Methylidynearsine (HC≡As): Synthesis and Direct Characterization by UV-Photoelectron Spectroscopy and Mass Spectrometry

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Electronic supplementary information (ESI)

Theoretical calculations at the B3LYP/6-311+G(d,p) level predict for this arsine two stable conformers **2a** and **2b** with an energy difference of ΔE = 0.55 kcal/mol (ΔG = 0.30 kcal/mol), the conformer **2a** being the most stable (Scheme 1S, Table 1S).

2a (*Cs*)
HF(neutral) =-3196.2324459u.a.
HF(cation)=-3195.8618851u.a.
ΔSCF = 10.08 eV

2b (*C1*)
HF(neutral)=-3196.2315595 u.a.
HF(cation)=-3195.8671921u.a.
ΔSCF = 9.91 eV

Scheme 1S

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Assignment of the ionizations is made considering theoretical IP estimations (Tables 1S and 2S) and by analogy with the previously described chloromethylarsine.[1S] The introduction of the second chlorine atom on the carbon atom induces only a minor IP shift (exp. IP: CH_3Cl n_{Cl} 11.29 eV; CH_2Cl_2 n_{Cl} 11.35 eV; $CHCl_3$ n_{Cl} 11.37 eV). In the case of the PE spectrum of arsine **2**, the first IP is linked with the ejection of an electron from the molecular orbital corresponding mainly to the antibonding combination of arsenic and chlorine lone pairs (in the same plane). The following bands are due to the chlorine atoms lone pairs, bonding combination of arsenic and chlorine lone pairs, and finally $\sigma_{As\text{-}H}$ and $\sigma_{As\text{-}C}$ ionizations (Table 2S).

Table 1S. Calculated (B3LYP/6-311G(d,p)) Geometrical Parameters (Distances in Å and Angles in deg) for **2a** and **2b**.

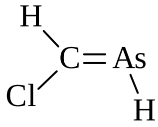
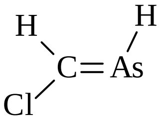
	2a	**2b**
As-H	1.527	1.522/1.526
As-C	2.018	2.015
$C\text{-}H^2$	1.083	1.085
$C\text{-}Cl^1$	1.799	1.805/1.800
$C\text{-}As\text{-}H^3$	92.9	93.7
$As\text{-}C\text{-}H^2$	112.9	109.0
Cl-C-As	109.7	108.8
$Cl\text{-}C\text{-}H^2$	106.5	106.0
$Cl\text{-}C\text{-}As\text{-}H^3$	72.5	77.8
$H^2\text{-}C\text{-}As\text{-}H^3$	46.1	167.0

Table 2S: Calculated and experimental ionization potentials for **2a** and **2b** (all values in eV, * ΔSCF, **Exp. IP)

2a	$-\varepsilon^{K-S}$	"corrected" IP x=1.96	TD-DFT	OVGF	Exp.
A'	7.69	9.65**	9.91*	9.94	9.65
A"	8.47	10.45	10.52	10.86	10.2
A'	8.82	10.78	10.94	11.23	11.3
A'	9.16	11.12	11.23	11.64	11.6
A"	9.35	11.31	11.79	11.85	11.8
A"	10.46	12.42	12.70	13.20	12.5

2b	$-\varepsilon^{K-S}$	"corrected" IP x=1.75	TD-DFT	OVGF	Exp. IP
A'	7.90	9.65**	10.08*	10.18	9.65
A"	8.53	10.28	10.71	10.85	10.2
A'	8.71	10.46	11.04	11.16	11.3
A'	9.21	10.96	11.24	11.63	11.6
A"	10.51	12.26	11.43	11.72	11.8
A"	11.59	13.34	12.74	13.18	12.5

Table 3S. Calculated (B3LYP/6-311G(d,p)) Total Energies and Geometrical Parameters of *Z* and *E* isomer of **4**.

