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Preparation and Properties of Pd(II) and Pt(II) Complexes of *N*-Picolinoyl-*S*,*S*-tetramethylenesulfilimine, *N*-Trimethylammoniopicolinamidate, and Related Ylides

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The reactions of *N*-picolinoyl-*S*,*S*-tetramethylenesulfilimine and *N*-trimethylammoniopicolinamidate with dichlorobis(benzonitrile)palladium(II) and dipotassium tetrachloroplatinate(II) afforded chelate complexes of formula MCl_2[Ylide]. The structures of the complexes were examined by IR and NMR spectroscopy, and determined as mononuclear complexes with ligands coordinated through two nitrogen atoms. A reverse relationship between pK_a values of the ylides and C=O stretching band frequency shifts on complex formation was found, and the nature of the coordination *via* ylidic nitrogen was discussed in terms of σ- and π-character of the ligands in the chelate complexes and several related bis-ylide complexes.

Carboxylic acid amides are anbidentate ligands and have potential coordination sites of nitrogen and carbonyl oxygen atoms. In most cases, they form complexes with a variety of Lewis acids *via* carbonyl oxygen in neutral media.[1] In alkaline media, however, amides liberate the hydrogen and form neutral complexes through anionic nitrogen atoms.[2] In the case of picolinamides, both cationic and neutral chelate complexes with transition metals were prepared and characterized;[3] the former has coordination through nitrogen and oxygen atoms, while the latter has coordination through two nitrogen atoms (**1** and **2**).

In this paper we describe a novel type of Pd(II) and Pt(II) complexes of sulfilimine (S–N ylide) and aminimide (N–N ylide) with picolinoyl group on ylidic nitrogen (**3** and **8**). These ylides have a close similarity to picolinamide anions in that they are bidentate *via* nitrogen atom in pyridine ring and anionic nitrogen with charge delocalized over adjacent carbonyl group. In contrast to amide anions, they are stable enough to be prepared and isolated by known procedures, and this would make it possible to elucidate directly the change in electronic state of the ligands upon complex formation. In addition, while each of the ylides has an anionic center, it has ammonium or sulfonium moiety adjacent to the ylidic nitrogen, and hence is a neutral molecule as a whole. The effect of the positively charged group on complex formation would be an interesting problem to examine.

An increasing number of reports have been published on metal–ylide complexes.[4] Many of them describe reactions of metal carbonyl with ylides,[5] and direct formation of metal–carbon bonds by reactions of metal salts with stable[6] and unstable[7] phosphorus and sulfur ylides. Several papers also describe the formation of metal complexes of sulfilimines and aminimides,[8] but chelate complexes of these ylides have not been reported so far except *ortho*-metallated *N*-(1-pyridinio)benzamidate complexes of transition metals.[9]

Results and Discussion

Preparation of Complexes. The complex formation of the ylides **3** and **8** occurred smoothly with dichlorobis(benzonitrile)palladium(II) in ethanol and with dipotassium tetrachloroplatinate(II) in water at room temperature. In all cases, the complexes were isolated as yellow or orange-yellow precipitates. The Pd(II) complexes were also prepared by reactions with disodium tetrachloropalladate(II) in ethanol or with dichloro(1,5-cyclooctadiene)palladium(II) in acetone, giving the same products as described above. The elemental analyses revealed that the complexes have equimolar compositions of MCl_2 (M=Pd or Pt) and ylides (Table 1), suggesting chelate structures for these complexes. *N*-Benzoyl- and *N*-acetylsulfilimines and aminimides formed complexes with two ylide molecules per metal atom (bis-ylide complexes). The thermal stability of the bis-ylide complexes is somewhat lower than that of the chelate complexes.

In the case of bidentate ligands, **3** and **8**, the reactions were carried out at the mole ratio of metal salt to ligand of 1 : 1 and 1 : 2, but no differences in the yield and spectroscopic properties of the products were observed. This indicates that the coordinating nitrogen atoms in the chelate complexes are not replaced by another ligand molecules, suggesting that the chelate formation is favored not only entropically but also energetically, resulting in the formation of stronger coordination bonds than those of bis-ylide complexes.

