The Displacement of Bonding Electrons found in the Ylide Bond of Aminimide–Palladium Complexes †

Shinji Tsuchiya * and Manabu Senō
Institute of Industrial Science, University of Tokyo, 7-22-1, Roppongi, Minato-Ku, Tokyo 106, Japan

A novel factor contributing to the stability of N-containing ylides has been clarified by *X*-ray photoelectron and i.r. spectroscopic measurements of aminimide–palladium complexes, $[\overline{PdCl_2\{R^1R^2R^3\overset{+}{N}N}C(O)R^4\}_2]$. An interaction through the σ bond between the quaternary nitrogen and the anionic nitrogen was observed in the ylide bond in the aminimide–palladium complexes.

The various factors contributing to the stability of ylides have been reported previously:[1] (*i*) the delocalization of electrons on the atom carrying the negative charge by an electron-withdrawing group; (*ii*) the stereoelectronic control;[2] (*iii*) the high polarization of the atom carrying the positive charge (electrostatic stabilization);[1,3] and (*iv*) the d_π–p_π interaction between a vacant 3*d* orbital of the positive heteroatom and a filled 2*p* orbital of an adjacent atom.[1,4] The ability of the positive heteroatom to stabilize an adjacent negative charge remains a particularly interesting phenomenon. Recently, we reported a new stabilizing effect caused by the strong interaction through the σ electrons, which we termed the electron displacement effect.[5] This effect was found by comparisons between the binding energies of positive heteroatoms in N-containing ylides and those in salts. That is, the electron density on the positive heteroatom of the ylide is higher than that of the salt and this higher electron density in the ylide arises from the displacement of bonding electrons to the positive atom. It was established that the coulombic potential, the reorganization energy, and the lattice energy do not contribute greatly to the binding energies of these compounds. In the present paper, we report novel evidence of the electron displacement effect by *X*-ray photoelectron spectroscopy (x.p.s.) and i.r. measurements of aminimide (ammonioamide) complexes of palladium.

Results and Discussion

The displacement of bonding electrons means that the electron cloud of the σ bond between the positive atom and the anionic atom in the ylide lies closer to the positive atom (S^+ or N^+).[5] This effect would lead to the increase of electron density on the positive atom. Polar covalent bonds are known when two atoms of different electronegativities form a covalent bond; the electrons are not shared equally between them, and the atom with greater electronegativity draws the electron pair closer to it.[6] However, a polar bond involving the displacement of bonding electrons is different from a polar covalent bond, for the following reasons. The polarization in polar covalent bonds arises from only the difference in electronegativities of each atom of which the covalent bond is composed. On the other hand, a polar bond involving the displacement of bonding electrons is found in the ylide, with the atoms having unusual valencies, and this displacement of bonding electrons occurs so as to neutralize the opposite charge on the heteroatoms of which the polar bond is composed. Consequently, the negative charge on the anionic

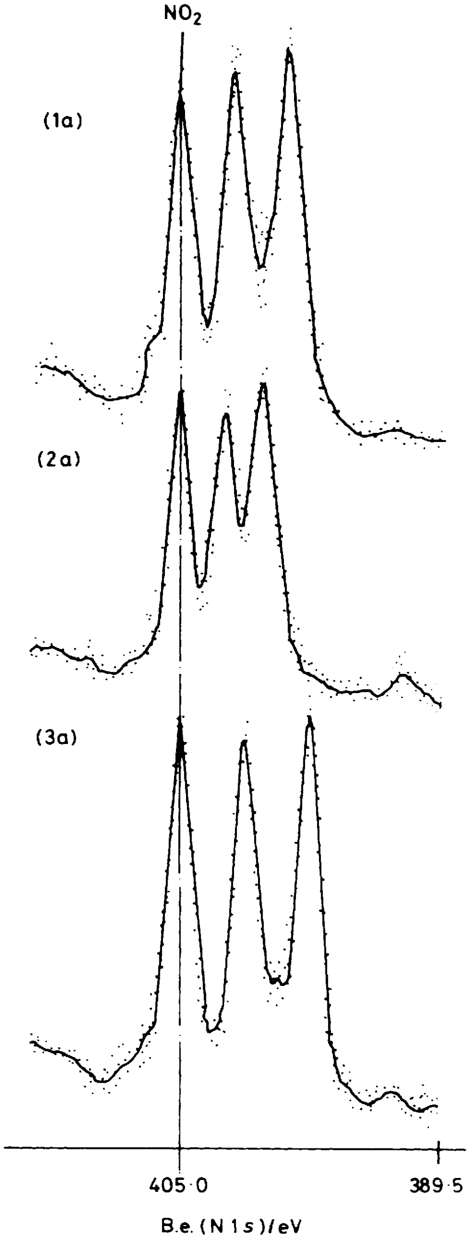
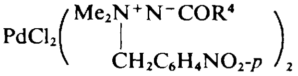


Figure. N 1*s* spectra of complex (1a), salt (2a), and aminimide (3a)

---

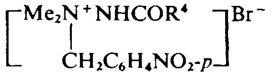
† *Non-S.I. unit employed*: 1 eV ≈ 1.60 × 10^{-19} J.

