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ORGANOMETALLIC DIAZOALKANES

X *. ^{13}C {^1H} PFT SPECTRA OF ORGANOMETALLIC DIAZOALKANES OF THE MAIN GROUP ELEMENTS

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Summary

Direct metal—carbon coupling constants $^1J(M—^{13}C)$ and chemical shift data are reported for the organometallic diazoalkanes $L_nMC(N_2)R$ [$L_nM = Me_3Si$; Me_3Ge; Me_3Sn; Me_3Pb; MeHg; $EtO_2C(N_2)CHg$; R = H; $(Me)_nM$; EtO_2C] and the compounds $Me_2MC(N_2)R'$ [M = As, Sb, Bi; R' = H; Me_2M; EtO_2C], including various other diazoalkanes of arsenic. Electron release by the methyl—metal substituents leads to strong shielding of the α-carbon atoms in heterodiazoalkanes.

Introduction

In the past few years examples of highly shielded carbon atoms in compounds with enhanced nucleophilic properties have been revealed by ^{13}C NMR spectroscopy [1]. Among the pure organic derivatives carbon suboxide C_3O_4 [2] ($\delta^{13}C$: —14.6 ppm), ketenes $R_1R_2C{=}C{=}O$ [3,4] ($\delta^{13}C$ ($H_2C{=}C{=}O$): 2.5 ppm, $\delta^{13}C(Ph_2C{=}C{=}O)$: 47.0 ppm), the isoelectronic diazoalkanes ($R_1R_2CN_2$ [5] ($\delta^{13}C(CH_2N_2)$: 23.1 ppm $\delta^{13}C$ (Ph_2CN_2): 62.5 ppm), ylides $R_3M—\bar{C}H_2$ of phosphorous [6,7,8] and arsenic [9] were throughly investigated.

Replacement of hydrogen or organic substituents by organometallic groups in the foregoing series of compounds leads to even more powerful nucleophilic reagents. The effect is convincingly demonstrated in organometallic ketenes [10] ($\delta^{13}C(Et_3Sn)_2C{=}C{=}O$: —20.5 ppm!), in metal complexes $Ph_3PC(H)R \rightarrow MCl$ [11] ($\delta^{13}C$ from —4.1 to —5.9 ppm) and in organometallic benzyl derivatives $PhCH_2—ML_n$ [12,13,14].

We describe below a ^{13}C NMR study of organometallic diazoalkanes $L_nMC(N_2)R$. A reaction mechanism for the formation of different organometallic diazo-

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alkanes, their differing kinetic stabilities in 1,3-dipolar cycloaddition reactions [15] (Huisgen Reaction) and their tendency to form metalorganic phosphazines [16] (Staudinger Reaktion) can all be rationalized in terms of different nucleophilicity at the reactive site, expressed in ^{13}C NMR shifts of the α-carbon atoms.

Our approach neglects conformational consequences of metal methyl interactions [13,14] which would be of importance in determining the inductive and hyperconjugative effects of those groups. Information about steric effects are said to be more easily obtained from PE spectroscopy, as e.g. with $PhCH_2HgCl$ [17].

Results and discussion

Geometries [18] and energies [19] of the parent compound CH_2N_2 were estimated and symmetry orbital shapes [20] with orbital energies (obtained from PE spectra) were correlated. The influence of substituents at the α-carbon atom in diazomethanes is effectively represented by the energy of the highest occupied molecular orbital $\psi_{HOMO} \equiv 2\, b_{1(\pi)}$ of a π-type [21]. Although orbital sequences and energies in diazomethanes were obtained from the excited molecules, viz. the corresponding radical cations, ground-state phenomena as observed with ^{13}C NMR may serve as a basis for the interpretation of different charge densities at α-carbon atoms in metalorganic diazoalkanes.

In Tables 1 and 2 we present ^{13}C NMR data for diazomethanes and diazoacetic esters of Group IV B, V B and II B elements, with mercury as the representative of the last group.

I. Group IV B and II B diazoalkanes

Resonance signals $\delta(^{13}C—N_2)$ in compounds $(Me_3M)_2CN_2$, Me_3MCHN_2 and $Me_3MC(N_2)CO_2Et$ are shifted to higher field compared with the parent organic derivatives and follow the sequence $M = Si < Ge < Sn \approx Pb$. There is an anomaly for the lead diazomethane $(Me_3Pb)_2CN_2$ but there is now ample evidence for nonlinear correlations of NMR data with other parameters, e.g. electronegativity. In $(Me_3Sn)_2CN_2$ ($\delta\,^{13}CN_2$: 5.8 ppm) we find a highly "anionic" α-C-atom in accordance with the nucleophilic power of this substance; in the lead compound $(Me_3Pb)_2CN_2$ ($\delta\,^{13}CN_2$: 1.9 ppm) shielding may be influenced by the diamagnetic anisotropy of the element, hybridization effects, or polarity in the metal—methyl carbon bonds.

