in the α position are not equivalent (and this also affects the signals of the hydrogens in the β position), and therefore separate

Table 1. Crystallographic Data for 6

empirical formula	$C_{21}H_{11}NO_9Os_3$
fw	991.91
cryst color, habit	orange block
cryst dimens (mm^3)	0.30 × 0.25 × 0.25
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	9.199(10)
b (Å)	13.332(11)
c (Å)	17.704(12)
β (deg)	95.83(5)
V (Å^3)	2160(3)
temp (K)	153(2)
Z	4
ρ_{calcd} (Mg/m^3)	3.050
F(000)	1776
radiation, monochromator	Mo Kα (λ = 0.710 73 Å), graphite
μ(Mo Kα) (cm^{-1})	176.59
diffractometer	Stoe four-circle
scan type; limiting indices	ω/θ; $-9 \le h \le 9$, $-13 \le k \le 14$, $-18 \le l \le 19$
θ range for collcn (deg)	3.02−22.52
abs corr	semiempirical
max and min transmission	0.329, 0.143
total no. of reflns	3917
no. of unique reflns	2816 (R_{int} = 0.0349)
data/restraints/parameters	2814/0/197
R1; wR2[a]	0.0358, 0.0975
goodness of fit	1.180
largest peak, hole (e Å^{-3})	2.686, −1.512

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$, where x and y are constants adjusted by the program; Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$ where n is the number of reflections and p the number of parameters.

(8) Coles, N.; Harris, M. C. J.; Whitby, R. J.; Blagg, J. *Organometallics* **1994**, *13*, 190−199. Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486−4494. Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 2088−2097. Durfee, L. D.; Fanwick, P. E.; Rothwell, J. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720−4722.

(9) Dawoodi, Z.; Mays, M. J.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *219*, 103−113.

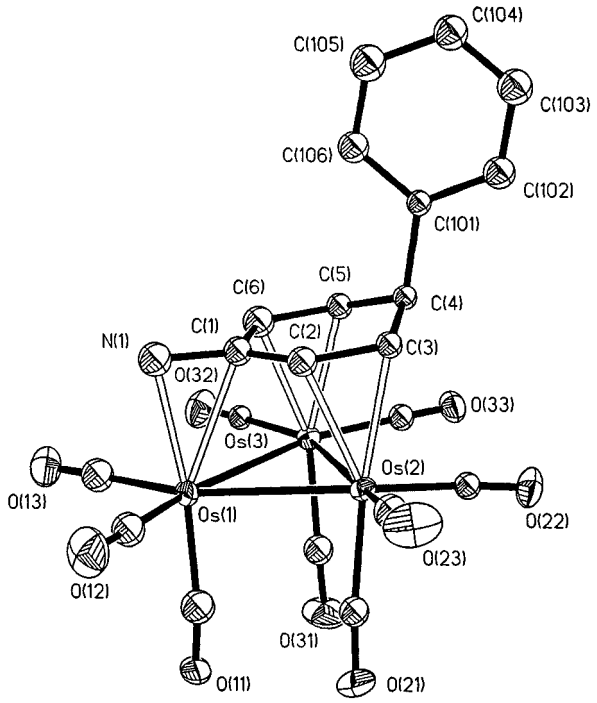


Figure 1. Molecular structure of **6** drawn with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Os(1)−Os(2) 2.911(2), Os(1)−Os(3) 2.900(2), Os(2)−Os(3) 2.877(3), N(1)−C(1) 1.35(2), Os(1)−N(1) 2.266(11), Os(1)−C(1) 2.407(12), Os(3)−C(6) 2.300(13), Os(3)−C(5) 2.330(12), Os(2)−C(2) 2.266(13), Os(2)−C(3) 2.282(11), C(1)−C(2) 1.42(2), C(1)−C(6) 1.46(2), C(6)−C(5) 1.41(2), C(2)−C(3) 1.43(2), C(5)−C(4) 1.48(2), C(3)−C(4) 1.53(2), Os(1)−C(11) 1.890(14), C(11)−O(11) 1.13 (2); Os(3)−Os(1)−Os(2) 59.36(5), Os(3)−Os(2)−Os(1) 60.12(6), Os(2)−Os(3)−Os(1) 60.52(4).

peaks are obtained. Since the inversion does not stop at even −80 °C, the expected multiplicity cannot be observed.

The ^{13}C NMR spectrum of **6** confirms the existence of a fluxional process. Two broad but very weak peaks at 49.8 and 44.4 ppm are assigned to the carbon atoms in the α and β positions to the imine group. There is also a broad peak at a chemical shift of 177.6 ppm, which can be assigned to the carbonyl ligands undergoing a fluxional process.

