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Preparations and Properties of the $\overset{-}{N}–\overset{+}{S}$ and $\overset{-}{N}–\overset{+}{N}$ Ylide Complexes with Palladium(II) and Platinum(II) Dichlorides

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Palladium(II) and platinum(II) dichloride complexes with the stable sulfilimine ($PhC(O)\overset{-}{N}\overset{+}{S}Me_2 = Y_S$) or aminimide ($PhC(O)\overset{-}{N}\overset{+}{N}Me_3 = Y_N$), $MCl_2(L)(L')$ ($M = Pd, Pt; L = Y_S, Y_N; L' = PPh_3, PPh_2Me, PPhMe_2$) were prepared. The carbonyl stretching bands of Y_S and Y_N shift to high frequencies upon complex formation, indicating the coordination of Y_S or Y_N to the metal through the negatively charged nitrogen atom. All the complexes are demonstrated to have a trans-configuration around the metal atom. Infrared and ^1H NMR spectra reveal that the coordination bond in the Y_S complexes is stronger than that in the Y_N ones, and that the platinum(II) complexes are more stable than the palladium(II) ones. In addition, the coordination abilities of both Y_S *and* Y_N *are shown to be weaker than those of ylides having a* $\overset{-}{C}H–\overset{+}{X}$ *skeleton.*

Introduction

From the viewpoint that a negatively charged ylide carbon has a coordinating ability to metal ions, reactions of ylides with metal ions have been investigated by many workers.

Recently, the authors reported the preparation and properties of palladium(II) and platinum(II) dihalide complexes with some $\overset{-}{C}H–\overset{+}{X}$ (X = S, N, P, As) ylides, which involve the ylide carbon–metal bond.[1,2] Compounds with a $\overset{-}{N}–\overset{+}{X}$ moiety are isoelectronic with the $\overset{-}{C}H–\overset{+}{X}$ ylide, and they are expected to coordinate through the nitrogen toward metal ions. This expectation was evidenced from our recent studies on some stable S,S-dimethyl-N-benzoylsulfilimine (Y_S) and the analogous imine complexes of palladium(II) and platinum(II) dihalides, $MX_2(Y_S)_2$ and $MX_2(Y_S)(L)$ (M = Pd, Pt; X = Cl, Br; L = PPh_3, Me_2SO).[3,4] Most recently, McWhinnie *et al.*[5] reported several metal complexes of the $\overset{-}{N}–\overset{+}{N}$ ylides.

The X-ray studies of the $\overset{-}{C}H–\overset{+}{X}$ ylide complexes have elucidated that the ylide carbon undergoes a rehybridization from sp^2 to sp^3 upon coordination to form a metal–carbon σ-bond.[6–8] On the other hand, the imine nitrogen atom in the complexes of $\overset{-}{N}–\overset{+}{X}$ ylides is in a sp^2 hybrid, which is assumed not to change upon complexation. Thus, it is of interest to study the coordination of $\overset{-}{N}–\overset{+}{X}$ ylides to metal ions in comparison with the $\overset{-}{C}H–\overset{+}{X}$ ylides.

This paper reports the preparations of several S,S-dimethyl-N-benzoylsulfilimine (Y_S) and trimethylamine-benzimide (Y_N) complexes with palladium(II) and platinum(II) dichlorides and their structures. The interaction between the ylides and the metal ions is also discussed on the basis of infrared and ^1H NMR spectra.

Experimental

Starting Materials

S,S-Dimethyl-N-benzoylsulfilimine ($PhC(O)\overset{-}{N}\overset{+}{S}Me_2 = Y_S$)[9] and trimethylamine-benzimide ($PhC(O)\overset{-}{N}\overset{+}{N}Me_3 = Y_N$)[10] were prepared according to the literature.

Preparation of Dichloro(tertiary phosphine)(S,S-dimethyl-N-benzoylsulfilimine)- and -(trimethylamine-benzimide)palladium(II)

The ylide (Y_S or Y_N, 0.75 mmol) was added to a suspension of bis(triphenylphosphine)dichloro-μ,μ′-dichlorodipalladium(II)[11] (0.25 mmol) in 1,2-dichloroethane (30 ml). The mixture was refluxed for about 3 hr to give an almost transparent solution. The solution was filtered and the filtrate was concentrated to about 10 ml under reduced pressure. Petroleum ether (*ca.* 20 ml) was added to the solution to give a precipitate of bis(triphenylphosphine)dichloro-μ,μ′-dichlorodipalladium(II). After the precipitate was filtered off, further additions of petroleum ether to the filtrate afforded orange crystals of $PdCl_2(PPh_3)(L)$ (75 and 55% yields for L = Y_S and Y_N, respectively). One molar 1,2-dichloroethane contained in the latter crystals was confirmed by ^{1}H NMR spectra. When the precipitation was performed in the presence of a large excess of Y_S or Y_N, $PdCl_2(PPh_3)(L)$ was directly obtained without precipitation of the dimeric chloro-bridged palladium complex. The Y_S complex was previously obtained by the reaction of $PdCl_2(Y_S)_2$ with PPh_3 in acetonitrile.[3]

The corresponding methyldiphenyl- and dimethylphenylphosphine complexes, $PdCl_2(L)(L')$ ($L = Y_S$, Y_N; $L' = PPh_2Me$, $PPhMe_2$) were similarly prepared by using appropriate phosphorus ligands in place of PPh_3 (60–70% yields). On the addition of petroleum ether to the resultant solution, however, no dimeric chloro-bridged palladium complex precipitated, probably because of its good solubility in petroleum ether.

Preparation of Dichloro(tertiary phosphine)(S,S-dimethyl-N-benzoylsulfilimine)- and -(trimethylamine-benzimide)platinum(II)

To a stirred suspension of bis(triphenylphosphine)-dichloro-μ,μ'-dichlorodiplatinum(II)[12] (0,25 mmol) in 1,2-dichloroethane (20 ml) was added a small excess of the appropriate ylide. The solution was filtered and the filtrate was evaporated to a volume of about 10 ml. Petroleum ether (*ca.* 30 ml) was added to the solution to give pale yellow crystals of $PtCl_2(PPh_3)(L)$ (54 and 57% yields for $L = Y_S$ and Y_N, respectively). The methyldiphenylphosphine and dimethylphenylphosphine analogs were prepared in the same way (60–85% yields).

The melting points and analytical data for the complexes are summarized in Table I.

Physical Measurements

Infrared, ^{1}H NMR spectra and molecular weights were measured as described previously.[1]

Results and Discussion

The imine Y_S may be stabilized by the delocalization of electronic charge on the nitrogen atom to the sulfur. This effect would be caused by means of d_π–p_π interaction, which is supported by analogy with a sulfilimine, $p\text{-}MePhSO_2\overset{-}{N}\overset{+}{S}Me_2$; the structure was determined by X-ray analysis.[13] On the other hand, in the aminimide Y_N there may be no such interaction between the onium group and the adjacent nitrogen atom. The X-ray crystallographic study[14] of Y_N showed that the $\overset{-}{N}$–$\overset{+}{N}$ bond length is essentially that of a single bond.

The electronic charges on the nitrogen atom of Y_N as well as Y_S are likely to be delocalized to the carbonyl group. This is evidenced by the occurrence of the $\nu(C{=}O)$ bands at 1539 cm^{-1} (Y_S) and 1557 cm^{-1} (Y_N),[15] which are fairly lower than those (1700 cm^{-1}) of common organic carbonyl compounds. Upon complex formation, however, the $\nu(C{=}O)$ band of the Y_S and Y_N ligands shifted to a higher frequency by 64–78 cm^{-1} and 46–57 cm^{-1} respectively, as shown in Table II. This fact confirms that Y_S and Y_N coordinate to the metal atom through the negatively charged nitrogen atom, as was mentioned in the previous paper.[3] In addition, the magnitude of the high frequency shifts of the $\nu(C{=}O)$ upon coordination would serve as a measure of the coordination ability of these ligands. It is therefore suggested that Y_S is a stronger ligand than Y_N. This is supported by the fact that the protonated ylides, S,S-dimethyl-N-benzoylsulfilimine hydrochloride[9] and 1-benzoyl-2,2,2-trimethylhydrazonium iodide[10] exhibit the $\nu(C{=}O)$ at 1700 and 1675 cm^{-1}, respectively. It is to be noted that the coordination shift of the $\nu(C{=}O)$ band in either Y_S or Y_N complexes is smaller than that of the corresponding $\overset{-}{C}H$–$\overset{+}{S}$ ylide complexes (130–140 cm^{-1}),[1,2]

TABLE I. Melting Points and Elemental Analyses of the Ylide–Metal Complexes.[a]