In metalorganic diazoacetic esters we generally find less shielding of the diazonium carbon atom and little change from the shifts noted for the parent $HC(N_2)CO_2Et$. The influence of the electron withdrawing carboxylic ester ligand and the diazonium group outweighs metal—methyl interactions. In $Hg[C(N_2)CO_2Et]_2$ we even find a large downfield shift of the diazo carbon atom resonance signal, $\delta(^{13}CN_2)$ 72.6 ppm, compared to 46.3 ppm of $HC(N_2)CO_2Et$. One explanation may be an interaction of electron acceptor groups across the *sp*-hybridized mercury atom. This assumption is supported by the $^1J(^{13}C—^{199}Hg)$ value of 2032 Hz, denoting *s*-character in the polarized Hg—C bond. Although the diazocarbon atom is formally *sp*^{2}-hybridized $^1J(^{13}C—^{199}Hg)$ is found in the range associated with pure *sp*-carbon atoms, e.g. $(C_6H_5—C{\equiv}C—)_2Hg$ with 2584 Hz [22].

Coupling constants $^1J(M—^{13}CH_3)$ were observed for all methyl—metal diazo-

TABLE 1

$^{13}C\{^1H\}$PFT SPECTRA (δ, ppm) OF ORGANOMETALLIC DIAZOALKANES OF Si, Ge, Sn, Pb and Hg

Compound	Solvent/T^b	$\delta M-^{13}CH_3$	$\delta M-^{13}C(N_2)$	$J^a\ M-^{13}CH_3$	$J^a\ M-^{13}C(N_2)$	$\delta O^{13}CH_2$	$\delta OCH_2{}^{13}CH_3$	$\delta\ ^{13}C{=}O$	Reference
$Me_3SiC(N_2)CO_2Et$	C_6D_6/T	4.8	42.9	58.4	not observed	59.8	14.3	167.6	28
$Me_3GeC(N_2)CO_2Et$	C_6D_6/T	−2.1	43.7	not observed	not observed	60.0	14.1	167.0	29
$Me_3SnC(N_2)CO_2Et$	C_6D_6/T	−8.3	38.4	^{117}Sn: 367.5 ^{119}Sn: 385.2	286.5 300.0	60.8	14.5	169.8	30
$Me_3PbC(N_2)CO_2Et$	C_6D_6/T	3.2	37.8	316.3	195.2	60.2	14.6	160.6	31
$MeHgC(N_2)CO_2Et$	C_6D_6/T	9.5	38.1	1146.4	not observed	60.1	14.2	170.7	31
$Hg[C(N_2)CO_2Et]_2$	C_6D_6/T	—	72.6	—	2,033	61.1	14.4	162.3	31
Me_3SiCHN_2	C_6D_6/T	−1.6	19.1	62.2	not observed				
Me_3GeCHN_2	C_6D_6/T	−1.9	19.3	not observed	not observed	—	—	—	27
$Me_3Ge)_2CN_2$	C_6D_6/T	−1.0	17.3	not observed	not observed	—	—	—	27
$(Me_3Sn)_2CN_2$	C_6D_6/T	−7.9	5.8	^{117}Sn: 348.9 ^{119}Sn: 365.2	208.2 217.2	—	—	—	32
$(Me_3Pb)_2CN_2$	C_6D_6/T	1.0	1.9	278.5	228.0	—	—	—	31
$(MeHg)_2CN_2$	Pyridine-d_5/								
	−20°C	12.4		1,085/1,061					31
	T	12.7		1,061					

[a] $J(^{13}C-M)$: ^{29}Si: 7.61%; $^{117,119}Sn$: 7.67/8.68%; ^{207}Pb: 8.899%; ^{199}Hg: 16.86% (% natural abundance).

[b] $T = 38°C$.

TABLE 2

$^{13}C\{^1H\}$PFT SPECTRA (δ, ppm) OF ORGANOMETALLIC DIAZOALKANES OF As, Sb and Bi[a]