Structure of Complexes. The sulfilimines and aminimides used as ligands have an ambidentate character with resonance structures such as shown in **3a**—**c** and **8a**—**b**. The difference between a sulfilimine and an aminimide is that the former has dπ-pπ interaction between sulfur and ylide nitrogen, making the S–N bond length shorter than ordinary single bond length,[10] while the latter does not have such interaction; the single bond character of N–N linkage and shortening of N–C(carbonyl) bond have been proved by X-ray analysis.[11] These ylides form stable sulfonium and ammonium salts by treatment with aqueous HCl in acetone except for **3** and **8**, whose HCl salts were not isolated. The IR spectral data of these ylides and salts are collected in Table 2. It is evident that the ylides have large contribution from the enolate form structures such as **3c** and **8b**, as manifested by low carbonyl stretching frequencies similar to those of carboxylate ions. The C=O bands shift as much as 105—160 cm^{-1} to higher frequencies, while the C=N stretching bands shift down from 1290—1350 to 1220—1274 cm^{-1} in going from ylides to their salts,[12] indicating that

Table 1. Melting points and elemental analyses of complexes

Complex		Mp(°C)	Found %			Calcd %		
			C	H	N	C	H	N
$PdCl_2[(CH_2)_4S{=}NCOC_5H_4N]$	**14**	216—217(d)	30.66	3.16	7.12	31.15	3.14	7.27
$PtCl_2[(CH_2)_4S{=}NCOC_5H_4N]$	**15**	185—188(d)	25.10	2.62	5.85	25.32	2.56	5.91
$PdCl_2[(CH_2)_4S{=}NCOC_6H_5]_2$	**16a**	168—170(d)	44.76	4.57	5.15	44.64	4.44	4.73
$PdCl_2[(CH_2)_4S{=}NCOC_6H_4CH_3\text{-}p]_2$	**16b**	181—182(d)	46.91	4.34	4.52	46.49	4.89	4.52
$PdCl_2[(CH_2)_4S{=}NCOC_6H_4Cl\text{-}p]_2$	**16c**	168—169(d)	40.91	3.58	5.04	40.00	3.67	4.24
$PdCl_2[(CH_2)_4S{=}NCOCH_3]_2$	**17**	198—200(d)	30.69	4.85	6.54	30.81	4.75	5.99
$PdCl_2[(CH_3)_3\overset{+}{N}\text{-}\overset{-}{N}COC_5H_4N]$	**18**	219—220(d)	30.03	3.68	11.45	30.32	3.68	11.78
$PtCl_2[(CH_3)_3\overset{+}{N}\text{-}\overset{-}{N}COC_5H_4N]$	**19**	196—197(d)	23.27	2.88	8.70	24.28	2.95	9.44
$PdCl_2[(CH_3)_3\overset{+}{N}\text{-}\overset{-}{N}COC_6H_5]_2$	**20**	210—211(d)	44.25	5.13	10.22	45.00	5.30	10.50
$PdCl_2[(CH_3)_3\overset{+}{N}\text{-}\overset{-}{N}COCH_3]_2$	**21**	207—208(d)	27.70	6.57	14.18	29.32	5.92	13.68
$Pd[(CH_3)_2N\overset{-}{N}COC_5H_4N]_2$	**22**	262—263	44.16	4.71	19.94	44.19	4.65	19.33
$PdCl_2[(CH_2)_4S{=}NCOC_6H_5]PPh_3$	**24**	193—195	53.82	4.28	2.13	53.84	4.37	2.17
$PdCl_2[(CH_2)_4S{=}NCOCH_3]PPh_3$	**25**	208—210	49.35	4.44	2.31	49.29	4.49	2.40

Table 2. IR data of sulfilimines, aminimides, and their salts (cm^{-1})

Compound		C=O st.	Aromatic ring st.	C-N st.	S-N st.	Aromatic C-H def.
$(CH_2)_4S{=}NCOC_5H_4N$	**3**	1547	1587	1330	785	750
$(CH_2)_4S{=}NCOC_6H_5$	**4a**	1527	1590	1335	780	780, 720
$(CH_2)_4\overset{+}{S}\text{-}NHCOC_6H_5\ Cl^-$	**5a**	1674	1595	1246	—	784, 690
$(CH_2)_4S{=}NCOC_6H_4CH_3\text{-}p$	**4b**	1540	1590	1335	800	843
$(CH_2)_4\overset{+}{S}\text{-}NHCOC_6H_4CH_3\text{-}p\ Cl^-$	**5b**	1645	1609	1260	—	840
$(CH_2)_4S{=}NCOC_6H_4Cl\text{-}p$	**4c**	1536	1587	1336	795	846
$(CH_2)_4\overset{+}{S}\text{-}NHCOC_6H_4Cl\text{-}p\ Cl^-$	**5c**	1683	1594	1253	—	846
$(CH_2)_4S{=}NCOCH_3$	**6**	1540	—	1290	788	—
$(CH_2)_4\overset{+}{S}\text{-}NHCOCH_3\ Br^-$	**7**	1700	—	1220	—	—
$(CH_3)_3\overset{+}{N}\text{-}\overset{-}{N}COC_5H_4N$	**8**	1560	1605	1350	—	750
$(CH_3)_3\overset{+}{N}\text{-}\overset{-}{N}COC_6H_5$	**9**	1560	1600	1334	—	726
$(CH_3)_3\overset{+}{N}\text{-}NHCOC_6H_5Cl^-$	**10**	1692	1598	1272	—	705
$(CH_3)_3\overset{+}{N}\text{-}\overset{-}{N}COCH_3$	**11**	1575	—	1335	—	—
$(CH_3)_3\overset{+}{N}\text{-}NHCOCH_3\ Cl^-$	**12**	1695	—	1274	—	—
$(CH_3)_2N\text{-}NHCOC_5H_4N$	**13**	1675	1587	1306	—	740