Complexes	M.p. (°C)	C % Found (Calcd)	H % Found (Calcd)	N % Found (Calcd)
$PdCl_2(PPh_3)(Y_S)$	159–160	52.07(52.23)	4.15(4.22)	2.29(2.26)
$PdCl_2(PPh_2Me)(Y_S)$	154–155	47.33(47.29)	4.37(4.33)	2.62(2.51)
$PdCl_2(PPhMe_2)(Y_S)$	120.5–122	41.07(41.11)	4.60(4.47)	2.84(2.82)
$PdCl_2(PPh_3)(Y_N)C_2H_4Cl_2$	194(dec.)	50.11(50.27)	4.60(4.64)	3.88(3.91)
$PdCl_2(PPh_2Me)(Y_N)$	196(dec.)	49.61(49.71)	4.96(4.90)	5.10(5.04)
$PdCl_2(PPhMe_2)(Y_N)$	143.5–145	43.64(43.79)	5.17(5.10)	5.66(5.67)
$PtCl_2(PPh_3)(Y_S)$	163–164	45.14(45.70)	3.52(3.69)	1.93(1.97)
$PtCl_2(PPh_2Me)(Y_S)$	147–148	40.56(40.81)	3.57(3.74)	2.24(2.16)
$PtCl_2(PPhMe_2)(Y_S)$[b]	141–142	34.91(34.88)	3.71(3.79)	2.33(2.39)
$PtCl_2(PPh_3)(Y_N)$	186.5–187	47.32(47.60)	3.95(4.14)	3.89(3.97)
$PtCl_2(PPh_2Me)(Y_N)$	175–176	42.55(42.87)	4.22(4.22)	4.32(4.35)
$PtCl_2(PPhMe_2)(Y_N)$[b]	138.5–141	37.03(37.12)	4.14(4.33)	4.73(4.81)

[a] Y_S: $PhC(O)\overset{-}{N}\overset{+}{S}Me_2$, Y_N: $PhC(O)\overset{-}{N}\overset{+}{N}Me_3$. [b] Molecular weights in chloroform: $PtCl_2(PPhMe_2)(Y_S)$, 544 (Calcd. 582); $PtCl_2(PPhMe_2)(Y_N)$ 498 (Calcd. 494).

TABLE II. Relevant Infrared Frequencies of the Ylide–Metal Complexes in Nujol Mulls, cm^{-1}.[a]

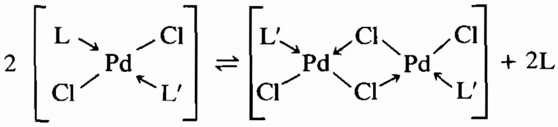
Complexes	ν(C=O)	ν(M–Cl)
Y_S	1539	
$PdCl_2(PPh_3)(Y_S)$	1608	350
$PdCl_2(PPh_2Me)(Y_S)$	1610	354
$PdCl_2(PPhMe_2)(Y_S)$	1603	354
$PtCl_2(PPh_3)(Y_S)$	1617	337
$PtCl_2(PPh_2Me)(Y_S)$	1617	337
$PtCl_2(PPhMe_2)(Y_S)$	1606	344
Y_N	1557	
$PdCl_2(PPh_3)(Y_N)$	1610	346
$PdCl_2(PPh_2Me)(Y_N)$	1611	343
$PdCl_2(PPhMe_2)(Y_N)$	1603	346
$PtCl_2(PPh_3)(Y_N)$	1614	337
$PtCl_2(PPh_2Me)(Y_N)$	1613	334
$PtCl_2(PPhMe_2)(Y_N)$	1607	331

[a] Y_S: $PhC(O)\overset{-}{N}\overset{+}{S}Me_2$; Y_N: $PhC(O)\overset{-}{N}\overset{+}{N}Me_3$.

suggesting the weaker coordination of Y_S and Y_N to the palladium(II) and platinum(II) than the $\overset{-}{C}H\text{–}\overset{+}{S}$ ylides. Table II also shows that the ν(C=O) frequency is somewhat higher in the platinum(II) complexes than in the palladium(II) analogs with a given ligand.

All the complexes exhibit only one metal–chlorine stretching band in the range 331–354 cm^{-1}, indicating a *trans*-configuration around the palladium or platinum atom. The ν(C=O) frequency of the $PPhMe_2$ complexes is lower than that of the corresponding PPh_2Me and PPh_3 complexes. This is consistent with the assumption that the *trans*-influence increases in the order PPh_3 < PPh_2Me < $PPhMe_2$.

The ^1H NMR spectra of the palladium complexes showed weak signals of the free ylides as well as those of the complexed ylides. At low temperatures the S–Me signal of the free ylide weakens in its intensity, while it becomes strong and broad with raising temperature. Finally, the S–Me signals merge at 86° C in chlorobenzene. Therefore, the complexes may be suggested to exist in the following equilibrium in solution. On the contrary, the platinum complexes of Y_S and Y_N exhibit no signal of the free ligand dissociated at room temperature. This is in agreement with the molecular weight determination, which indicated that $PtCl_2(PPhMe_2)(L)$ is monomeric in solution.



L = Y_S, Y_N; L' = PPh_3, PPh_2Me, $PPhMe_2$

Table III summarizes ^1H NMR data of Y_S, Y_N and their complexes in dichloromethane. The S–Me and N–Me signals shift to downfields upon complex formation. If the magnitude of these shifts is taken as a measure of the strength of the metal–nitrogen bond of the complexes, the Y_S complexes appear to be more stable than the Y_N ones, and the Pt–N bond is rather stronger than the Pd–N bond.

