

## Enhanced Electrophilicity of Co-ordinated Ethylene in a Cationic Platinum(II) Complex

Luciana Maresca<sup>a</sup> and Giovanni Natile<sup>b</sup>

<sup>a</sup> *Istituto di Chimica Generale ed Inorganica, Università di Venezia, Italy*

<sup>b</sup> *Cattedra di Chimica Generale ed Inorganica, Facoltà di Farmacia, Università di Bari, Italy*

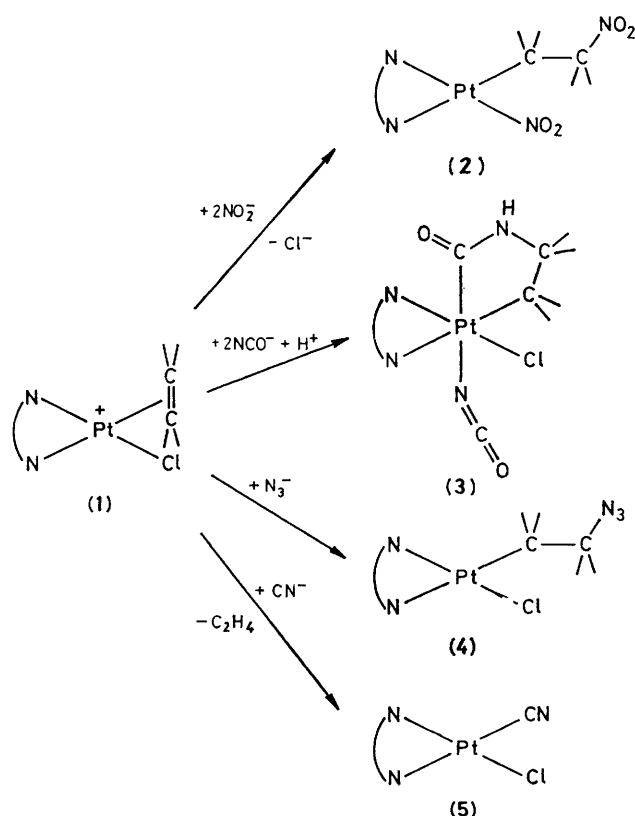
The complex  $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}(\text{tmen})]^+$  (tmen = *N,N,N',N'*-tetramethylethylenediamine), in which ethylene is unsymmetrically bound to the metal, reacts with  $\text{NO}_2^-$ , and  $\text{N}_3^-$  to give stable addition products.

The activation of co-ordinated olefins towards nucleophilic attack has been a topic of great interest for several years.<sup>1</sup>

The source of activation has recently been discussed by Eisenstein and Hoffmann<sup>2</sup> who have suggested that it might result from a slipping of the metal fragment along the double-bond axis which causes an increase in the overlap population between the  $\pi^*$  orbital of the olefin and the electron pair of the nucleophile. We now report a platinum complex with ethylene in which such asymmetry, observed in the ground state, is accompanied by an unusually high reactivity towards nucleophiles.

The cationic complex  $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}(\text{tmen})]^+$  (1) (tmen = *N,N,N',N'*-tetramethylethylenediamine), recently prepared by us, exhibits, upon *X*-ray analysis,<sup>3</sup> an interesting deviation of the ethylene axis from the expected orthogonal position, the angle between this axis and the co-ordination plane being  $80^\circ$ . The tilting of the  $\text{C}_2\text{H}_4$  molecule causes the two carbon atoms to be at different distances from the metal [2.176(9) and 2.242(11) Å, respectively] and is accompanied by a considerable elongation of the carbon-carbon bond which reaches the value of 1.470(17) Å. Although we could not exclude the possibility that some of the observed features arose from steric interactions between ethylene and the adjacent ligands, they are far too significant to be explained on the basis of non-bonding interactions.<sup>4</sup>

We decided to test the reactivity of this substrate towards nucleophilic attack. It is to be noted that although ethylene complexes of several transition metals can react with nucleophiles such as alcohols, sulphides, phosphines, phosphites, thiocyanate, and in some cases the cyanide ion,<sup>5</sup> those of platinum(II) have so far been reported to react only with amines.<sup>6</sup> Therefore, we chose those nucleophiles which are



Scheme 1. N—N = *N,N,N',N'*-Tetramethylethylenediamine.