protonation occurred at ylidic nitrogen to form salts such as **5** and **10**.

As shown in Table 3, the C=O bands of the ylides shift to higher frequencies on complex formation, and this seems to indicate that coordination to metal occurs through ylidic nitrogen. In view of the Pd–Cl stretching bands of Pd(II) complexes, there seems to be two groups of complexes; one includes **16a**—**c**, **24**, and **25** which have only one Pd–Cl absorption band at 323—345 cm^{-1}, and another one includes **14**, **17**, **18**, **20**, and **21** which have two Pd–Cl bands at 327—331 and 346—368 cm^{-1}. The former is considered to have *trans*-configuration and the latter has *cis*-configuration around the Pd atom.

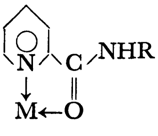
In the case of picolinoyl ylides **3** and **8**, the absorption bands due to in-plane deformation of pyridine ring[3f)] appear at 615 and 623 cm^{-1} respectively, and these bands shift to higher frequencies (655—665 cm^{-1}) on complex formation. Furthermore, the lack of IR bands characteristic of the bridging M–Cl–M stretching mode that would be expected below 300 cm^{-1} rules out binuclear structures.[13)] These and analogous considerations on the Pt(II) complexes, **15** and **19**, lead to the conclusion that the structures of **14**, **15**, **18**, and **19** are best represented by **A** and **B** in Fig. 1. In the NMR spectrum of **18**, protons of the pyridine ring, as well as protons of methyl groups, show down field shift in comparison with the free ligand **8**, and this also implies the chelate ring formation through two nitrogen atoms.

One of the structurally related Pd(II) complexes of picolinamides is shown in Fig. 1 (**C**).[3f)] In this case, the amide groups coordinate to metal *via* anionic nitrogens, forming a 1:2 metal-amide complex. The C=O band of the complex **C** appears at 1625 cm^{-1} which

Table 3. IR data of complexes (cm^{-1})[a)]

Complexe	C=O st.	Aromatic ring st.	C–N st.	Aromatic C–H def.	Pyridine[b)] def.	M–Cl	Δ_1	Δ_2	Δ%	pK_a
14[c)]	1665	1605	1316	762	655	346, 329	29	118	80	(2.62)
15[c)]	1665	1605	1310	752	665	342, 327	29	118	80	(2.62)
16a	1625	1578	1282	776, 712	—	323, 300	49	100	67	2.62
16b	1595	1606	1320	835	—	325	50	55	52	2.72
16c	1595		1310	843	—	328	88	59	40	
17	1594	—	1316	—	—	368, 328	106	54	34	3.45
18[d)]	1655	1600	1326	762	656	356, 328	37	95	72	4.42
19[d)]	1656	1610		757	656	308, 302	36	96	73	4.42
20	1610	1596	1340	755, 696	—	362, 327	82	50	38	4.40
21	1600	—	1327	—	—	361, 331	95	25	21	5.48
22	1626, 1598[e)]		1345	762	—	—				
24	1605	1574	1322	724, 687	—	340	69	78	53	2.62
25	1604	1585	1298	—	—	345	96	64	38	3.45
f)	1625		—				35	101	74	7.75
g)	1630	1580	—	750, 695	—	330	50	122	71	8.10

a) Δ_1 and Δ_2 are C=O frequency differences between salts and complexes, and between complexes and ylides, respectively. Δ% is $\Delta_2/(\Delta_1+\Delta_2)\times 100$. b) Pyridine in plane deformation band.[3f)] In free ligands this bands appear near 615 cm^{-1}. c) Values of Δ were calculated using $\nu_{C=O}=1694\ cm^{-1}$ for the salt of **3**. d) Values of Δ were calculated using $\nu_{C=O}=1692\ cm^{-1}$ for the salt of **8**. e) Two absorption bands of almost equal intensities were observed. f) $PdCl_2[(C_6H_5)_3P=CHCOC_6H_5]_2$, Ref. 6a. g) $PdCl_2[(CH_3)_2S=CHCOC_6H_5]_2$, Ref. 6c.



