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ISOLATION OF PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF THE $\overset{+}{S}$-$\overset{-}{N}$ YLIDE

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Several new stable ylide complexes formed between palladium(II) and platinum(II) dihalides and S,S-dimethyl-N-benzoyl- or S,S-dimethyl-N-p-methylbenzoylsulfilimine were isolated and the coordination through the ylide-nitrogen atom is concluded.

Introduction

A few studies on metal complexes containing coordinating ylides have been reported.[1-4] Most recently we have isolated several stable methylphenylsulfonium p-chlorophenacylide $[(CH_3)C_6H_5\overset{+}{S}\overset{-}{C}HC(O)C_6H_4Cl\text{-}p]$ complexes with palladium(II) halides and the coordination to the metal via the methine carbon of the ylide has been concluded on the basis of IR and PMR spectra of the complexes.[5] It is of interest to investigate metal complexes of $\overset{+}{S}$-$\overset{-}{N}$ ylides which are isoelectronic with the $\overset{+}{S}$-$\overset{-}{CH}$ ylide. In this paper will be reported an isolation of stable palladium(II) and platinum(II) complexes of S,S-dimethyl-N-benzoyl- or S,S-dimethyl-N-p-methylbenzoylsulfilimine.

Experimental

S,S-Dimethyl-N-benzoyl- (Y_H) and S,S-dimethyl-N-p-methylbenzoylsulfilimines (Y_{CH_3}) were prepared according to the literature.[6]

To an ethanol solution of palladium sodium chloride was added an excess amount of Y_H in ethanol, and orange-yellow precipitates ($PdCl_2.2Y_H$) obtained were washed with ethanol several times, and dried under reduced pressure. To a suspension of the bis-ylide complex in acetonitrile was added an acetonitrile solution containing an equimolar triphenylphosphine and the solution was refluxed to give a homogeneous solution. The solution was concentrated and allowed to stand at -10°～0°C. The orange-yellow crystals ($PdCl_2.(Y_H)(P(C_6H_5)_3)$) obtained were recrystallized from a mixture of petroleum ether (bp 30°～50°C) and dichloromethane. The corresponding Y_{CH_3} complexes and bis(ylide)palladium dibromide complexes were prepared in a similar way.

Bis(benzonitrile)platinum dichloride and more than twice molar amounts of Y_H were refluxed in 1,2-dichloroethane. The yellow crystals ($PtCl_2.2Y_H$) obtained were filtered, washed with dichloromethane and acetone, and dried under reduced pressure. The corresponding Y_{CH_3} complex was analogously prepared.

The properties and analytical data of the complexes are summarized in Table I.

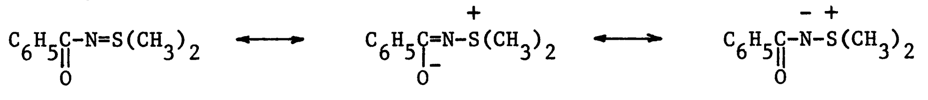
Table I. Melting points, elemental analyses and molecular weights of the ylide complexes.

Complexes	m.p. (°C)	C (%) Found (Calcd)	H (%) Found (Calcd)	N (%) Found (Calcd)	M.w.[a] Found (Calcd)
$PdCl_2.2Y_H$	180-	39.31	4.38	5.20	
	182.5	(40.03)	(4.11)	(5.19)	
$PdBr_2.2Y_H$	183-	33.99	3.73	4.34	
	184.5	(34.38)	(3.53)	(4.46)	
$PdCl_2.(Y_H)(P(C_6H_5)_3)$	154-	51.73	4.29	2.39	586
	156	(52.23)	(4.22)	(2.26)	(621)
$PtCl_2.2Y_H$	216-	34.12	3.49	4.59	
	218.5	(34.40)	(3.53)	(4.46)	
$PdCl_2.2Y_{CH_3}$	167.5-	41.60	4.44	4.78	
	170	(42.30)	(4.62)	(4.92)	
$PdBr_2.2Y_{CH_3}$	173-	36.30	4.06	4.17	
	174.5	(36.58)	(3.99)	(4.27)	
$PdCl_2.(Y_{CH_3})(P(C_6H_5)_3)$	158-	52.76	4.45	2.43	563
	159.5	(52.97)	(4.45)	(2.21)	(635)
$PtCl_2.2Y_{CH_3}$	227-	36.34	4.00	4.46	
	228.5	(36.59)	(3.99)	(4.27)	

a: Measured in chloroform, in concentrations (～7 x 10^{-3} mole/l).