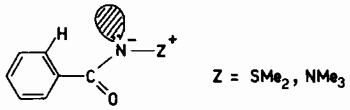
The *ortho*-proton signals of the phenyl ring of Y_S showed a small downfield shift (–0.13 ~ –0.25 ppm), and those of Y_N showed a slight upfield shift (0.02 ~ 0.17 ppm) upon complexation. The *ortho*-proton signals of free Y_S and Y_N are subject to the para-

TABLE III. ^1H NMR Parameters of the Ylide–Metal Complexes in Dichloromethane at 24° C.[a]

Complexes	Chemical Shifts (ppm)			Coupling Constants (Hz)	
	δ(S–Me or N–Me)	δ(*ortho*-H)	δ(P–Me)	$^2J(^{31}P\text{–}CH_3)$	$^3J(^{195}Pt\text{–}P\text{–}CH_3)$
$PhC(O)\overset{-}{N}\overset{+}{S}Me_2$ (= Y_S)	2.76	8.05			
$PdCl_2(PPh_3)(Y_S)$	3.26 (–0.50)	8.30 (–0.25)			
$PdCl_2(PPh_2Me)(Y_S)$	3.22 (–0.46)	8.28 (–0.23)	1.92	12.0	
$PdCl_2(PPhMe_2)(Y_S)$	3.18 (–0.42)	8.22 (–0.17)	1.70	12.8	
$PtCl_2(PPh_3)(Y_S)$	3.27 (–0.51)	8.21 (–0.16)			
$PtCl_2(PPh_2Me)(Y_S)$	3.26 (–0.50)	8.19 (–0.14)	1.87	11.7	33.2
$PtCl_2(PPhMe_2)(Y_S)$	3.22 (–0.46)	8.18 (–0.13)	1.67	11.8	32.8
$PhC(O)\overset{-}{N}\overset{+}{N}Me_3$ (= Y_N)	3.42	7.98			
$PdCl_2(PPh_3)(Y_N)$	3.81 (–0.39)	7.96 (+0.02)			
$PdCl_2(PPh_2Me)(Y_N)$	3.78 (–0.36)	7.92 (+0.06)	1.82	12.0	
$PdCl_2(PPhMe_2)(Y_N)$	3.76 (–0.34)	7.89 (+0.09)	1.57	12.6	
$PtCl_2(PPh_3)(Y_N)$	3.87 (–0.45)	7.85 (+0.13)			
$PtCl_2(PPh_2Me)(Y_N)$	3.86 (–0.44)	7.82 (+0.16)	1.81	11.2	32.3
$PtCl_2(PPhMe_2)(Y_N)$	3.83 (–0.41)	7.81 (+0.17)	1.56	11.7	32.0

[a] The values in parentheses are $\delta_{free} - \delta_{complexed}$.

magnetic anisotropy effect of the nitrogen atom located closely to the proton, as illustrated in (A).



(A)

This effect should decrease upon coordination of the ylide, because of the interaction between the nitrogen and metal atoms, which results in an upfield shift of the *ortho*-proton. On the other hand, the inductive effect of the metal would cause a downfield shift of the signals. These mutually opposite effects explain the observed small downfield or slightly upfield shift. The similar phenomenon was reported on the complexation of 2,2′-dipyridyl and picolinaldimines with metal ions.[16–18] It should be noted here that the upfield or downfield shift of the signals in the Y_S or Y_N complex is fairly small compared with the corresponding $\overset{-}{C}H\text{–}\overset{+}{S}$ complexes, in which a large downfield shift (–0.5 ~ –0.6 ppm) was detected. Thus, the ^1H NMR spectra also indicate that the coordination abilities of Y_S and Y_N are weaker than those of the $\overset{-}{C}H\text{–}\overset{+}{S}$ ylides.

The platinum(II) complexes at room temperature display the spin–spin coupling between the (P–)Me protons and the platinum nucleus, which may also serve as a measure of the *trans*-influence of the ylide ligands. The $^3J(^{195}Pt\text{–}P\text{–}CH_3)$ values obtained in the present complexes were 32.0–32.8 Hz, which are larger than the values in the analogous $\overset{-}{C}H\text{–}\overset{+}{X}$ (X = S, N, P, As) ylide complexes (23–25 Hz).[2] This indicates that the *trans*-influence of Y_S and Y_N is smaller than that of the $\overset{-}{C}H\text{–}\overset{+}{X}$ complexes. On the other hand, the S–Me and N–Me signals move to downfields with decreasing number of methyl groups on the phosphorus atom, indicating the same result of the *trans*-influence of the phosphorus ligands as suggested by the infrared spectra.

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