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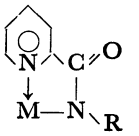

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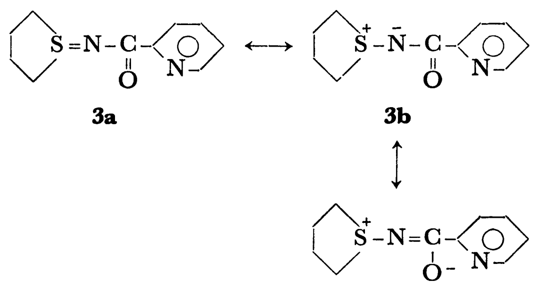
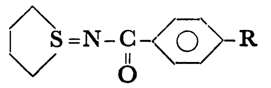


3a **3b** **3c**



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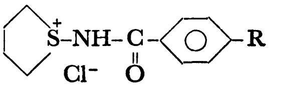

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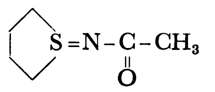
R=H (a), CH_3 (b), Cl (c)



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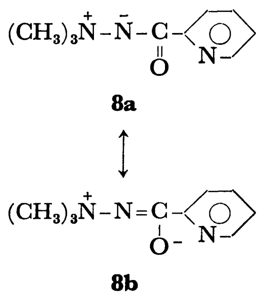
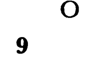


8a **8b**



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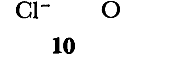

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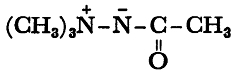
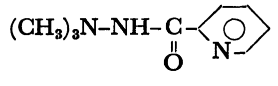


$(CH_3)_3\overset{+}{N}-\overset{-}{N}-\underset{\underset{O}{\|}}{C}-CH_3$

11



13

is the same frequency as the C=O band of **16a**. Considering that the basicity of the anionic ligand and hence the strength of metal–ligand bonding is thought to be much higher in the former complex than the latter, it is obvious that the metal–ligand bond strength can not be estimated by the observed C=O band shift. In fact, including a hydrazide complex **D** (*vide infra*), the order of basicity (pK_a of the corresponding amide hydrogens) of the anionic nitrogens is expected to be **C**>**D**>**B**>**A**, while the C=O frequency is in the order **C**<**D**<**B**<**A**.

The degree of higher shift of C=O band on complex

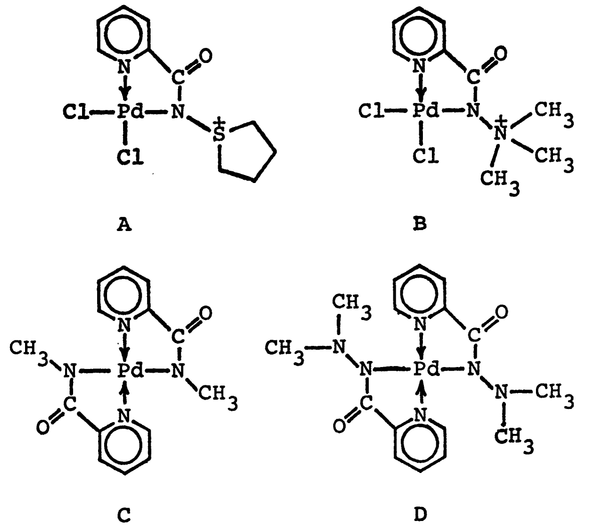
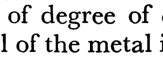


Fig. 1. Structures of chelate complexes.

formation is quite different between the aminimides and the sulfilimines, and among the ylides with different substituents on the carbonyl group. In order to visualize these structural effects, the C=O frequency differences between the salts and the complexes (Δ_1), and those between the complexes and the ylides (Δ_2) are summerized in Table 3, together with the percentages of $\Delta\% = \Delta_2/(\Delta_1+\Delta_2)$ ($\Delta_1+\Delta_2$ equal to the frequency differences between the ylides and the salts). Since the attempted preparations of the salts of the picolonoyl ylides, **3** and **8**, were unsuccessful, the values of Δ_1 and $\Delta\%$ of **14, 15, 18**, and **19** were calculated using hypothetical values of 1694 and 1692 cm^{-1} for the salts of **3** and **8**, respectively. These values were calculated on assumption that the values of $\Delta_1+\Delta_2$ of the *N*-picolinoyl compounds are equal to those of *N*-benzoyl compounds. Table 3 also includes the values for the P–C and S–C ylides calculated from the reported data and the pK_a values of the salts of the ylides. The value of $\Delta\%$ is considered to be a measure of degree of σ-bonding between dsp^2 hybridized orbital of the metal ion and sp^2 orbital of the ylidic nitrogen.