Compound	Solvent/*T*	$\delta M{-}^{13}CH_3$	$\delta M{-}^{13}C(N_2)$	$\delta O^{13}CH_2$	$\delta OCH_2{}^{13}CH_3$	$\delta\, ^{13}C{=}O$	$\delta N{-}^{13}CH_3$	Reference
$(Me_2Sb)_2CN_2$	Toluene-d_8 −30°C	0.7	−1.1	—	—	—	—	33
Me_2AsCHN_2	Toluene-d_8 −30°C	9.5	24.1	—	—	—	—	26
$(Me_2As)_2CN_2$	C_6D_6/*RT*	9.9	24.7	—	—	—	—	33
$Me_2BiC(N_2)CO_2Et$	Toluene-d_8 −20°C	11.9	26.3	61.5	15.5	166.0	—	33
$Me_2SbC(N_2)CO_2Et$	C_6D_6/*RT*	0.5	34.3	61.1	15.0	168.5	—	33
$Me_2AsC(N_2)CO_2Et$	C_6D_6/*RT*	9.3	45.7	60.5	14.5	166.0	—	33
$MeAs[C(N_2)CO_2Et]_2$	Toluene-d_8 −20°C	6.8	27.2	61.2	14.4	160.0	—	34
$MeAs(NMe_2)C(N_2)CO_2Et$	C_6D_6/*RT*	9.7	46.4	60.7	14.5	166.7	42.4	34
$(Me_2N)_2AsC(N_2)CO_2Et$	C_6D_6/RT	—	38.4	60.6	14.5	167.1	40.1	34
$HC(N_2)CO_2Et$	C_6D_6/*RT*	—	46.3	61.1	14.7	167.1	—	5
H_2CN_2	$CDCl_3$/0°C	—	23.1	—	—	—	—	5

[a] $(Me_2Bi)_2CN_2$ was too unstable for obtaining ^{13}C NMR Spectra (see Ref. 33).

alkanes and are of the same magnitude as those reported for simple alkyls of silicon [23], tin [24], lead [25] and mercury [25]. The order ${}^1J(\text{M—}{}^{13}\text{CH}_3) > {}^1J(\text{M—}{}^{13}\text{CN}_2)$ parallels the different states of hybridization of the carbon atoms.

II. Group V B diazoalkanes

Among compounds of this group in the diazomethane series $(\text{Me}_2\text{Bi})_2\text{CN}_2$ was too unstable to give reliable ^{13}C NMR spectra, but in $(\text{Me}_2\text{Sb})_2\text{CN}_2$ ($\delta^{13}\text{CN}_2$: —1.1 ppm) shielding is of the same order as in the tin compound $(\text{Me}_3\text{Sn})_2\text{CN}_2$. On passing from antimony to arsenic there is a remarkable fall in shielding: diazoalkanes of arsenic show resonance signals $\delta^{13}\text{CN}_2$ close to that of CH_2N_2. From the data in Tables 1 and 2 we find support for a tentative mechanism rationalizing the formation of moderately stable monosubstituted diazomethanes L_nMCHN_2 ($\text{L}_n\text{M} = \text{Me}_2\text{As}$ [26] or Me_3Ge [27]). According to our model a competition reaction of both diazo compounds CH_2N_2 and a first intermediate L_nMCHN_2 with a metal amide takes place:

$$\text{L}_n\text{MNR}_2 + \text{CH}_2\text{N}_2 \xrightarrow{-\text{HNR}_2} \text{L}_n\text{MCHN}_2 \xrightarrow[-\text{HNR}_2]{+\text{L}_n\text{MNR}_2}$$

$$(\text{L}_n\text{M})_2\text{CN}_2 \text{ or } \underset{(\text{excess})}{\text{CH}_2\text{N}_2} \xrightarrow[-\text{HNR}_2]{+\text{L}_n\text{MNR}_2} \text{L}_n\text{MCHN}_2$$

We find empirically that only those derivatives L_nMCHN_2 will be of appreciable kinetic stability which show comparable $\delta(^{13}\text{CN}_2)$ values for the parent CH_2N_2 and both possible metalorganic diazocompounds:

$\delta^{13}\text{C}(^{13}\text{CH}_2\text{N}_2) \approx \delta^{13}\text{C}(\text{L}_n\text{M}^{13}\text{CHN}_2) \approx \delta^{13}\text{C}[(\text{L}_n\text{M})_2{}^{13}\text{CN}_2]$, e.g.:

CH_2N_2: 23.1 ppm; $\text{Me}_2\text{AsCHN}_2$: 24.1 ppm; $(\text{Me}_2\text{As})_2\text{CN}_2$: 24.75 ppm
CH_2N_2: 23.1 ppm; $\text{Me}_3\text{GeCHN}_2$: 19.3 ppm; $(\text{Me}_3\text{Ge})_2\text{CN}_2$: 17.3 ppm.

We summarize our ^{13}C NMR results for heterodiazoalkanes of Group IV B and II B elements by the statement, that the α-carbon atoms experience strong shielding as a result of effects of the metal—methyl groups, exceptions occurring where interaction with strong electron-withdrawing substituents overrides this effect. The same behaviour is mainly observed for heterodiazoalkanes of the Group V B elements, but interaction of the "lone-pair" on arsenic may play an important role in the interpretation of widely scattered ^{13}C NMR shifts in the arsenic series.

Experimental

Organometallic diazoalkanes were prepared according to the literature quoted in Tables 1 and 2.