	Z 	***E*** 
E_{total} u.a.	-2735.3819574	-2735.3816715
ΔE= E_{tot}(Z) - E_{tot}(E) kcal/mol	0.179	
C-As	1.795 Å	1.799 Å
C-Cl	1.737 Å	1.739 Å
As-H	1.530 Å	1.531 Å
C-H	1.084 Å	1.083 Å
H-As=C	97.7°	92.0°
As=C-Cl	129.3°	123.2°
As=C-H	119.5°	125.2°

Experimental Section

General: ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker ARX400 spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane (^{1}H), and solvent (^{13}C, $CDCl_3$, δ 77.0 ppm). The NMR spectra were recorded using $CDCl_3$ as solvent. HRMS (high-resolution mass spectrometry) experiments were performed on a Varian MAT 311 instrument. The cell containing compound **2** or **3** was directly connected to the spectrometer. To record the mass spectra of compounds **4** and **1**, a cooled cell containing arsine **2** and the reactor containing sodium carbonate were directly connected to the mass spectrometer.

UV-Photoelectron Spectroscopy

Photoelectron spectra were recorded with Helectros 0018 spectrometer equipped with a 127° cylindrical analyzer using 21.21 eV He I radiation as a photon source and monitored by a microcomputer supplemented with a digital-to-analogue converter. Helium ionization at 4.98 eV and nitrogen ionizations at 15.59 and 16.98 eV were used for calibration. The spectra contain 2000 points and are accurate to 0.1 eV.

Computational Details

The calculations were performed using the Gaussian 98[2S] and MOLCAS[3S] (for CASPT2) program packages. The 6-311G(d,p) basis set was used for all calculations since the inclusion of polarization functions is necessary for the accurate description of the neutral molecules containing arsenic atom and their cations. Geometry optimizations were carried out at DFT[4S] level of theory with the B3LYP [5S] functional and confirmed as true minima *via* frequency analysis, which was also used to calculate zero-point energies (ZPEs) without scaling. Ionization energies were calculated with ΔSCF-DFT which means that separate SCF calculations are performed to optimize the orbitals of the ground state and the appropriate ionic state ($IE = E_{cation} - E_{neut.mol.}$). TDDFT [6S] approach provides a first principles method for the calculation of excitation energies within a density functional context taking into account the low lying ion calculated by ΔSCF method. The vertical ionization potentials of the compounds **1, 2**, **4** were also calculated at the *ab initio* level according to OVGF [7S] method. In this case the effects of electron correlation and reorganization are including beyond the Hartree-Fock approximation and the self-energy part was expanded up to third order. CASPT2 [3S] refers to multiconfigurational SCF *ab initio* calculations in which all excitations are taken into account in a certain orbital space (the active space), with second order perturbation corrections added afterwards. To compare the ionization potentials resulting from these rigorous methods of calculation, we proceeded also to the currently used estimation of ionization potentials. Indeed, quite recent works [8S] have shown that ε_i^{KS} could be linked up to experimental vertical ionization potentials (IP_v) by uniform shift $x = \left| -\varepsilon_i (HOMO) - IP_v^{exp} \right|$. This approach gives a remarkable agreement with experimental values and is justified by the fact that the first calculated vertical ionization potential lies very close to experimental values. Stowasser and Hoffman [9S] have shown that the localization of KS orbitals are very similar to those obtained after HF calculations.

Density functional theory (DFT) has been shown to predict various molecular properties successfully.[9S] The advantages of the most employed method of calculations of the first ionization energies (ΔSCF – DFT calculations) have been thoroughly demonstrated.[10S] On the other hand, the frequently used estimation of IPs by "shifting" of calculated Kohn-Sham energies (a not very rigorous process, but nicely working) has also proved its efficacy. Nevertheless, we have to consider that each theoretical method of approaching ionization potentials is limited by the calculation procedure. In the ΔSCF method we have to take into account that the single-configuration approximation is not valid when several ions of the same symmetry are near in energy. For TDDFT approach, the configuration interaction processes is based on the quality of the evaluation of the low lying ion described by ΔSCF method. In the Outer Valence Green's Function (OVGF) calculation, the quality of the theoretical results depends on the validity of the Hartree-Fock approximation. The limitation of CASPT2 methods is the limit of active space (10 electrons or 9 for the ions in 12 molecular orbitals in our case), so it is reserved for rather small-size molecules.