There is a tendency that the sulfilimine complexes have somewhat higher values of $\Delta\%$ than the aminimide complexes with the same substituents on the carbonyl carbon. This may indicate that the latter has smaller σ-bond character than the former. In the case of carboxylate complexes such as metal complexes of amino acids, the stretching frequency of the coordinated carboxyl group becomes higher as the metal–oxygen bond becomes stronger.[14] Therefore, it may be considered that the coordination in the sulfilimine complexes is stronger than that in the aminimide analogs. However, the conclusion is somewhat dubious, because the observed basicity of the sulfilimines is lower than the aminimides, and hence the latter is expected to have stronger electrostatic interactions with metal ions.

An alternative explanation for these results is that the metal-ylide coordination is appreciably of ionic character with π-electron delocalized over N–C–O atoms (**E**).



(**E**)

Chelate complexes cannot have a coordination like **E**. A similar complex of an anionic ligand, acetamidopentaamminecobalt(III) perchlorate [Co(NHCOCH$_3$)(NH$_3$)$_5$](ClO$_4$)$_2$, has been reported by Schneider *et al.*[2b)] The complex has C=O stretching band at 1560 cm^{-1}, and X-ray analysis revealed that C=O bond length is longer than ordinary double bonds, indicating electron delocalization over N–C–O atoms.

It should be noted that the chelate complexes have larger σ-bond character than the bis-ylide complexes as seen in Table 3, and that the complexes of *N*-acetyl ylides have remarkably larger ionic character; the C=O bands appear closer to those of free ylides rather than salts.

One of the distinguishable characteristics of ylide ligands is that they have a positively charged group adjacent to the coordination site. In order to evaluate the effect of the charged group, a complex of 2′,2′-dimethylpicolinohydrazide (**13**) was prepared by the reaction with disodium tetrachloropalladate(II) in an alkaline medium. The proposed structure of the complex (**22**) is shown in Fig. 1 (**D**), and the comparison of C=O bands of **B** and **D** (Table 3) suggests that the latter has a little larger ionic character. It is interesting that by complex formation the NMR bands of methyl and pyridine-6-CH protons of 2′,2′-dimethylpicolinohydrazide show down field shift by 0.25 and 1.36 ppm, respectively. The magnitude of the shift of pyridine-6-CH protons is larger than that expected from the electronic deshielding by coordination of pyridine N atom, and this was ascribed to the van der Waal's interaction with methyl groups of another ligand in the complex.

Ligand Exchange Reactions. The complexes prepared in the present study have relatively low solubilities in water and ordinary organic solvents, making it difficult to study the reactions in solution. However, it was found that the NMR spectra of bis-ylide complexes **16** in DMSO-d_6 were essentially the same with those of free ligands, suggesting that the ligands in these complexes were readily replaced by the solvent molecules. On the contrary, the spectra of the chelate complexes **18** and **22** observed under the same condition were unchanged for more than one week.

The heterogeneous reaction of the complexes with equimolar triphenylphosphine were carried out in refluxing acetonitrile. The bis-sulfilimine Pd(II) complexes **16a** and **17** afforded monosubstituted complexes PdCl$_2$(Ylide)PPh$_3$ in 76 and 60% yields, respectively, while the chelate complexes did not give monsubstituted complexes, but mixtures of PdCl$_2$(PPh$_3$)$_2$ and unreacted complexes were obtained together with small amounts of unidentified products.

Experimental

Melting points are uncorrected. IR spectra were taken on JASCO IRA-2 and DS-403G spectrometer, and NMR spectra were recorded on a Hitachi R-20A spectrometer (60 MHz) using TMS as an internal standard. Elemental analyses were performed on a Perkin Elmer 240 analyzer.

