Organometallics **2001,** *20,* 4454−4456

Methyl Group Transfer from $ZnMe_2$ to Arsenic(III), an Alternative Pathway to Deprotonation of $[CyNHAs(\mu\text{-}NCy)]_2$

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Received April 20, 2001

*Summary: Attempted metalation of the dimer $[CyNHAs(\mu\text{-}NCy)]_2$ (**1**) with $ZnMe_2$ gives the novel complex $[\{MeAs(NHCy)(NCy)\}ZnMe]_2$ (**2**), a reaction formally involving transfer of a Zn-bonded Me group to the As(III) center, rather than the anticipated deprotonation of the CyNH groups. **2** has an unusual ladder structure in the solid state, composed of a central $(ZnMe)_2$ dimer unit coordinated by two $[MeAs(NHCy)(NCy)]^-$ anions.*

In recent years the coordination chemistry of anionic ligands containing group 15/nitrogen frameworks has been a focus of a number of studies.[1,2] Imido anions, such as $[E(NR)_3]^{3-}$ (E = As, Sb) and $[E_2(NR)_4]^{2-}$ (E = P, As, Sb, Bi), are readily prepared by various synthetic routes. These include the condensation reactions of $E(NMe_2)_3$ with primary amines (RNH_2) and their lithiates (RNHLi)[1] and the deprotonation of $[E(NHR)_3]$ and $[(RNH)E(\mu\text{-}NR)_2]_2$ with organo alkali metal reagents.[2] Such anions are usually stable in transmetalation reactions, the reactions of the alkali metal derivatives with a variety of transition and main group metal sources providing a simple strategy for the assembly of a broad range of heterometallic cages, containing well-defined mixed-element stoichiometries.[1−3] So far, our studies in this area have mainly concerned imido ligands of the heavier group 15 elements (E = Sb and Bi).[1a] However, we have recently become interested in the corresponding P and As ligands.[4] Reported here is a study of the reaction of the dimer $[(CyNH)As(\mu\text{-}NCy)]_2$ with $ZnMe_2$, a reaction that follows an entirely different course to the simple deprotonation pathway previously encountered in the synthesis of this class of compounds.[2]

Previously, it had been shown that deprotonation of the dimeric arsazene $[(DippNH)As(\mu\text{-}NDipp)]_2$ (Dipp = 2,6-$^{i}Pr_2C_6H_3$) with $[Zn\{N(SiMe_3)_2\}_2]$ gives $[Zn\{As(NDipp)_2\}_2]$, containing the $[As(NDipp)_2]^-$ anion.[5] The starting material in our study, $[(CyNH)As(\mu\text{-}NCy)]_2$ (**1**) (Cy = cyclohexyl), was prepared by the 1:2 reaction of $As(NMe_2)_3$[6] with $CyNH_2$, the dimeric nature of **1** being confirmed by (EI) mass spectrometric investigations ($[MH]^+$ $m/z = 541$).[7] Surprisingly, however, the reaction of **1** with $ZnMe_2$ does not give the target complex $[\{As_2(NCy)_4\}(ZnMe)_2]$, containing the $[As_2(NCy)_4]^{2-}$ dianion (Scheme 1).[8] Instead, the product is $[\{MeAs(NHCy)(NCy)\}ZnMe]_2$ (**2**), resulting from an unexpected alternative to simple deprotonation, the formal transfer of the Zn-bonded Me group to the As(III) center (Scheme 1).[9] Initial evidence for the unusual nature of **1** was apparent in IR and ^{1}H NMR spectroscopic studies. The IR spectrum indicated that the N−H protons of the CyNH groups had been retained, while the ^{1}H NMR

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(6) The purity of the $As(NMe_2)_3$ used in reactions was confirmed by elemental analysis, ^{1}H NMR spectroscopy, and EI MS. These studies illustrate that the precursor is chlorine-free. In addition, there were no $ClAs(NMe_2)_2$ or $Cl_2As(NMe_2)$ impurities present that could account for the trivial formation of **1** by substitution of Cl for Me.