Results and Discussion

The $\overset{+}{S}\text{-}\overset{-}{N}$ ylide is stabilized by the following delocalization of the negative charge.[7)]



$$C_6H_5\underset{\underset{\displaystyle O}{\|}}{C}\text{-}N=S(CH_3)_2 \longleftrightarrow C_6H_5\underset{\underset{\displaystyle O^-}{|}}{C}=N\text{-}\overset{+}{S}(CH_3)_2 \longleftrightarrow C_6H_5\underset{\underset{\displaystyle O}{\|}}{C}\text{-}\overset{-}{N}\text{-}\overset{+}{S}(CH_3)_2$$

(A) (B) (C)

The ν(C=O) of the free ylides observed at a very low frequency (ca. 1535 cm^{-1}) indicates an important contribution of the canocical structure (B). As is summarized in Table II, the ν(C=O) frequency shifts by ca. 70 cm^{-1} to higher frequencies upon coordination to the metals, suggesting the coordination of the ylide via the nitrogen atom. This result is compared with the frequency shift of ν(C=O) of methylphenylsulfonium p-chlorophenacylide upon complex formation.[5)] In view of the ν(M-X) frequencies shown in Table II being close to those of some square planar palladium(II) and platinum(II) complexes,[8,9)] we propose that the bis(ylide)palladium dibromide and the (ylide)(triphenylphosphine)palladium dichloride have a trans-configuration and the platinum complexes have a cis-one around the

Table II. IR[a] and PMR[b] data of ylides and their metal complexes

Compounds	ν(C=O)	ν(M-X)	Compounds	ν(C=O)	ν(M-X)
Y_H[c]	1539	——	Y_{CH_3}[d]	1532	——
$PdCl_2.2Y_H$	1610	343, ?[e]	$PdCl_2.2Y_{CH_3}$	1604	330, ?[e]
$PdBr_2.2Y_H$	1608	260	$PdBr_2.2Y_{CH_3}$	1604	261
$PdCl_2.(Y_H)(P(C_6H_5)_3)$	1608	348	$PdCl_2.(Y_{CH_3})(P(C_6H_5)_3)$	1610	350
$PtCl_2.2Y_H$	1611	326, ?[e]	$PtCl_2.2Y_{CH_3}$	1610	339, 326

Compounds	δ(S-CH_3)	δ(o-H)	δ(m-H or m,p-H)	δ(p-H)
Y_H	2.76	8.05	7.38	——
$PdCl_2.(Y_H)(P(C_6H_5)_3)$	3.28	8.25	f	——
Y_{CH_3}	2.73	7.96	7.16	2.35
$PdCl_2.(Y_{CH_3})(P(C_6H_5)_3)$	3.36	8.22	f	2.46

a: Measured in Nujol mulls, in cm^{-1}. b: Measured in dichloromethane relative to tetramethylsilane as the internal standard, in ppm. c: $Y_H = C_6H_5C(O)\overset{-}{N}\overset{+}{S}(CH_3)_2$. d: $Y_{CH_3} = p\text{-}CH_3C_6H_4C(O)\overset{-}{N}\overset{+}{S}(CH_3)_2$. e: Obscured by ligand bands. f: Obscured by phenyl proton signals of triphenylphosphine.

metal atom, although the configuration of bis(ylide)palladium dichloride complexes is not evident.

The bis-ylide complexes are too insoluble in common organic solvents to measure PMR spectra.10) In the PMR spectra of (ylide)(triphenylphosphine)palladium complexes in dichloromethane the S-CH_3 and phenyl-ring proton signals occur at lower fields than those of the free ylides, which is due to decrease of electron densities on the ylide upon coordination. In addition, weak proton signals due to dissociated ylide are observed in the solution, whose intensity decreases with lowering temperature. This partial dissociation is also concluded from the molecular weight determination.

References

1) N. A. Nesmeyanov, V. M. Novikov, and O. A. Reutov, J. Organometal. Chem., 4, 202 (1965).

2) P. A. Arnup and M. C. Baird, Inorg. Nucl. Chem. Letters, 5, 65 (1968).

3) J. Buckle, P. G. Harrison, T. J. King, and J. A. Richards, Chem. Comm., 1104 (1972).

4) J. Buckle and P. G. Harrison, J. Organometal. Chem., 49, C17 (1973).

5) H. Koezuka, G. Matsubayashi, and T. Tanaka, in contribution in Inorg. Chem.

6) A. J. Papa, J. Org. Chem., 35, 2837 (1970).

7) H. Kise, G. F. Whitfield, and D. Swern, Tetrahedron Letters, 21, 1761 (1971).

8) J. R. Ferrano, Low-frequency Vibrations of Inorganic and Coordination Compounds, p. 165, Plenum Press, N. Y. (1971).

9) J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, Inorg. Chem., 11, 1280 (1972).

10) Bis-ylide complexes are soluble in dimethylsulfoxide, where the ylide molecules are, however, substituted completely by solvent molecules.

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