

## Metal-Ylide Complexes: Mercury(II), Cadmium(II) & Palladium(II) Complexes of Ambidentate Sulphonium Ylides

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Synthesis of Hg(II), Cd(II) and Pd(II) halide complexes with stable sulphur ylides, phenacylidene dimethylsulphurane and 4-methoxyphenacylidene dimethylsulphurane is described. The function of sulphonium group as the non-coordinated counter ion is supported by IR and NMR data. The  $\nu$  (C=O) bands of the complexes are higher than those of free ylides and approach those of the completely protonated onium salts. This indicates coordination via methine carbon atom. The structures of the complexes have been elucidated on the basis of elemental analyses, anion exchange and IR and NMR data.

Although synthetic applications of ylides are well known<sup>1-6</sup>, only a few metallation reactions of ylides, in particular of sulphonium ylides, have been reported. This is despite the fact that the ylides, being strong nucleophilic reagents, may be used as versatile carbon donor ligands for metals in different oxidation states<sup>7-10</sup>. Preliminary studies have shown promise in this respect since the resulting metal ylide complexes have been found to be stable. Prompted by this, we have extended our preliminary studies to synthesise a

series of transition metal halide complexes with sulphur ylides. In the present note, we report the generation and reaction of carbonyl stabilized sulphur ylides as ligands for various metal ions.

Dimethyl sulphide (1) on reaction with phenacyl bromide (2a), and 4-methoxyphenacyl bromide (2b) at reflux temperature afforded phenacyl dimethylsulphonium bromide (3a) and 4-methoxyphenacyl dimethylsulphonium bromide (3b) respectively (Scheme 1). The sulphonium salts 3a-b on treatment with aqueous sodium hydroxide afforded phenacylidene dimethylsulphurane (4a) in 94% yield (m.p. 57-58°C) and 4-methoxyphenacylidene dimethylsulphurane (4b) in 93% yield (m.p. 90-91°C).

Melting points reported are uncorrected. NMR spectra (CDCl<sub>3</sub>) were run on a Varian EM-390 spectrometer using TMS as an internal standard. IR spectra were recorded on a Perkin Elmer 298 infrared spectrophotometer. Cephadex column was used for anion exchange. All the reactions were carried out under nitrogen atmosphere.

### Synthesis of metal-ylide complexes: general procedure

A solution of metal halide (1.0 mmol) in methanol (20.0 ml) was added dropwise to a solution of sulphurane (2.0 mmol) in methanol (20.0 ml). Immediately after the complete addition, a precipitate started forming which was further stirred for 2 hr at room temperature and then isolated by suction filtration. After washing with methanol and diethyl ether, it was dried *in vacuo* over CaSO<sub>4</sub> (Table 1).

Table 1—Yields and Analytical Data of Metal Ylide Complexes (6a-f)

Product M <sub>2</sub> (Ylide) <sub>2</sub> X <sub>4</sub>	M	X	R	m.p. (°C)	Yield (%)	Found (Calc.), %		
						C	H	X
6a	Hg	Cl	H	194-95	53	26.81 (26.81)	2.18 (2.65)	15.99 (15.12)
6b	Hg	I	H	170-72	61	18.81 (18.91)	1.88 (1.89)	40.00 (40.03)
6c	Cd	I	H	190(d)	58	21.92 (21.96)	2.22 (2.19)	46.44 (46.48)
6d	Pd	Cl	H	185(d)	64	33.69 (33.67)	3.31 (3.36)	19.99 (19.92)
6e	Pd	Cl	4-OCH <sub>3</sub>	188(d)	66	33.97 (34.16)	3.12 (3.62)	18.82 (18.37)
6f	Hg	I	4-OCH <sub>3</sub>	165-67	57	19.04 (19.84)	1.82 (2.10)	37.68 (38.22)

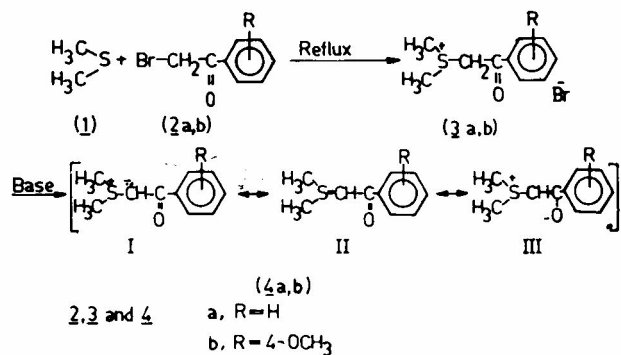
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Table 2—IR and NMR Spectral Data of 3,4 (a,b) and 6 (a-f)