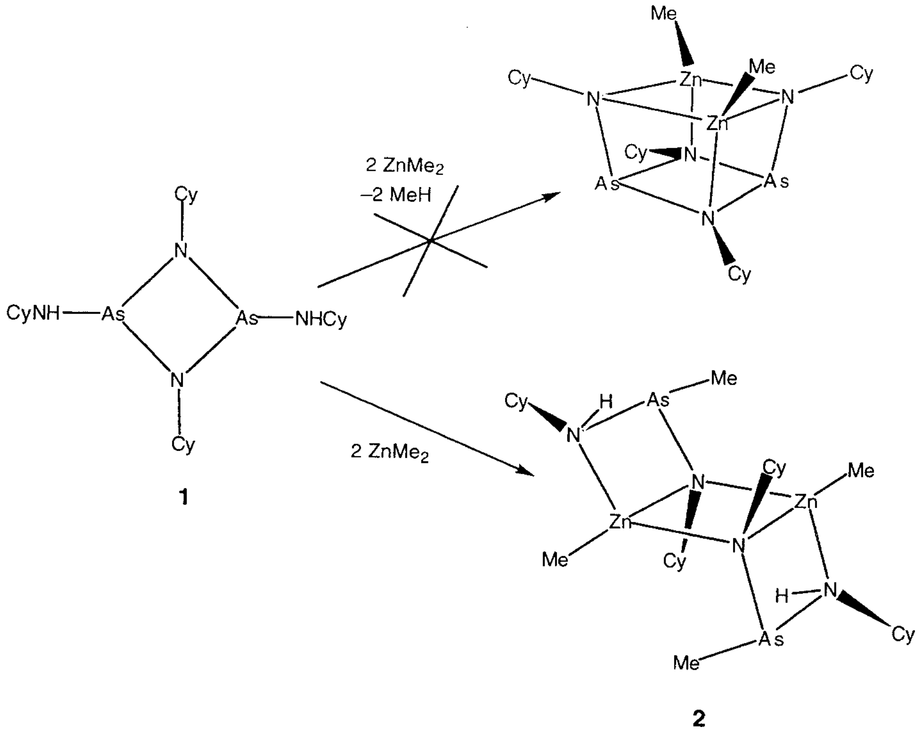
(7) Synthesis of **1**: the complex was produced by the 1:2 reaction of $As(NMe_2)_3$ with $CyNH_2$ in hexane, under argon. Removal of the solvent gives **1** as a semisolid. Attempts to purify further the complex have so far failed. Anal. Found: C, 52.0, H 8.5, N 9.8. Cald for $C_{24}H_{46}N_4As_2$: C 53.3, H 8.6, N, 10.4. EI-MS dominant $[MH]^+$ 541.

(8) The $[As_2(NCy)_4]^{2-}$ dianion is obtained from the reaction of $[Me_2NAs(\mu\text{-}NCy)]_2$ with CyNHLi, see: Beswick, M. A.; Harron, E. A.; Hopkins, A. D.; Raithby, P. R.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1999**, 107.

(9) Synthesis of **2**: To a hexane solution of $As(NMe_2)_3$ (1.0 mL, 2.5 mmol, 2.5 mol L^{-1} solution in toluene) under argon was added $CyNH_2$ (0.57 mL, 5.0 mmol). On addition the solution became slightly cloudy. The reaction was completed by bringing the mixture briefly to reflux. $ZnMe_2$ [1.25 mL, 2.5 mmol, 2.0 mol L^{-1} solution in toluene] was added to the mixture at −78 °C. The solution produced was allowed to warm to room temperature and then briefly brought to reflux. The quantity of solvent was reduced to ca. 2 mL under vacuum, causing the precipiation of a white solid. Toluene (2 mL) was added, and the solid was heated into solution. Storage at room temperature gave crystals of **2**. Yield of crystals 0.15 g (16.5%) (the relatively low yield appears to be a consequence of the high solubility of the complex; if crystallised at −10 °C, yields as high as 35.5% (10 mmol scale) are obtained). Mp: 153−160 °C. IR (Nujol, NaCl), ν/cm^{-1} 3262(w) (N−H str.), other bands at 1306(w), 1257(s), 1062(s), 1025(s), 968(m), 887(w), 842(w), 797(s). ^{1}H NMR (400.16 Mz, toluene-d_8, +25 °C), δ/ppm = 3.03 (1H, mult., α-C−H of Cy), 2.83 (1H, mult., α-C−H of Cy), 1.45 (s, 3H, Me-As), 2.10−0.69 (overlapping mult., 20H, β- to δ-Cy), −0.28 (s, 3H, Me-Zn). Anal. Found: C 46.0, H 7.8, N 7.8. Calcd for $C_{28}H_{58}N_4Zn_2As_2$: C 46.0, H 8.0, N 7.7.