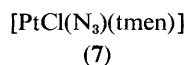
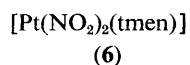
known to be the least reactive towards ethylene and the most reactive towards platinum(II). The ions  $\text{NO}_2^-$ ,  $\text{NCO}^-$ ,  $\text{N}_3^-$ , and  $\text{CN}^-$  lead to ligand substitution, instead of olefin addition, even with  $[\text{Fe}(\eta^2\text{-C}_2\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^+$  which is one of the most reactive and thoroughly studied substrates. The results are summarized in Scheme 1.†

It should be noted that compounds (2) and (3) contain two moles of nucleophile per mole of starting complex, and that these were the only products isolated irrespective of the ratio of reactants.

Compound (4), although containing only one mole of azide per mole of complex, required the use of a large excess of nucleophile and a lower reaction temperature (ca. 0 °C) in order to increase the conversion of (1) to greater than 70%.

The cyanide ion, even when used in less than stoichiometric amounts, led to ethylene substitution and formation of (5) [ $\nu(\text{CN})$  2140  $\text{cm}^{-1}$ ]. However there was some evidence that a complex resulting from the attack of  $\text{CN}^-$  on ethylene might be formed in a small yield [ $\nu(\text{CN})$  2200  $\text{cm}^{-1}$ ] but it could not be isolated in a pure state.

Compounds (2) and (4), either in the solid state or in contact with a solvent, released ethylene to give the corresponding substitution products  $[\text{Pt}(\text{NO}_2)_2(\text{tmen})]$  (6) and  $[\text{PtCl}(\text{N}_3)(\text{tmen})]$  (7). The reaction was much slower for (2) than for (4).



From these results it appears that ethylene, which in complex (1) is unsymmetrically bonded to the metal, is indeed strongly activated towards nucleophilic attack and competes with the metal centre, to give addition rather than substitution reactions, even when the nucleophiles used are among the most reactive towards platinum(II). This, we believe, represents the highest degree of activation that one can expect from the co-ordination of an olefin to a metal atom.

† All the reactions were carried out in water or methanol at temperatures between 0 and 20 °C. The new compounds precipitated out of solution as white solids and were fully characterized by elemental analysis, i.r. and  $^1\text{H}$  n.m.r. spectra, and conductivity measurements.

The authors are grateful to Consiglio Nazionale delle Ricerche (C.N.R.), Roma, for financial support and to Miss S. Boesso for technical assistance.

Received, 16th September 1982; Com. 1104

## References

- 1 J. Chatt, L. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 1957, 2496; J. K. Stille and R. A. Morgan, *J. Am. Chem. Soc.*, 1966, **88**, 5135; A. De Renzi, R. Palumbo, and G. Paiaro, *ibid.*, 1971, **93**, 880; S. J. Betts, A. Harris, R. N. Haszeldine, and R. V. Parish, *J. Chem. Soc. A*, 1971, 3699; L. F. Hines and J. K. Stille, *J. Am. Chem. Soc.*, 1972, **94**, 485; W. T. Wipke and G. L. Goeke, *ibid.*, 1974, **96**, 4244.
- 2 O. Eisenstein and R. Hoffmann, *J. Am. Chem. Soc.*, 1980, **102**, 6148; 1981, **103**, 4308.
- 3 A. Tiripicchio, M. Tiripicchio-Camellini, L. Maresca, G. Natile, and G. Rizzardi, *Cryst. Struct. Commun.*, 1979, **8**, 689.
- 4 M. A. M. Meester and K. Olie, *Cryst. Struct. Commun.*, 1975, **4**, 725; M. A. M. Meester, D. J. Stufkens, and K. Vrieze, *Inorg. Chim. