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METAL-YLIDE COMPLEXES: MERCURY(II), CADMIUM(II), COBALT(II), AND NICKEL(II) COMPLEXES OF AMBIDENTATE SULFONIUM YLIDES *

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Summary

The mercury(II), cadmium(II), cobalt(II) and nickel(II) halide complexes with stable sulfur ylides have been prepared from phenacylidenedimethylsulfurane, 4-chlorophenacylidenedimethylsulfurane, 4-methylphenacylidenedimethylsulfurane, and 4-methoxyphenacylidenedimethylsulfurane. The presence of the sulfonium ions as the non coordinated counter ions is confirmed by IR and NMR data. The ν(C=O) frequencies of the complexes are high relative to those of free ylides and approach those of the completely protonated onium salts, indicating that coordination is via the methine carbon atoms.

Introduction

Although the synthetic applications of ylides are well known in organic chemistry [1–6], only a few metalations of these ylides, and in particular of sulfonium ylides, have been reported, despite the fact that the ylides are powerful nucleophilic reagents and provide versatile ligands for metals in their various oxidation states, and form some useful chelates and complexes [7–10]. The few such studies carried out have shown a great deal of potentials due to the marked stability of the metal ylide complexes. We thus decided to synthesize a series of transitional metal halide complexes with various sulfur ylides, and we describe below the preparation of some carbonyl-stabilized sulfur ylides and their use as ligands for various metals, with the objective of examining the coordination behaviour of the ylides and studying the configuration of the complexes.

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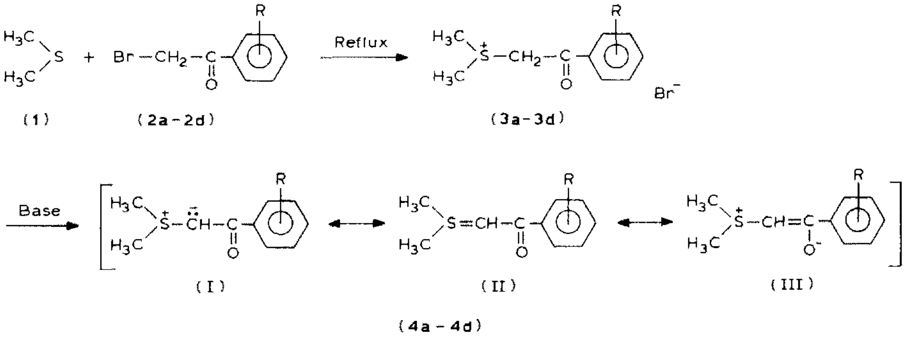
Results and discussion

Dimethyl sulfide (**1**) reacted with phenacyl bromide (**2a**), 4-chlorophenacyl bromide (**2b**), 4-methylphenacyl bromide (**2c**), and 4-methoxyphenacyl bromide (**2d**) at reflux temperature to give the corresponding phenacyldimethylsulfonium bromides (**3a**–**3d**). The sulfonium salts **3a**–**3d** on treatment with aqueous sodium hydroxide gave the phenacylidenedimethylsulfuranes **4a**, **4b** and **4d** as solids and **4c** as a yellow oil (Scheme 1). The identification of the sulfonium salts and their ylides was based on the IR and NMR spectral data (Table 1).

SCHEME 1



(2, 3 and 4 a, R = H, b, R = 4-Cl, c, R = 4-CH_3, d, R = 4-OCH_3)

The reaction of the ylides **4a**–**4d**, with various transition metal halides (MX_2, where M = metal and X = halogen) (**5a**–**5q**) in methanol gave 53–68% yields of the ylide metal halide complexes (**6a**–**6q**) $[M_2(\text{Ylide})_2X_4]$, presumably containing bridging X^- group (Scheme 2). Electron-donating substituents of the phenyl ring of the sulfonium ylides increased the ease of the complex formation as judged by the yields of the products (**6a**–**6q**) (Table 2). The reaction seemed to have proceeded via intermediate ylide carbanion. The sulfonium ylides used here may be represented by the canonical structures I–III (Scheme 1), and the values of the carbonyl stretching frequencies observed for the ylides **4a**–**4d** suggest an important contribution of enolate structure III, lone pair of electrons formally on the ylide carbanion being considerably delocalized. The ylides thus have two potential coordination sites towards metal halide; coordination through the carbonyl oxygen would result in a low frequency shift of ν(C=O), owing to an increased enolate ion character (cf. the form III) coordination through the nucleophilic methine carbon would result in a high frequency shift because of increased carbonylcharacter (cf. the form I). The

SCHEME 2

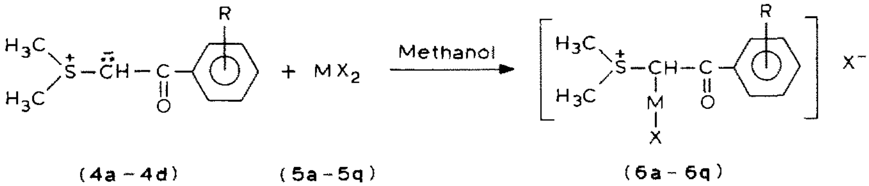


TABLE 1

IR AND NMR SPECTRAL DATA FOR **3**, **4a–4d** AND **6a–6q**

Product	IR data (KBr) ν (cm^{-1})				^{1}H NMR data (CDCl$_3$) δ(ppm)	
	Aromatic C–H stretching vibrations	C=O	C–S	C–M	Aliphatic H	Aromatic H
3a	3000	1670	820	–	–	–
3b	2960	1680	810	–	–	–
3c	2990	1680	820	–	2.33 S, CH$_3$; 3.36 S, CH$_3$; 4.2 S, CH$_2$	7.00–8.12m
3d	3010	1690	830	–	2.00 S, CH$_3$; 3.50 S, CH$_2$; 3.70 S, OCH$_3$	6.50–8.20m
4a	2950	1600	840	–	2.97 S, CH$_3$; 4.33 S, CH	7.24–7.90m
4b	2900	1620	860	–	–	–
4c	2980	1610	850	–	–	–
4d	2950	1580	850	–	–	–
6a	3410	1665	780	720	–	–
6b	3300	1665	810	710	–	–
6c	3600	1610	800	680	–	–
6d	3320	1640	800	690	–	–
6e	3400	1625	810	700	–	–
6f	3400	1630	840	700	–	–
6g	3410	1635	820	720	–	–
6h	3500	1665	850	740	–	–
6i	3400	1670	800	710	–	–
6j	3500	1620	810	720	–	–
6k	3600	1620	800	730	–	–
6l	3400	1625	830	760	–	–
6m	3400	1630	840	740	–	–
6n	3600	1620	790	730	2.30 S, CH$_3$; 4.20 S, CH$_2$	6.20–8.40m
6o	3500	1620	810	750	–	–
6p	3550	1664	820	720	–	–
6q	3500	1660	810	730	–	–

ν(C=O) bands of the complexes were in fact formed at higher frequencies than those of the original ylides, and so the coordination is through the methine carbon. The NMR data were also in accordance with the expectation. Although the analytical data obtained for the adducts were generally in good agreements with the indicated formulations, they did not unequivocally rule out the presence of small amounts of other salts, which might be expected in view of the high halide mobility likely encountered in these systems.

The anion exchange method confirmed that the complexes were 1/1 adducts. Except for **6a** [11] the metal ylide complexes, compounds **6** are new. (Table 2).

Experimental

Melting points were determined on a Gallenkaamp apparatus and are uncorrected. The NMR spectra (CDCl$_3$) were recorded on a Varian A60 spectrometer

TABLE 2

STRUCTURE AND PHYSICAL PROPERTIES OF METAL YLIDE COMPLEXES (**6a**–**6q**)

Product	M	X	R	M.p. (°C)	Yield (%)	Elemental analysis (Found (Calcd) (%)) C	H	X
6a	Hg	Cl	H	194–195	53	26.81 (26.81)	2.18 (2.65)	15.99 (15.12)
6b	Hg	Br	H	180–181	61	22.34 (22.19)	2.28 (2.21)	29.81 (29.59)
6c	Cd	Cl	H	197–198	57	33.05 (33.02)	3.36 (3.30)	19.59 (19.53)
6d	Ni	Cl	H	165(dec.)	57	38.78 (39.74)	3.39 (3.87)	22.98 (22.92)
6e	Co	Cl	H	158–159	54	39.73 (39.31)	4.21 (3.87)	23.88 (23.43)
6f	Hg	Cl	4-CH_3	200(dec.)	64	28.34 (23.38)	3.11 (3.01)	15.82 (15.26)
6g	Hg	Br	4-CH_3	183–184	66	23.88 (23.82)	2.51 (2.52)	28.91 (28.88)
6h	Cd	Cl	4-CH_3	265(dec.)	58	34.99 (34.97)	3.80 (3.70)	18.99 (18.81)
6i	Cd	I	4-CH_3	140–141	55	23.33 (23.55)	2.61 (2.49)	45.74 (45.32)
6j	Ni	Cl	4-CH_3	160(dec.)	60	40.80 (40.77)	4.35 (4.32)	21.98 (21.93)
6k	Co	Cl	4-CH_3	210–211	53	40.76 (40.74)	4.38 (4.32)	21.96 (21.91)
6l	Hg	Cl	4-OCH_3	178–179	68	27.13 (27.44)	2.98 (2.91)	14.80 (14.76)
6m	Hg	Br	4-OCH_3	180–181	66	23.67 (23.15)	2.45 (2.40)	28.87 (28.38)
6n	Cd	Cl	4-OCH_3	260(dec.)	60	33.21 (33.55)	3 67 (3.54)	18.45 (18.05)
6o	Cd	I	4-OCH_3	170–171	62	27.71 (27.70)	2.86 (2.93)	53.66 (53.31)
6p	Hg	Cl	4-Cl	171–172	58	26.67 (26.63)	2.41 (2.44)	15.81 (15.75)
6q	Hg	Br	4-Cl	151–155	55	22.44 (22.23)	2.08 (2.03)	29.67 (29.65)

using TMS as internal standard. The IR spectra were recorded on a Perkin–Elmer Infracord instrument. The anion exchange was carried out on a Cephadex Column. All the reactions were carried out under nitrogen.

*Synthesis of metal–ylide complexes (**6a**–**6q**); general procedure:*

A solution of the metal halide (**5a**–**5q**) (1.0 mmol) in methanol (20 ml) was added dropwise to a solution of the sulfurane (**4a**–**4d**) (2.0 mmol) in methanol (20 ml). Immediately after the complete addition a precipitate rapidly began to form. The mixture was stirred for a further 2 h at room temperature, and the solid was then filtered off, washed with methanol and diethyl ether, and dried in vacuo over calcium sulfate.

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