Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

NITROSO-DERIVATIVES OF FOURTH MAIN GROUP ELEMENTS

J. JAPPY AND P. N. PRESTON
Department of Chemistry, Heriot-Watt University, Edinburgh EH1 1HX, Scotland (Great Britain)

(Received June 3rd, 1969)

In the last few years several fourth main group organometallic compounds have been prepared which incorporate a simple chromophore attached to the metal atom, *e.g.*,

$$\geqslant M-\overset{|}{C}=O^{1a,b},\ \geqslant MN_3{}^{2,3},\ \geqslant M-N=N-^{4,5},\ \geqslant M-N=C\lessgtr^{6}.$$

Compounds of this type are of considerable value in assessing the contribution of vacant metal *d*-orbitals to the bond between the metal atom and the chromophore. West[7] has applied qualitative molecular orbital theory to explain on a general basis the effects of metalloid substitution on the spectra of simple chromophores; this treatment has been successfully used in relation to the bathochromic shifts observed in the n-π^* transition of silylketones[7] and silylketimines[6], and the hypsochromic shift is one of the transitions of silylazides[3]. Recently the validity of West's approach[7] has been questioned, for carbonyl derivatives at least, by Yates *et al.*[8]; their simple and extended H.M.O. calculations support the conclusion that the σ-donor (inductive) properties of the metal atom are primarily responsible for the spectral shifts and that p_π–d_π or p_{π^*}–d interactions are unimportant.

West[7] has discussed the situation in compounds of the type M–A=B in which A possesses both a lone pair and π-orbitals, *e.g.*, $\geqslant M-N=N$, $\geqslant M-N=C\lessgtr$. Figure 1 shows the result of raising the energy of n, π, and π^* levels by induction from the electropositive metal and their lowering by interaction with vacant *d*-orbitals. On this basis bathochromic shifts are successfully predicted for $\geqslant M-N=N-$ and $\geqslant M-N=C\lessgtr$ but assessment of the magnitude of interaction of the *d*-orbitals with n, π, and π^*

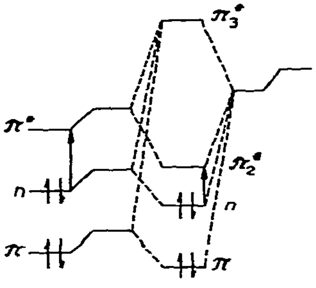

Fig. 1. Energy levels showing the influence of a metalloid substituent with unfilled *d* orbitals. Only one nonbonding pair is indicated (n), as in $M-N=C\lessgtr$ (ref. 7).

levels is difficult and hypsochromic shifts may arise; the need for examination of new types of compound in this category has been emphasised[7].

An especially interesting case is the group of compounds $\geqslant$M–N=O in which two *n*–π* transitions are possible, *viz.*, *n*–π*(N) and *n*–π*(O) absorptions [which appear[9] in C-nitroso derivatives at 630–790 ($\varepsilon \simeq 1$–60) and 270–300 nm ($\varepsilon \simeq 80$) respectively]. We now report the results of our attempts to prepare such compounds by using the organometallic route[10] used hitherto[11] only for C-nitroso compounds:

i.e.

$$\mathrm{ArMgX + NOCl \longrightarrow ArNO}$$

$$\geqslant\mathrm{MLi} + \mathrm{NOCl} \xrightarrow[< -30^{\circ}]{\mathrm{TFH}} \geqslant\mathrm{MNO} + \mathrm{LiCl}$$

Deep green solutions [(IV)–(IX)] or blue solutions (II) are obtained by allowing 3% solutions of the appropriate lithium reagent to react with 5% solutions of nitrosyl chloride in tetrahydrofuran (THF) at −78°. From the method of preparation, and the appearance of new bands in the absorption spectra of the solutions (Table 1), we tentatively suggest that this generally applicable reaction produces the desired compounds.

TABLE 1

SPECTROSCOPIC DATA FOR ORGANOMETALLIC NITROSO DERIVATIVES

Compound		Absorption spectra[a]		
		ν(N=O)(cm^{-1})	*n*–π*(O)(nm)	*n*–π*(N)(nm)
Me_3CNO[12]	(I)	1630	298	678
Me_3SnNO	(II)	1590	362	626
Ph_3CNO[13]	(III)	1640		*ca.* 710
Ph_3SiNO	(IV)	1590		*ca.* 715
Ph_3GeNO	(V)	1595		*ca.* 715
Ph_3SnNO	(VI)	1590		*ca.* 715
Ph_3PbNO	(VII)	1595		*ca.* 715
$(MeSi)_3SiNO$	(VIII)	Not measured		*ca.* 715
$Ph_2MeSiNO$	(IX)	1590		*ca.* 715

[a] Measured below −25°.

The products are thermally unstable in solution; in each case the solutions decolourise when warmed above *ca.* −10°, decomposition being accompanied by loss of the band near 1590 cm^{-1} and by evolution of an unidentified gas. Hydrolysis of the resultant pale yellow solutions provides products of the type $\geqslant$MOH and/or $\geqslant$M–O–M$\leqslant$. The absence of compounds of the type $\geqslant$MH in the hydrolysis product suggests that the metallic lithium reagent is consumed quantitatively during reaction with nitrosyl chloride. It is noteworthy however that triphenyltin chloride was isolated as one product from the decomposition of (VI) suggesting that the lithium reagent may be converted* to the chloride as well as to Ph_3SnNO; clearly the observed decomposition products in all cases may arise from two sources.

One feature of interest in the IR spectra is the shift to higher wavelength of the N=O stretching frequency compared with the organic analogues; this trend is parallel-

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* In our hands conversion from Ph_3SnCl/Li to Ph_3SnLi has been high (*cf.* ref. 17).

ed by the behaviour[14] of acyl and aroyl derivatives of group IV organometallic compounds. The UV and visible absorption spectra show remarkable trends: on the basis of Wests[7] approach the hypsochromic shift in the n–π^*(N) band of (II) relative to (I) can be rationalised on the basis that interaction of the metal d-orbitals is greater with the n-level than with π^*; the corresponding data for (IV)–(VII), however, suggest that this approach may be invalid and that induction by the metal atom may be a critical factor. The bathochromic shift in the n–π^*(O) band of (II) is similar to the situation in the analogous ketones.

We are presently attempting to obtain definitive chemical evidence for the presence of these compounds but our initial efforts to isolate adducts from 2+2 cycloaddition reactions or from insertion reactions into the Sn–N bond of (II) and (VI) have been unsuccessful.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen. Ph_3SiLi[15], Ph_3GeLi[16], Ph_3SnLi[17], Ph_3PbLi[17], Me_3SnLi[18], $(Me_3Si)_3SiLi$[19], and $Ph_2MeSiLi$[15] were prepared by literature methods. In all the reactions a solution of 5% nitrosyl chloride[20] in THF was added dropwise to a stirred 3% solution of the lithium reagent in THF at −78°. Absorption spectra were measured below −25° under anhydrous conditions.

ACKNOWLEDGEMENT

We thank the S.R.C. for a research grant (to J.J.), Midland Silicones for a gift of diphenyldichlorosilane, and Professor G. J. M. van der Kerk for gifts of triphenylchlorogermane and trimethyltin chloride.

REFERENCES

1 (a) A. G. Brook, *J. Amer. Chem. Soc.*, 79 (1957) 4373;
(b) G. J. D. Peddle, *J. Organometal. Chem.*, 14 (1968) 139.
2 J. S. Thayer and R. West, *Inorg. Chem.*, 3 (1964) 406.
3 J. S. Thayer and R. West, *Inorg. Chem.*, 3 (1964) 889.
4 C. Krüger and U. Wannagat, *Z. Anorg. Allg. Chem.*, 326 (1964) 288, 296, 304.
5 *Chem. Eng. News*, Aug. 5th (1968), p. 39: description of work by N. Wiberg *et al.*
6 Lui-Heung Chan and E. G. Rochow, *J. Organometal. Chem.*, 9 (1967) 231.
7 R. West, *J. Organometal. Chem.*, 3 (1965) 314.
8 F. Agolini, S. Klemenko, I. G. Csizmadia and K. Yates, *Spectrochim. Acta, Part A*, 24 (1968) 169.
9 B. G. Gowenlock and W. Lüttke, *Quart. Rev. (London)*, 12 (1958) 321.
10 B. Oddo, *Gaz. Chim. Ital.*, 39 (1909) 659.
11 E. Robson, J. M. Tedder and D. J. Woodcock, *J. Chem. Soc., C*, (1968) 1324.
12 W. D. Emmons, *J. Amer. Chem. Soc.*, 79 (1957) 6522.
13 W. Schlenk, L. Mair and C. Bornhardt, *Ber.*, 44 (1911) 1169.
14 A. G. Brook, *Advan. Organometal. Chem.*, 7 (1968) 95.
15 H. Gilman, D. J. Peterson and D. Wittenberg, *Chem. Ind. (London)*, (1958) 1479.
16 H. Gilman and C. W. Gerow, *J. Amer. Chem. Soc.*, 77 (1955) 4675.
17 H. Gilman, O. L. Marrs and See-Yuen Sim, *J. Org. Chem.*, 27 (1962) 4232.
18 C. Tamborski, F. E. Ford and E. Soloski, *J. Org. Chem.*, 28 (1963) 237.
19 H. Gilman and C. L. Smith, *J. Organometal. Chem.*, 14 (1968) 91.
20 C. C. Addison and R. Thomson, *J. Chem. Soc.*, (1949) 5218.