10.1021/om010326w CCC: $20.00

Scheme 1



spectrum showed the presence of two, 1:1 Me environments (δ −0.28 for the Zn-Me and δ 1.45 for the As-Me groups). The difference in the behavior of **1** with $ZnMe_2$ and $[(DippNH)As(\mu\text{-}NDipp)]_2$ with $[Zn\{N(SiMe_3)_2\}_2]$[5] may (in part) be accounted for by the greater steric demands involved in the latter reaction. In situ variable-temperature ^1H NMR studies of the reaction mixture reveal that the transfer reaction from Zn to As is, however, relatively slow even at 70 °C. One possible mechanism involves Me-addition to and opening of the dimer **1**.[10] However, this process appears to be less likely thermodynamically than the alternative of deprotonation and the formation of the target complex $[\{As_2(NCy)_4\}(ZnMe)_2]$.[11] A more plausible explanation may involve addition of Me to the As(III) centers of $[\{As_2(NCy)_4\}(ZnMe)_2]$ itself, followed by reprotonation with **1** (this may account for the relatively low yields of **2** obtained, 16.5−35.5%).[12]

A low-temperature X-ray crystallographic study of **2**[13] reveals that the complex has an unusual “four-rung” ladder structure in the solid state, resulting from the association of two crystallographically independent [{MeAs(NHCy)(NCy)}ZnMe] ring units (Figure 1). Ladder structures of this type are more common for s-block metal complexes,[14] such as the lithium amido and phosphido complexes $[\{H_2C(CH_2)_4NLi\}_2\cdot TMEDA]_2$ [TMEDA = $(Me_2NCH_2)_2$][15] and $[LiP^tBu_2\cdot THF]_4$,[16] and have

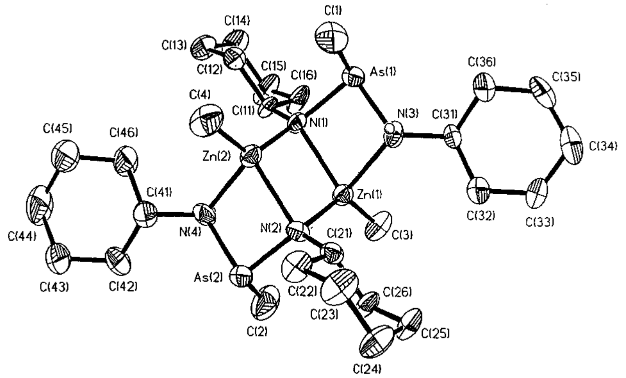


Figure 1. Ladder structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Key bond lengths (Å) and angles (deg); As(1)−N(1) 1.868(6), As(1)−N(3) 1.894(6), As(1)−C(1) 1.955(8), As(2)−N(2) 1.846(6), As(2)−N(4) 1.917(6), As(2)−C(2) 1.93(1), Zn(1)−N(1) 2.135(5), Zn(1)−N(2) 2.052(5), Zn(1)−N(3) 2.241(7), Zn(1)−C(3) 2.002(8), Zn(2)−N(1) 2.053(5), Zn(2)−N(2) 2.141(6), Zn(2)−N(4) 2.220(8), Zn(2)−C(4) 1.955(5), N−As−N mean 90.8, As−NH(Cy)−Zn (within AsN_2Zn rings) 90.9, As−N(Cy)−Zn (within AsN_2Zn rings) mean 95.2, N−Zn−N (within AsN_2Zn rings) mean 75.6, N−Zn−N (within Zn_2N_2 ring) mean 92.4, Zn−N−Zn (within Zn_2N_2 ring) mean 87.6, As(1)−N(1)−Zn(2)/As(2)−N(2)−Zn(1) mean 120.0, N(3)−Zn(1)−N(2)/N(4)−Zn(2)−N(1) mean 100.6.

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(10) Alternatively, the formation of **2** could be considered to derive from addition of $ZnMe_2$ across the As═N bond of the monomer [(CyNH)As═NCy]; see for example: Andrews, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1997**, 1183. Andrews, P. C.; Nichols, P. J.; Raston, C. L.; Roberts, B. A. *Organometallics* **1999**, *18*, 4247.

(11) Model ab initio STO-3G calculations investigating reactions of $ZnMe_2$ with a [As(NHMe)(NMe)] monomer show that Me addition to As(III) is 82.0 kJ mol^{-1} more favorable than N−H deprotonation. However, this ignores the key effect of entropy (i.e., particularly that associated with the formation of CH_4 in the deprotonation reaction).

(12) ^{31}P NMR studies provide some evidence for the electropositive nature of P in $[(RN)_2P]^-$ anions (δ 340−390); for example, see: (a) Brask, J. K.; Chivers, T.; Krahn, M. L.; Parvez, M. *Inorg. Chem.* **1999**, *38*, 290. (b) Nieke, E.; Frost, M.; Nieger, M.; von der Gönna, V.; Ruban, A.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1994,** *33*, 2111. (c) Detsch, R.; Nieke, E.; Nieger, M.; Schoeller, W. W. *Chem. Ber.* **1992**, *125*, 1119.