Preparation of Sulfilimines, Aminimides, and Their Salts. N-*Picolinoyl*-S,S-*tetramethylenesulfilimine (3)*: To a solution of 4.59 ml (0.052 mol) of tetrahydrothiophen in 30 ml of methanol was added dropwise 5.62 ml (0.050 mol) of *t*-butyl hypochlorite at −50—−45 °C. To the resulting mixture a solution of 6.10 g (0.050 mol) of picolinamide and 1.20 g (0.054 mol) of sodium in 40 ml of methanol was added dropwise keeping the temperature between −55 and −45 °C.[15)] After 3 h reaction, the mixture was allowed to warm up to room temperature, evaporated by a rotary evaporator under vacuum, and the residue was extracted by 60 ml of dichloromethane. By evaporation of dichloromethane, crude **3** was obtained in 90% yield. Pure **3** was obtained by recrystallization from a mixture of benzene and petroleum ether. Mp 78—80 °C. Found: C, 57.29; H, 5.97; N, 13.44%. Calcd for $C_{10}H_{12}N_2OS$: C, 57.66; H, 5.82; N, 13.45%. NMR (CDCl$_3$) δ=1.7—2.8 (4H, m, C–CH$_2$–C), 3.38 (4H, br. t, J=8 Hz, CH$_2$S), 7.15—7.50 (1H, m, Py-4-CH), 7.75 (1H, t, J=8 Hz, Py-5-CH), 8.12 (1H, d, J=8 Hz, Py-3-CH), 8.77 (1H, d, J=5 Hz, Py-6-CH).

N-*Benzoyl- and* N-*(*p-*Substituted Benzoyl)*-S,S-*tetramethylenesul-*

filimines (4a—c): These sulfilimines were prepared and purified by similar methods to that described above. Analytical and NMR data are shown: **4a**, mp 116—117 °C. Found: C, 64.03; H, 6.71; N, 6.71%. Calcd for $C_{11}H_{13}NOS$: C, 63.73; H, 6.33; N, 6.76%. NMR ($CDCl_3$) δ=1.7—2.7 (4H, m, C–CH_2–C), 3.25 (4H, br. t, *J*=8 Hz, CH_2S), 7.37 (3H, t, *J*=3 Hz, *m*- and *p*-CH), 7.9—8.2 (2H, m, *o*-CH). **4b**, mp 99—100 °C. Found: C, 65.61; H, 6.92; N, 6.40%. Calcd for $C_{12}H_{15}NOS$: C, 65.11; H, 6.85; N, 6.33%. NMR ($CDCl_3$) δ=1.7—2.5 (4H, m, C–CH_2–C), 2.35 (3H, s, CH_3), 3.25 (4H, br. t, *J*=8 Hz, CH_2S), 7.12 (2H, d, *J*=8 Hz, *m*-CH), 7.93 (2H, d, *J*=8 Hz, *o*-CH). **4c**, mp 106—108 °C. Found: C, 54.46; H, 5.14; N, 6.04%. Calcd for $C_{11}H_{12}NOSCl$: C, 54.65; H, 5.01; N, 5.80%. NMR ($CDCl_3$) δ=1.7—2.6 (4H, m, C–CH_2–C), 3.25 (4H, br. t, *J*=7 Hz, CH_2S), 7.28 (2H, d, *J*=8 Hz, *m*-CH), 7.97 (2H, d, *J*=8 Hz, *o*-CH).

1-(Benzoylamino and p*-Substituted Benzoylamino)thiolanium Chlorides (5a—c)*: These sulfonium chlorides were prepared by the method reported previously.[16]

N*-Acetyl-*S,S*-tetramethylenesulfilimine (6) and 1-Acetylaminothiolanium Bromide (7)*: These compounds were also reported in a literature.[17]

N*-Trimethylammoniopicolinamidate (Trimethylamine-picolinimide) (8)*: A modified method of McKillip and Slagel[18] was employed for the syntheses of aminimides **8**, **9**, and **11**. Thus, a mixture of 10.43 g (0.0516 mol) of 1,1,1-trimethylhydrazinium iodide, 7.08 g (0.0516 mol) of methyl picolinate, and 6.02 g (0.0536 mol) of potassium *t*-butoxide in 60 ml of *t*-butyl alcohol was heated with stirring at 60—65 °C for 4.5 h. The precipitate was separated by filtration and the filtrate was evaporated to dryness under vacuum. The residue was recrystallized from ethyl acetate, and a hygroscopic solid was obtained which was identified as **8** by IR and NMR. Yield 70%, mp 148—149 °C. NMR ($CDCl_3$) δ=3.56 (9H, s, CH_3), 7.1—7.5 (1H, m, Py-4-CH), 7.75 (1H, t, *J*=7 Hz, Py-5-CH), 8.11 (1H, d, *J*=8 Hz, Py-3-CH), 8.66 (1H, d, *J*=5 Hz, Py-6-CH).