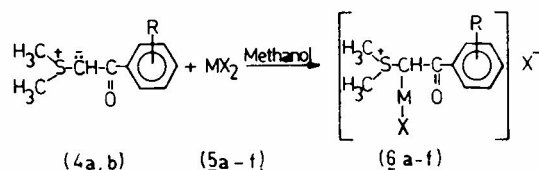
Product	IR Data (KBr) (cm <sup>-1</sup> )				<sup>1</sup> H NMR Data: δ (ppm)	
	νC-H (aromatic)	νC=O	νC-S	νC-M	Aliphatic H	Aromatic H
3a	3000	1670	820	—	2.94(s), CH <sub>3</sub> ; 5.75(s), CH <sub>2</sub>	6.90-8.20 m
3b	3010	1690	830	—	2.00(s), CH <sub>3</sub> ; 5.50(s), CH <sub>2</sub> ; 3.70(s), OCH <sub>3</sub>	6.50-8.20 m
4a	2950	1600	840	—	2.97(s), CH <sub>3</sub> ; 4.33(s), CH	7.24-7.90 m
4b	2950	1580	850	—	—	—
6a	2970	1650	790	700	3.00(s), CH <sub>3</sub> ; 4.80(s), CH	7.20-8.40 m
6b	2980	1630	810	720	2.92(s), CH <sub>3</sub> ; 4.60(s), CH	7.00-8.10 m
6c	3000	1640	840	720	—	—
6d	2970	1620	810	700	—	—
6e	2950	1610	830	720	2.60(s), CH <sub>3</sub> ; 3.80(s), OCH <sub>3</sub> ; 5.20(s), CH	6.80-8.40 m
6f	2970	1620	830	710	2.92(s), CH <sub>3</sub> ; 3.90(s), OCH <sub>3</sub> ; 4.80(s), CH	6.70-7.90 m

The structural assignment of sulphonium salts and their ylides has been made on the basis of IR and NMR data (Table 2). The reaction of ylides **4a-b** in methanol medium with a variety of transition metal halides (**5a-f**) afforded metal halide complexes of ylides (**6a-f**) in 53-66% yields. The complexes have the general formula M<sub>2</sub>(Ylide)<sub>2</sub>X<sub>4</sub> presumably involving bridging X<sup>-</sup> group. It was found that the electron donating substituents in the phenyl ring of the sulphonium ylides accelerated the complex formation reaction because of the enhanced electron density at methine carbon of ylide, and in these cases the yields of the products were also higher (Table 1). The reactions seem to proceed via the formation of ylide carbanion as the intermediate. The sulphonium ylides used here may be represented by the canonical structures I-III (Scheme 1) and the



carbonyl stretching bands observed for the ylides **4a-b** suggest an important contribution of enolate structure III, the lone pair on the ylide carbanion remaining considerably delocalised. The ylide has two coordination sites, i.e., carbonyl oxygen and methine carbon. Coordination through the carbonyl oxygen would have decreased ν(C=O), and coordination through the nucleophilic methine carbon would have increased νC=O. The participation of lone pair at the

methine carbon atom in the coordination with metal atom can be established on the basis of IR spectra of ylide complexes **6a-f**. These showed a sharp band in the region 1620-1650 cm<sup>-1</sup> while the precursor ylides (**4a-b**) exhibited a strong band in the region 1580-1600 cm<sup>-1</sup> (Table 2). The M-X group, which was introduced into the sulphurane to form a metallated sulphonium salt, raised the frequency of the carbonyl group relative to that of the free ylide because of the conjugation between the M-C and C=O bonds in addition to the increase due to contributing structures I and II. Therefore, coordination of metal halide through the methine carbon site is inferred. This observation is in agreement with that of Koezuka *et al.*<sup>10</sup> who observed that a peak at 1578 cm<sup>-1</sup> for ν(C=O) of methyl phenyl sulphonium phenacylide (SY) was raised to 1620-1633 cm<sup>-1</sup> in its palladium halide complexes, PdX<sub>2</sub>(SY)<sub>2</sub>. The NMR data also corroborate this view<sup>10</sup> for the reported ylide-metal complexes e.g. PdCl<sub>2</sub>(PPhMe<sub>2</sub>) (SY) [values in δ (ppm)]; ylide CH, 5.08; CH<sub>3</sub>, 3.0, 2.71; *ortho*-protons of phenyl ring, 8.2. PdCl<sub>2</sub>(PMe<sub>3</sub>) (PY): ylide-CH, 5.01; CH<sub>3</sub>, 2.85; *ortho* protons of phenyl ring, 8.3. It was observed that though the analytical data obtained for the compounds were, in general, in good agreement with the indicated formulations, they did not unequivocally rule out the presence of small amounts of other mixed salts, especially in view of the



high halide mobility anticipated in these systems. Elemental analyses and ion exchange techniques using sodium nitrate and aqueous methanol indicated that the complexes were 1:1 adducts (Scheme 2). All the metal ylide complexes except 6a<sup>11</sup> are new (Table 2).

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