Synthesis of compounds (1)-(4)

Caution: Low-boiling arsenic compounds are potentially highly toxic molecules. All reactions and handling should be carried out in a well-ventilated hood.

Dichloromethylarsonic acid dichloride (3). In an 250 mL three necked flask equipped with a dropping funnel, a low temperature thermometer, an efficient stirring bar and a nitrogen inlet were introduced dry pentane (15 mL), diethyl ether (15 mL) and THF (60 mL).

Dichloromethane (4.25 g, 50 mmol) freshly distilled on P_4O_{10} was added and the flask was immersed in a cold bath. When the temperature of the solution arose -95 °C, n-BuLi (30 mL, 48 mmol) was very slowly added (30 min). At the end of the addition, the reaction mixture was stirred at -95 °C for 15 min. The solution was then cooled at -110 °C and a suspension of arsonic trichloride (11.1 g, 60 mmol) in THF (30 mL) previously cooled at about -50 °C was quickly added to the reaction mixture. An increase of the temperature up to -70 °C was observed. After 5 min of stirring, the cold bath was removed and the reaction mixture was allowed to warm to room temperature. The solvent was then removed in vacuo and a crude mixture of arsine **3** was obtained. Analysis by ^1H NMR spectroscopy of this mixture showed the presence of dichloromethylarsonic dichloride and bis(dichloromethylarsonic chloride) in a 3:1 ratio. A pure sample was obtained using a vacuum line by removing the solvents in vacuo and selective trapping of compound **3** in a trap cooled at -20 °C. Compound **3** (2.66 g, 11.5 mmol, yield: 24 %) was kept at low temperature (-30 °C). ^1H NMR (400 MHz, $CDCl_3$) δ: 6.01 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 69.0 (t, $^1J_{CH}$ = 183.9 Hz). HRMS: $M^{+\cdot}$ for $CHAs^{35}Cl_4$ calcd: 227.8048, found: 227.805. (Spectroscopic characterization of the impurity: bis(dichloromethyl)arsonic chloride: ^1H NMR (400 MHz, $CDCl_3$) δ: 6.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 65.6).

Dichloromethylarsine (2). The apparatus already described for the preparation of 2-propynylphosphine was used.[11S] A vacuum line was equipped with two cells with stopcocks. The flask containing the reducing mixture (Bu_3SnH, 8.7 g, 30 mmol and small amounts of duroquinone) was attached to the vacuum line, cooled to -10 °C and degassed. Compound **3** (460 mg, 2 mmol) diluted in tetraglyme (5 mL) was then slowly added with a flex-needle through the septum for about 15 min. During and after the addition, the dichloromethylarsine **2** that formed was distilled off in vacuo from the reaction mixture. A cold trap (-30 °C) selectively removed the less volatile products and the arsine **2** was condensed in a second cold trap (-90 °C) to remove the most volatile products (mainly AsH_3). This cell was disconnected from the vacuum line and the dichloromethylarsine **2** (103 mg, yield: 32 %) was kept at low temperature (77 K). For analysis by NMR spectroscopy, arsine **2** was distilled in vacuo and condensed with an NMR solvent ($CDCl_3$) on a cold finger equipped at the bottom with an NMR tube. ^1H NMR ($CDCl_3$) δ: 4.30 (d, 2H, $^3J_{HH}$ = 3.7 Hz); 6.27 (t, 1H, $^3J_{HH}$ = 3.7 Hz). ^{13}C NMR ($CDCl_3$) δ: 56.4 (t, $^1J_{CH}$ = 180.7 Hz). IR (gas phase, ν, cm^{-1}):

2962 (m), 2103 (m, ν_{AsH}), 800 (vs), 665 (s). HRMS: $M^{+\cdot}$ for $CH_3As^{35}Cl_2$ calcd: 159.8828, found: 159.883. (m/z (%): 162 (20), 160 (24, $M^{+\cdot}$), 126 (20), 124 (65, ClCH=As$H^{+\cdot}$), 91 (25), 90 (80), 89 (80), 85 (70), 83 (100, $CHCl_2^{+\cdot}$).