N-Trimethylammoniobenzamidate (**9**), mp 167—168 °C, (lit,[19] 168—169 °C), and *N*-trimethylammonioacetamidate (**11**), mp 124—126 °C (lit,[20] 122.5—123 °C), were prepared in similar manners and converted to hydrochloric acid salts. **9**; Found: C, 67.49; H, 7.93; N, 15.22%. Calcd for $C_{10}H_{14}N_2O$: C, 67.37; H, 7.93; N, 15.72%. NMR ($CDCl_3$) δ=3.42 (9H, s, CH_3), 7.2—7.5 (3H, m, *m*- and *p*-CH), 7.8—8.1 (2H, m, *o*-CH). **10**; mp 178—179 °C. Found: C, 56.32; H, 7.15; N, 13.11%. Calcd for $C_{10}H_{15}N_2OCl$: C, 55.93; H, 7.06; N, 13.05%. NMR (DMSO-d_6) δ=3.80 (9H, s, CH_3), 7.4—7.7 (3H, m, *m*- and *p*-CH), 7.8—8.1 (2H, m, *o*-CH). Ylide **11** was very hygroscopic and could not analyzed. NMR ($CDCl_3$) δ=1.79 (3H, s, C–CH_3), 3.36 (9H, s, N–CH_3). **12**, mp 198—199 °C. Found: C, 39.17; H, 8.54; N, 18.18%. Calcd for $C_5H_{13}N_2OCl$: C, 39.49; H, 8.60; N, 18.34%. NMR (DMSO-d_6) δ=2.02 (3H, s, C–CH_3), 3.63 (9H, s, N–CH_3).

2′,2′-Dimethylpicolinohydrazide (13): This compound was prepared by the reaction of 1,1-dimethylhydrazine with picolinic acid in the presence of dicyclohexylcarbodiimide in dichloromethane.[21] Picolinic acid (4.9 g, 0.04 mol) was added to a solution of 8.2 g (0.04 mol) of dicyclohexylcarbodiimide and 2.4 g (0.04 mol) of 1,1-dimethylhydrazine in 160 ml of dichloromethane, and the solution was stirred at room temperature for 2 h. The precipitate was removed by filtration, and the filtrate was extracted by three portions of 50 ml of 3 M HCl. After the extract was neutralized by sodium carbonate, the product was extracted by chloroform and dried over anhydrous sodium sulfate. The evaporation of chloroform gave crude **13** in 78% yield. After several recrystallization from benzene-hexane or cyclohexane, pure **13** was obtained, mp 67—68 °C. Found: C, 57.79; H, 6.75; N, 24.92%. Calcd for $C_8H_{11}N_3O$: C, 58.15; H, 6.72; N, 25.44%. NMR ($CDCl_3$) δ=2.72 (6H, s, CH_3), 7.25—7.50 (1H, m, Py-4-CH), 7.80 (1H, t, *J*=7 Hz, Py-5-CH), 8.18 (1H, d, *J*=7 Hz, Py-3-CH), 8.45 (1H, d, *J*=4 Hz, Py-6-CH), 8.65 (1H, br. s, NH).

Preparation of Complexes. *Dichloro(*N*-picolinoyl-*S,S*-tetramethylenesulfilimine)palladium(II) (14)*: To a solution of 0.763 g (3.66 mmol) of **3** in 60 ml of benzene 1.26 g (3.29 mmol) of dichlorobis(benzonitrile)palladium(II) was added. After overnight reaction with stirring, an orange-yellow precipitate was separated and dried *in vacuo*. Crude **14** (93% yield) was purified by recrystallization from DMSO. Alternative procedures for the preparation of **14** are the reaction of **3** with disodium tetrachloropalladate(II) in ethanol or with dichloro(1,5-cyclooctadiene) palladium(II) in acetone. In both cases the products were obtained as precipitates and identified as **14**.

*Dichloro(*N*-picolinoyl-*S,S*-tetramethylenesulfilimine)platinum(II) (15)*: A solution of 0.514 g (2.47 mmol) of **3** in 5 ml of water was added dropwise to a solution of 0.257 g (0.618 mmol) of dipotassium tetrachloroplatinate(II) in 5 ml of water. After 3 h reaction at room temperature, an orangered precipitate was separated, washed with water, and dried *in vacuo*; yield 66%.