In the case of the mononuclear amino-substituted carbene complex $(CO)_5CrC(Me)NMeH$, no isomerization was observed between the *Z* and *E* isomer under thermal conditions. However, upon treatment with a base, isomerization takes place. It is assumed that a proton is abstracted from the amino group and an anionic intermediate is formed. This intermediate shows similarities with an imino group, and there is considerable double bond character between the carbene carbon and the nitrogen atom. In this case, the isomerization can proceed *via* inversion at the nitrogen atom, a mechanism that is also discussed for the *syn*−*anti* isomerization of Schiff bases. The advantage of an inversion mechanism compared to a "rotation" is a significantly lower activation energy.[10] This low activation energy may be responsible for the fact that the inversion of the hydrogen in imine complex **6** still occurs at −80 °C, as observed in the ^1H NMR spectrum. However, an alternative mechanism to the inversion of the hydrogen at the imine nitrogen of complex **6** cannot be excluded, and it might be possible that the hydrogen can exchange between the two positions by a rapid protonation-deprotonation mechanism facilitated by traces of moisture which might be present.

Mononuclear Fischer carbene complexes such as $(CO)_5CrC(OCH_3)C_6H_4R$ (R = Ph, Me) react with ammonia[11] and primary and less crowded secondary amines[12] under substitution of the methoxy group to form amino-substituted carbene complexes. The methoxy group is a good leaving group and can easily be lost as methanol in a following step. This opens a general route for the preparation of heteroatom-substituted carbene complexes.[13] With tertiary amines ylidic complexes can be obtained.[14] In the case of the triosmium carbene complex **2**, one may assume that a zwitterionic addition product is formed in the first step of the reaction with ammonia. This zwitterionic complex can easily be deprotonated by an excess of ammonia, resulting in the formation of an anionic amino complex **5** which is stabilized by the formation of a substituted cyclohexadienyl ligand. This shows clearly the difference between mononuclear carbene complexes of the Fischer-type and the triosmium carbene complex **2**, besides some common features such as a metal in a low oxidation state stabilized by carbon monoxide ligands and the electrophilic behavior of the carbene carbon. First, there is no leaving group and therefore a substitution reaction cannot take place, and second, there are different products upon reactions with nucleophiles due to the unusual coordination of the carbene ligand to the osmium triangle. The hybridization of the carbene carbon in the triosmium complex **2** remains formally sp^2 after the nucleophilic attack because the cyclohexadienyl ring formed remains coordinated to the three osmium atoms by three electron pairs and consequently stabilizes the addition product, while in mononuclear Fischer carbene complexes the change of hybridization of the carbene carbon from sp^2 to sp^3 in the adduct and back to sp^2 after the loss of methanol is a general feature.

The coordinaton of a conjugated ligand to more than two metal atoms results, usually, in a decrease of its reactivity. Here, however, the reactivity of the carbene carbon is enhanced relative to that of mononuclear complexes with carbene ligands without heteroatoms. These react under more forcing conditions compared to those bearing a heteroatom. The reason for this enhanced reactivity can also be the delocalization obtained by the formation of the cyclohexadienyl ligand.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen using standard

(10) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1968**, *15*, 147−155.

(11) Klabunde, U.; Fischer, E. O. *J. Am. Chem. Soc.* **1967**, *89*, 7141−7142. Fischer, E. O.; Kollmeier, H.-J. *Chem. Ber.* **1971**, *104*, 1339−1346.

(12) Baikie, P. E.; Fischer, E. O.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1967**, 1199−1200. Conner, J. A.; Fischer, E. O. *J. Chem. Soc. A* **1969**, 578−584. Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1969**, *16*, 275−282. Fischer, E. O.; Heckl, B.; Werner, H. *J. Organomet. Chem.* **1971**, *28*, 359−365. Fischer, E. O.; Leupold, M. *Chem. Ber.* **1972**, *105*, 599−608.

(13) Dötz, K. H. In *Reactions of Coordinated Ligands*; Brateman, P. S., Ed.; Plenum Press: New York 1986; pp 285.

(14) Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G.; Weiss, K. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 563−564. Kreissl, F. R.; Fischer, E. O. *Chem. Ber.* **1974**, *107*, 183−188.

Schlenk techniques, and the solvents were distilled and dried prior to use. Infrared spectra were recorded on a Perkin-Elmer Fourier-transform spectrometer using 0.5 mm solution cells, ^{1}H NMR and ^{31}P NMR spectra using a Bruker AM 400 spectrometer, and mass spectra on a FAB MS 902 instrument. Separation of the products was achieved on laboratory-prepared glass plates coated to a thickness of 1 mm with Merck Kieselgel 60 F_{254}. Purification on TLC plates was carried out under air using a mixture of dichloromethane and hexane (40:60).