^{13}C NMR spectra

Spectra were run on Varian XL 100 (for low-temperature experiments) or on Varian CFT 20 spectrometers equipped with a Fourier transform accessory. Off resonance spectra were useful in assigning resonance signals unambiguously to the ($^{13}\text{CN}_2$) group in L_nMCHN_2. Generally signals of the α-carbon atoms in $(\text{L}_n\text{M})_2\text{CN}_2$ were of minor intensity, since these atoms have long relaxation times due to lack of neighbouring hydrogen nuclei, and considerable broadening of these signals was also observed. Spectra of good quality were usually obtained with aquisition times of 0.4—0.8 sec and 30—50 thousand scans but some spectra required more than 100,000 scans.

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References

1 B.E. Mann, Advan. Organomet. Chem., 12 (1974) 135.
2 E.A. Williams, J.D. Cargioli and A. Ewo, J. Chem. Soc. Chem. Commun., (1975) 366.
3 J. Firl and W. Runge, Angew. Chem., 85 (1973) 671.
4 J. Firl and W. Runge, Z. Naturforsch., 29b (1974) 393.
5 J. Firl, W. Runge and W. Hartmann, Angew. Chem., 86 (1974) 274.
6 T.A. Albright, W.J. Freeman and E.E. Schweizer, J. Amer. Chem. Soc., 97 (1975) 940.
7 H. Schmidbaur, W. Buchner and D. Scheutzow, Chem. Ber., 106 (1973) 1251.
8 K.A. Ostoja Starzewski and M.F. Feigel, J. Organometal. Chem., 93 (1975) C20.
9 Y. Yamamoto and H. Schmidbaur, J. Chem. Soc. Chem. Commun., (1975) 668.
10 Yu. K. Grishin, S.V. Ponomarev and S.A. Lebedev, Zh. Org. Khim., 10 (1974) 404.
11 Y. Yamamoto and H. Schmidbaur, J. Organometal. Chem., 97 (1975) 479.
12 W. Adcock, B.D. Gupta, W. Kitching, D. Dodrell and M. Geckle, J. Amer. Chem. Soc., 96 (1974) 7360.
13 D. Dodrell, M.L. Bullpitt, C.J. Moore, C.W. Fong, W. Kitching, W. Adcock and B.D. Gupta, Tetrahedron Letters, 9 (1973) 665.
14 M. Bullpitt, W. Kitching, W. Adcock and D. Dodrell. J. Organometal. Chem., 116 (1976) 187.
15 R. Grüning and J. Lorberth, J. Organometal. Chem., in press.
16 P. Krommes and J. Lorberth, J. Organometal. Chem., 120 (1976) 131.
17 H. Schmid and A. Schweig, J. Chem. Soc. Chem. Commun., (1975) 667.
18 A.P. Cox, L.F. Thomas and J. Sheridan, Nature, 181 (1958) 1000.
19 J.M. Andre, M.C. Andre, G. Leroy and J. Weiler, Int. J. Quantum Chem., 3 (1969) 1013.
20 W.L. Jorgensen and L. Salem, The Organic Chemist's Book of Orbitals, Academic Press, New York, 1973.
21 E. Heilbronner and H.-D. Martin, Chem. Ber., 106 (1973) 3376.
22 L.A. Fedorov, Z.A. Stumbrevichyute, A.K. Prokof'ev and E.I. Fedin, Dokl. Akad. Nauk SSSR, 209 (1973) 134.
23 G.C. Levy, D.M. White and J.D. Cargioli, J. Magn. Resonance, 8 (1972) 280.
24 H.G. Kuivila, J.L. Considine, R.H. Sarma and R.J. Mynott, J. Organometal. Chem., 111 (1976) 179.
25 G. Singh, J. Organometal. Chem., 99 (1975) 251.
26 P. Krommes and J. Lorberth, J. Organometal. Chem., 110 (1976) 195.
27 P. Krommes and J. Lorberth, J. Organometal. Chem., 127 (1977) 19.
28 U. Schöllkopf and N. Rieber, Angew. Chem., 79 (1967) 238, 906; idem, Angew. Chem. Int. Ed. Engl., 6 (1967) 261, 884; idem, Chem. Ber., 102 (1969) 488.
29 M.F. Lappert, J. Lorberth and J.S. Poland, J. Chem. Soc. A, (1970) 2954.
30 J. Lorberth, J. Organometal. Chem., 15 (1968) 251.
31 J. Lorberth, J. Organometal. Chem., 27 (1971) 303.
32 M.F. Lappert and J. Lorberth, J. Chem. Soc. Chem. Commun., (1967) 836.
33 P. Krommes and J. Lorberth, J. Organometal. Chem., 93 (1975) 339.
34 P. Krommes and J. Lorberth, J. Organometal. Chem., 97 (1975) 59.