(13) Crystal data for **2**: $C_{28}H_{58}As_2N_4Zn_2$, M = 731.36, space group $P\bar{1}$, Z = 2, a = 8.1835(5) Å, b = 9.8676(5) Å, c = 23.3327(8) Å, α = 81.031(3)°, β = 81.754(3)°, γ = 66.919(2)°, V = 1705.10(15) Å^3, μ(Mo Kα) = 3.354 mm^{-1}, T = 180(2) K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 15 944 reflections collected, 7684 were independent (R_{int} = 0.055). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final R1 = 0.045 [$I > 2\sigma(I)$] and wR2 = 0.135 (all data).[20]

only rarely been observed elsewhere in the periodic table, e.g., the heterometallic imido/amido Sn(II) ladder $[(MesNHLi{\cdot}2THF)_2\{Sn(\mu\text{-}Nma)\}_2]$ (ma = 2-MeOC$_6$H$_4$).[17] While a number of amido-Zn complexes have been structurally characterized previously,[18] to our knowledge, none of these have ladder structures similar to **2**, and the structure and composition of the complex is entirely novel.

The As centers within the two independent [MeAs(NHCy)NCy)]$^-$ anions of **2** have similar, distorted pyramidal geometries. This geometry and the compression of the C−As−N and N−As−N angles [range 90.6(3)−102.9(3)°] below that expected for pure sp^3 hybridization are typical of As(III) and symptomatic of the presence of a lone-pair. The As−N bond lengths in these anions are within the range of values previously observed in imido and amido As(III) compounds, the bonds made with the μ_3-bridging imido-NCy centers [As(1,2)−N(1,2) mean 1.86 Å] being shorter than those involving the μ_2-bridging amido-NHCy centers [As(1,2)−N(3,4) 1.91 Å]. The central Zn$_2$N$_2$ ring fragment of **2** is almost rectangular in shape [Zn−N−Zn mean 87.6°, N−Zn−N mean 92.4°], with each of the Zn centers having similar, highly distorted pseudo-tetrahedral coordination geometries [the N−Zn−N and C−Zn−N angles about each falling over a large range of 75.7(2)−132.3(3)°]. The shortest Zn−N bonds are found within the Zn$_2$N$_2$ dimer unit, reflecting the high degree of negative charge carried by the imido-N centers of the [MeAs(NHCy)NCy)]$^-$ anions. The shortest of all are those connecting the two [{MeAs(NHCy)(NCy)}ZnMe] units [Zn(1)−N(2) and Zn(2)−N(1) mean 2.052 Å], while the remaining Zn−N bonds within the Zn$_2$N$_2$ ring are significantly longer [Zn(1)−N(1) and Zn(2)−N(2) mean 2.139 Å]. This pattern of Zn−N bond lengths appears to mirror the steric effects of the Me and Cy substituents, which are *trans* with respect to the shorter Zn(1)−N(2) and Zn(2)−N(1) bonds but *cis* with respect to the longer Zn(1)−N(1) and Zn(2)−N(2) bonds. The very long Zn−N bonds made with the formally neutral amido-NHCy group of the [MeAs(NHCy)NCy)]$^-$ anions [Zn(1)−N(3) and Zn(2)−N(4) mean 2.23 Å] are similar to those observed between neutral Lewis base donor ligands and Zn[19] and can be described as coordinative interactions.

In summary, the results reported here show for the first time that simple deprotonation of group 15/nitrogen frameworks, commonly used in the generation of anionic ligand arrangements, is not the only reaction pathway available to these systems. The unusual Me-transfer reaction observed in the formation of **2** may well be a common feature of reactions involving less basic organometallic or metallo-organic reagents. This reaction has potentially useful synthetic applications and will be an interesting area of study in the future.

Acknowledgment. We gratefully acknowledge the EPSRC (A.D.B., A.R., A.D.W., D.S.W.), Churchill and Fitzwilliam Colleges (Cambridge) (Fellowship for A.D.H.), Evangelisches Studienwerk Villigst (R.W.), and the Cambridge European Trust (A.R.) for financial support. We also thank one of the referees for valuable communications concerning the nature of the reaction involved.

Supporting Information Available: Crystal data and an ORTEP diagram. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for **2** are available via the Cambridge Crystallographic Data Center (CCDC 170104).

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(18) In amides the Zn−N bond lengths are ca. 2.05−2.10 Å, for examples see: Bell, N. A.; Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr.* **1983**, *39C*, 1182. Davidson, M. G.; Elilio, D.; Less, L.; Martin, A.; Raithby, P. R.; Snaith, R.; Wright, D. S. *Organometallics* **1993**, *12*, 1. Olmstead, M. M.; Grigsby, W. J.; Chacon, D. R.; Hascall, T.; Power, P. P. *Inorg. Chim. Acta* **1996**, *251*, 273.

(19) Zn−N bond lengths in adducts are generally >2.10 Å. For a recent example see: Mimoun, H.; de Saint Laumer, J. Y.; Giannini, L.; Scopelliti, R.; Floriani, C. *J. Am. Chem. Soc.* **1999**, *121*, 6158.

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