Preparation of Amino Complex (5). A solution of the carbene complex **2** (150 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) was treated with NH_3 at room temperature under nitrogen. The color of the solution changed immediately from orange to yellow. A solution of DBU/CH_2Cl_2 (1 drop of DBU in 1 mL of CH_2Cl_2) was added, the solution was stirred further for 5 min, and $[N(PPh_3)_2]$-Cl (115 mg, 0.20 mmol) was added. The solvent was evaporated, and an oily yellow residue remained that was treated with *i*PrOH (3ml). During this procedure, the product formed yellow microcrystals which were filtered and washed with hexane (4 mL) under air and stored under nitrogen. **5**: yield 165 mg (0.11 mmol), 73% ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15−7.67 (m, 35 H, Ph), 4.52 (t, ^3J(H,H) = 2.4 Hz, 1 H, C*H*Ph), 3.80 (d, ^3J(H, H) = 8.3 Hz, 2 H, C*H*), 2.92 (s, 2 H, NH_2), 2.29 (dd, ^3J(H,H) = 8.3 Hz, 2.4 Hz, 2H, C*H*). IR (CH_2Cl_2): ν (cm^{-1}) 2040 (m), 1994 (s), 1983 (s), 1954 (m), 1931 (m), 1917 (sh). MS (negative ion FAB): a distinct molecular peak was not obtained. Anal. Found (calcd): C, 44.55 (44.53); H, 2.76 (2.73); N, 1.72 (1.82); P, 3.76 (4.04).

Preparation of the Imine Complex (6). A yellow solution of complex **5** (165 mg, 0.11 mmol) in dichloromethane (7 mL) was cooled to −78 °C under nitrogen. $[Ph_3C][BF_4]$ (50 mg, 0.15 mmol) dissolved in dichloromethane (3 mL) was added dropwise. After the mixture was stirred at −78 °C for 5 min, the orange-yellow solution was warmed to room temperature and stirred for 1 h. After the volume was reduced, the reaction solution was purified on TLC plates (SiO_2; CH_2Cl_2 (50%)/hexane (50%)) under air. **6** (R_f = 0.13) was isolated in 27% (29 mg, 0.03 mmol) yield as an orange-yellow powder, which was stored under nitrogen. (The cyclohexadienone complex **3a** (R_f = 0.45) and the carbene complex **2** (R_f = 0.62) were isolated as side products in 19% and 15% respectively.) ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.2−7.6 (m, Ph), 5.03 (t, ^3J(H,H) = 2.5 Hz, 1 H, C*H*Ph), 3.91 (s br, 2 H), 3.62 (s, 1 H, N*H*), 2.84 (d, br, 2 H). ^{13}C {^{1}H } NMR (400 MHz, CD_2Cl_2): δ 182.1 (CO), 177.6 (br, CO), 148.9 (*ipso*-C), 129.7 (2C, Ph), 128.1 (1C, Ph), 126.7 (2C, Ph), 52.0 (1C), 49.8 (br), 44.3 (br). The signal for the carbon atom of the imine group could not be clearly identified because of the poor signal-to-noise ratio of the spectra. IR (CH_2Cl_2): ν (CO)(cm^{-1}) 2082 (m), 2040 (s), 2028 (vs), 2006 (m), 1984 (m), 1956 (w), 1940 (sh). MS (positive ion FAB): *m*/*z* 998 (calcd 997). Anal. Found (calcd): C, 26.05 (25.28); H, 1.18 (1.10); N, 1.40 (1.40).

Crystallographic Analysis. The crystals of **6** suitable for X-ray diffraction analysis were obtained by layering a solution of complex **6** in dichloromethane with pentane under argon at room temperature. The crystals grew during the diffusion of both solvents. Data were collected on a Stoe four-circle diffractometer equipped with an Oxford Cryostream low-temperature apparatus, 2961 reflections collected in the range 6.04° < 2θ < 45.04°. A semiempirical absorption correction was applied. The structure was solved by a combination of direct methods and Fourier-difference techniques and refined by full-matrix least-squares on F^2 using SHELXL-93;[15] Os atoms, C atoms of the phenyl ring, and O atoms were refined anisotropically; all hydrogen atoms were in idealized positions (C−H 0.96 Å). All calculations were performed on a Viglen 486 PC computer.

Acknowledgment. We thank the European Union for a HCM-Fellowship and the EPSRC for a grant (for J.U.K.).

Supporting Information Available: ORTEP and cell-packing diagrams and tables of X-ray crystallographic data and structure refinement, atomic coordinates, bond lengths and angles, and hydrogen coordinates for **1** (8 pages). Ordering information is given on any current masthead page.

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(15) Sheldrick, G. M. *SHELXL-93, a computer programm for crystal structure determination*; University of Göttingen: Göttingen, Germany, 1993.