Table 1. N 1*s* and Pd 3*d* binding energies [b.e. (N 1*s*) for NO_2 = 405.0 eV] and ν(C=O) values for aminimide–palladium complexes, salts, and free aminimides [a]



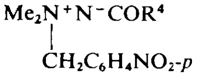
$$PdCl_2\left(\begin{array}{c}Me_2N^+N^-COR^4\\ |\\ CH_2C_6H_4NO_2\text{-}p\end{array}\right)_2$$

Complex (1)



$$\left[\begin{array}{c}Me_2N^+NHCOR^4\\ |\\ CH_2C_6H_4NO_2\text{-}p\end{array}\right]Br^-$$

Salt (2)



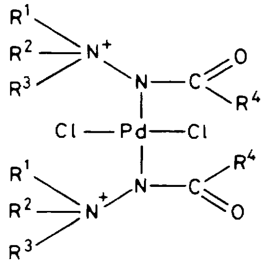
$$\begin{array}{c}Me_2N^+N^-COR^4\\ |\\ CH_2C_6H_4NO_2\text{-}p\end{array}$$

Aminimide (3)

Compound	R^4	B.e. (N 1*s*)/eV			B.e. (Pd 3*d*)/eV		ν(C=O)/cm⁻¹
		N^+	N^-	NH	$3d_{3/2}$	$3d_{5/2}$	
(1a)	OEt	402.0	398.6		341.9	336.6	1 660
(2a)	OEt	402.3		400.0			1 740
(3a)	OEt	401.1	396.9				1 640
(1b)	Me	402.0	398.5		342.0	336.6	1 610
(2b)	Me	402.5		400.1			1 690
(3b)	Me	401.3	397.4				1 580
(1c)	$C_6H_4NO_2$-*p*	401.9	398.6		*b*	*b*	1 625 [c]
(2c)	$C_6H_4NO_2$-*p*	402.1		400.0			1 675 [c]
(3c)	$C_6H_4NO_2$-*p*	401.5	397.6				1 580 [c]
(1d)	Ph	401.7	398.6		342.2	336.9	1 620
(2d)	Ph	402.2		400.1			1 690
(3d)	Ph	401.5	397.9				1 550
$PdCl_2$					342.5	337.1	

[a] Ref. 5*a*. [b] Not measured. [c] *para* Substituent.

nitrogen in the ylide is delocalized on the positive heteroatom and the ylide is stabilized. We termed this as the 'electron displacement effect' and we consider that this effect is one of the stabilizing factors in aminimides and sulphonioamides $(R^1R^2\overset{+}{S}-\overset{-}{N}R^3)$.[5] In order to gain further evidence of displacement of bonding electrons, palladium complexes with aminimides were synthesized. In this series of complexes, it is expected that, if the electron density on the anionic nitrogen atom decreases as a result of formation of the metal complex, the degree of displacement of bonding electrons decreases and the positive charge on the quaternary nitrogen atom increases compared with that of aminimide. Thus, we can confirm the effect of displacement of bonding electrons through x.p.s. measurements of these complexes. The compounds prepared were *trans*-bis(aminimide)dichloropalladium complexes (1).



(1)

These were characterised by elemental analyses, ¹H n.m.r. and i.r. spectroscopy, and conductivities as previously reported.[7] The N 1*s* binding energies (b.e.) were measured to estimate the electron densities on N^- and N^+.[8] X.p.s. and i.r. data are summarized in Table 1. Table 2 contains the ratios of changes in electron density on N^- and N^+ and the ratios of changes in ν(C=O) occurring as a result of complexation. The ratios were calculated as shown below.

$$\text{Ratio} = \frac{[\text{b.e. (N }1s\text{), complex}] - [\text{b.e. (N }1s\text{), ylide}]}{[\text{b.e. (N }1s\text{), salt}] - [\text{b.e. (N }1s\text{), ylide}]}$$

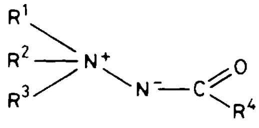
$$= \frac{[\nu(\text{C=O}),\text{ complex}] - [\nu(\text{C=O}),\text{ ylide}]}{[\nu(\text{C=O}),\text{ salt}] - [\nu(\text{C=O}),\text{ ylide}]}$$

Table 2. Ratios, Δ*R*, of change of charge on N^+ and N^- and of change of ν(C=O) on complexation

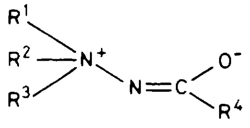
Complex	Δ*R*(N^-)	Δ*R*(N^+)	Δ*R*[ν(C=O)] *
(1a)	0.55	0.75	0.20
(1b)	0.41	0.58	0.27
(1c)	0.42	0.67	0.47
(1d)	0.32	0.29	0.50

* Calculated using the data of Table 1.