Chloromethylidenearsine (4) and Methylidynearsine (1). A cell containing the dichloromethylarsine **2** (43 mg, 0.27 mmol) was attached to the vacuum line equipped with a reactor connected to the mass or photoelectron spectrometer. Dry sodium carbonate (30 g), introduced in a reactor (ϕ: 2.5 cm, L = 30 cm) in half-section between two pads of glass wool, was heated to 110 °C (MS experiments) or 200 °C (UV-PES experiments) and, arsine **2** was slowly vaporized in the vacuum line. The gaseous flow was analyzed by photoelectron spectroscopy or mass spectrometry. Chloromethylidenearsine **4** was unambiguously observed as the main product (purity ~ 85 %) in the presence of small amounts of the precursor and carbon dioxide.

With a higher temperature of the base (250 °C in MS and 335°C in UV-PES), methylidynearsine **1** was observed as the main product (purity ~ 90 %) in the presence of carbon dioxide.

Fig. 2S. Mass spectra of compounds (2) and (4)

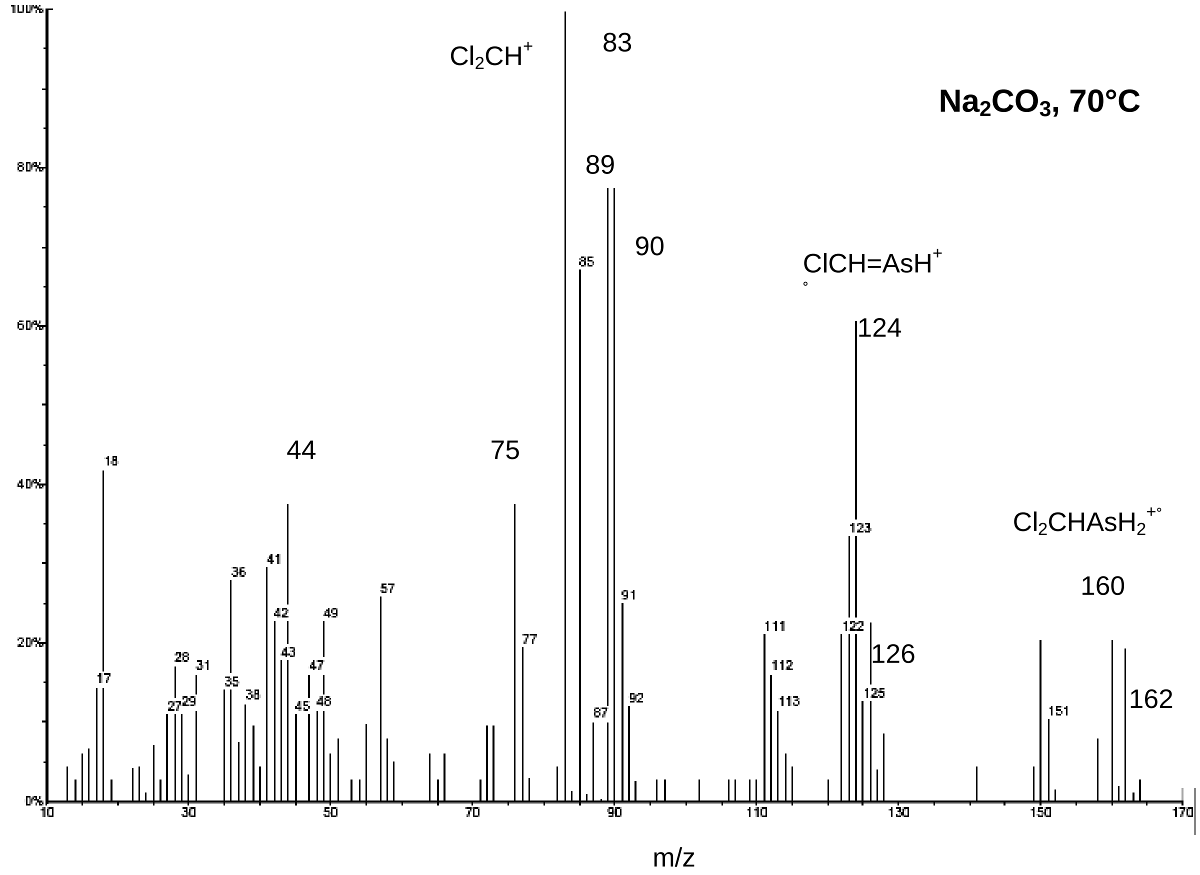


Fig. 2S (a). Mass Spectra of dichloromethylarsine **2**.

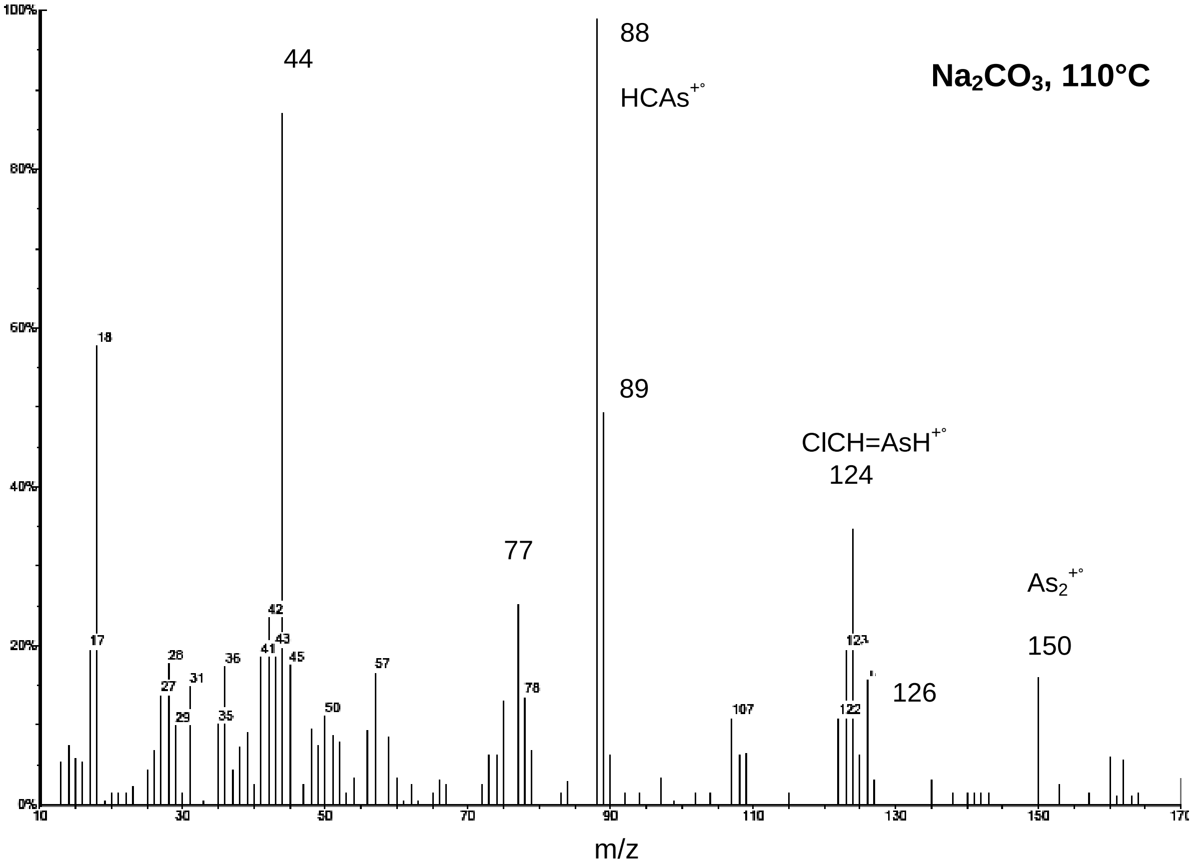


Fig. 2S(b). Mass Spectra of **2** vaporized on Na_2CO_3 at 110 °C.