*Dichlorobis(*N*-benzoyl-*S,S*-tetramethylenesulfilimine)palladium(II) (16a)*: A solution of 0.447 g (2.15 mmol) of **4a** in 5 ml of ethanol was added dropwise at room temperature to a solution of 0.376 g (1.08 mmol) of disodium tetrachloropalladate (II) in 25 ml of ethanol. The orange precipitate formed was filtered, washed with ethanol–water, and dried *in vacuo*; yield 95%. *p*-Methyl- and *p*-chlorobenzoylsulfilimine complexes of palladium(II) were prepared by similar methods. The NMR spectra of **15a**—**c** in DMSO-d_6 were essentially the same with those of **4a**—**c** respectively, indicating that the ylide ligands were replaced by the solvent. The complex **17** was prepared in tha same way.

*Dichloro(*N*-trimethylammoniopicolinamidate)palladium(II) (18)*: A solution of 0.555 g (3.09 mmol) of **8** in 5 ml of ethanol was added at room temperature to a solution of 0.598 g (1.56 mmol) of dichlorobis(benzonitrile)palladium(II) in 30 ml of ethanol. A brownish precipitate formed immediately. After 1 h reaction, the precipitate was separated, washed with ethanol, and dried *in vacuo*; yield 74%. NMR (DMSO-d_6) δ=3.68 (9H, s, CH_3), 7.4—8.4 (3H, m, Py-3,4,5-CH), 8.90 (1H, d, *J*=6 Hz, Py-6-CH). No significant change was observed in the spectrum of **18** in DMSO-d_6 after 1 week, indicating that the aminimide ligand was not displaced by the solvent. The reactions of **8** with disodium tetrachloropalladate(II) in ethanol and with dichloro(1,5-cyclooctadiene)palladium(II) in acetone also gave **18** in almost quantitative yields.

*Dichloro(*N*-trimethylammoniopicolinamidate)platinum(II) (19)*: A solution of 0.289 g (1.61 mmol) of **8** in 5 ml of water was added at room temperature to a solution of dipotassium tetrachloroplatinate(II) (0.666 g, 1.60 mmol) in 10 ml of water. After 6 h reaction, the precipitate was separated, washed with water, and dried *in vacuo*; yield 49%.

*Dichlorobis(*N*-trimethylammoniobenzamidate)palladium(II) (20) and Dichlorobis(*N*-trimethylammonioacetamidate)palladium(II) (21)*: These complexes were prepared by the reactions of disodium tetrachloropalladate(II) with two equivalents of the aminimides **9** and **11** in ethanol. Yields were 95 and 73%, respectively.

Bis(2′,2′-dimethyl-1′-picolinoyl-1′-hydrazino)palladium(II) (22): A solution of 0.712 g (4.31 mmol) of **13** and 0.172 g (4.31 mmol) of sodium hydroxide in 8 ml of ethanol was added dropwise to a solution of disodium tetrachloropalladate(II) (0.635 g, 2.16 mmol) in 30 ml of ethanol. After 2 h reaction at room temperature, the precipitate was separated by filtration, the filtrate was concentrated, and the solution was poured into 200 ml of water. After standing in a refrigerator overnight, the yellow crystal was filtered and dried *in vacuo*. Yield 83%. NMR ($CDCl_3$) δ=2.97 (6H, s, CH_3), 7.40—7.65 (1H, m, Py-4-CH), 8.02 (2H, d, J=4 Hz, Py-3- and -5-CH), 9.84 (1H, d, J=5 Hz, Py-6-CH).

Reactions of Pd (II) Complexes with Triphenylphosphine. A mixture of 0.228 g (0.591 mmol) of **14** and equimolar amount of triphenylphosphine in 15 ml of acetonitrile was refluxed for 4 h. The precipitate was separated by filtration and it was found to be a mixture of **14** and dichlorobis(triphenylphosphine)palladium(II) (**23**). The reaction of **18** with triphenylphosphine was also carried out in a similar way, and **23** was isolated in 40% yield. In the case of bis-sulfilimine complexes, **16a** and **17**, monosubstituted complexes, $PdCl_2[(CH_2)_4S{=}NCOC_6H_5](PPh_3)$ (**24**) and $PdCl_2[(CH_2)_4S{=}NCOCH_3](PPh_3)$ (**25**) were obtained as orange precipitates by cooling the reaction mixtures in 76 and 60% yields, respectively.

pK_a *Measurement of Aminosulfonium and Aminoammonium Chlorides.* pK_a values of the salts **5** and **7** were reported in a previous paper,16) and those of **10** and **12** were measure by a similar method.

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