A typical spectrum for an aminimide–palladium complex is shown in the Figure. The N 1*s* binding energies of the anionic nitrogen atom in the complex are higher than those of the corresponding free aminimide and Pd 3*d* binding energies in the complex are lower than those of $PdCl_2$. These results indicate a decrease in electron density on the anionic nitrogen atom of the aminimide component on co-ordination to the palladium ion. It is expected that the ratio of this decrease is reflected by the relative importance of the canonical structures (A) and (B) in the resonance hybrid description; that is, the ratio of change of electron density on N^- due to the complexation increases as (A) becomes more important relative to (**B**).



(A)



(B)

The experimental results support this tendency. This is also consistent with the i.r. data, as shown in Table 2; the frequencies of ν(C=O) become larger with increasing contribution of canonical structure (A). On the other hand, the ratios of change of ν(C=O) due to complexation decrease with increasing contribution of (A). The ν(C=O) absorption is not affected by complexation if the contribution of (A) is very large.

It is of particular interest to point out a correlation between the positive charge on N^+ and the electron density on N^-; the N 1*s* binding energies of the quaternary nitrogen atom increase with a decrease in electron density on the anionic nitrogen. This increase of positive charge on N^+ on complexation indicates a smaller contribution from the displacement of bonding electrons. In addition, if a lower N 1*s* binding energy of N^+ in the aminimide arises from the coulombic potential, the N 1*s* binding energy of N^+ in the metal complex should be the same as that of the salt because of the cancellation of negative charge on N^- by the metal cation. Also, a substituent effect should not be observed, for the same reasons. However, the N 1*s* binding energies of N^+ in aminimide–palladium complexes are lower than those of N^+ in the corresponding salt and the ratios of change also depend on the substituents. Thus, these results give clear evidence of an electron displacement effect which is enhanced by higher electron density on the anionic nitrogen atom and indicate that this effect is an important factor in the stabilization of the N-containing ylides. In addition, because of the electron displacement effects, the positive charge on the quaternary nitrogen atom in aminimides is very different from that having typical tetravalent bonding (*e.g.* 1.2 eV lower than that of the hydrazonium salt, reported previously[5]). The striking difference suggests that the nitrogen atom has a great variety of valency values depending on the electronic properties of adjacent atoms and substituents. In biological systems, the nitrogen atom in an organic compound co-ordinates to the metal ion and this complex forms electron-transfer intermediates or electron-transport systems. This important ability of nitrogen would arise because of the variable valency property discussed here.

Experimental

The aminimides were prepared by published methods.[1,9] The aminimide–palladium complexes were synthesized by the reaction of disodium tetrachloropalladate and aminimide in ethanol. The complexes were washed with ethanol after the reactions and recrystallized from nitromethane or chloroform–light petroleum (b.p. 30—60 °C).[7] *X*-Ray photoelectron spectra were determined using a JASCO ESCA-1 photoelectron spectrometer, with Mg-K_α radiation. The samples were examined as fine powders dusted onto double-sided sticky tape. As the N 1*s* binding energy of the nitro-group is not affected by the environment of the nitrogen atom,[5] the N 1*s* line of the nitro-group was taken as 405.0 eV.

References

1 T. L. Gilchrist and C. J. Moody, *Chem. Rev.*, 1977, **77**, 409; M. J. Mckillip, E. A. Sedor, B. M. Culbertson, and S. Wawzonek, *Chem. Rev.*, 1973, **73**, 255; A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966.
2 G. D. Andreetti, F. Bernardi, A. Bottoni, and A. Fava, *J. Am. Chem. Soc.*, 1982, **104**, 2176; G. Barbarella, P. Dembech, A. Garbesi, F. Bernardi, A. Bottoni, and A. Fava, *ibid.*, 1978, **100**, 200.
3 A. Streitwieser and J. E. Williams, *J. Am. Chem. Soc.*, 1975, **97**, 191.
4 B. M. Trost and L. S. Melvin, jun., 'Sulfur Ylides,' Academic Press, New York, 1975; C. Kissel, R. J. Holland, and M. C. Caserio, *J. Org. Chem.*, 1972, **37**, 2720.
5 (*a*) S. Tsuchiya and M. Senō, *J. Org. Chem.*, 1979, **44**, 2850; (*b*) S. Tsuchiya, M. Senō, and W. Lwowski, *J. Chem. Soc., Chem. Commun.*, 1982, 875; (*c*) S. Tsuchiya and M. Senō, *ibid.*, 1983, 413; (*d*) S. Tsuchiya, M. Senō, and W. Lwowski, *J. Chem. Soc., Perkin Trans. 2*, 1983, 887.
6 T. W. G. Solomons, 'Organic Chemistry,' Wiley, New York, 1976.
7 M. Senō and S. Tsuchiya, *J. Chem. Soc., Dalton Trans.*, 1977, 751.
8 'Electron Spectroscopy,' ed. D. A. Shirley, North-Holland, Amsterdam, 1972; M. Senō and S. Tsuchiya, *J. Electron Spectrosc. Relat. Phenom.*, 1976, **8**, 165; M. Senō, S. Tsuchiya, and S. Ogawa, *J. Am. Chem. Soc.*, 1977, **99**, 3014.
9 S. Wawzonek and E. Yeakey, *J. Am. Chem. Soc.*, 1960, **82**, 5718.

Received 7th June 1983; *Paper* 3/942