References

1S A. Chrostowska, A. Dargelos, V. Lemierre, J.-M. Sotiropoulos, P. Guenot and J.-C. Guillemin, *Angew. Chem., Int. Ed.* 2004, **43**, 873-875.

2S Gaussian 98, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratman, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. Martin, D. J. Fox, D. T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Jonhson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.

3S *MOLCAS* Version 5., Lund University, Sweden, 2000.

4S (a) R. G. Parr and W. Yang, Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989; (b) M. J. Frish, G. W. Trucks and J. R. Cheeseman, *Systematic Model Chemistries Based on Density Functional Theory: Comparison with Traditional Models and with Experiment in: Recent Development and Applications of Modern Density Functional Theory, Theoretical and Computational Chemistry* (Ed.: J. M. Semminario), 1996, vol 4, pp. 679-707, Elsevier Science B. V.

5S (a) A. D. Becke, *Phys. Rev*. 1988, **38,** 3098-3100; (b) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652; (c) C. Lee, W. Yang and R. G. Parr, *Phys. Rev*., 1988, **B37**, 785-789.

6S (a) R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys.*, 1998, **109**, 8218 - 8224; (b) M. E. Casida, C. Jamorski, K. C. Casida and D. R. Salahub, *J. Chem. Phys*., 1998, **108**, 4439-4449.

7S (a) W. von Niessen, J. Schirmer and L. S. Cederbaum, *Comput. Phys. Rep.* 1984, **1**, 57-125; (b) J. V. Ortiz, *J. Chem. Phys.* 1988, **89**, 6348 – 6352.

8S (a) A. J. Arduengo, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Hermann, N. L. Jones, M. Wagner and R. West, *J. Am. Chem. Soc*., 1994, **116**, 6641-6649; (b) H. Muchall, N. Werstiuk, J. L. Pitters and M. S. Workentin, *Tetrahedron*, 1999, **55**, 3767-3778; (c) H. Muchall, N. Werstiuk, B. Choudury, J. Ma, M. S. Workentin and J. P. Pezacki, *Can. J. Chem*., 1998, **76,** 238-240; (d) H. Muchall, N. Werstiuk and B. Choudury, B. *Can. J. Chem*., 1998, **76**, 221-227; (e) H. Muchall and P. Rademacher, *J. Mol. Struct*., 1998, **471**, 189-194.

9S R. Stowasser and R. Hoffmann, *J. Am. Chem. Soc*., 1999, **121,** 3414-3420.

10S (a) S. Joantéguy, G. Pfister-Guillouzo and H. Chermette, H., *J. Phys. Chem.*, 1999, **103**, 3505- 3511 ; (b) A. Chrostowska, K. Miqueu, G. Pfister-Guillouzo, E. Briard, J. Levillain, and J.-L. Ripoll, *J. Mol. Spectrosc.*, 2001, **205**, 323-330 ; (c) R. Bartnik, P. Baylère, A. Chrostowska, A. Galindo, S. Lesniak and G. Pfister-Guillouzo, *Eur. J. Org. Chem.* 2003, 2475-2479 ; (d) V. Lemierre, A. Chrostowska, Dargelos and H. Chermette, *J. Phys. Chem. A*, 2005, **109**, 8348-8355.

11S J. Demaison, J.-C. Guillemin and H. Möllendal, *Inorg. Chem.*, 2001, **40**, 3719-3724.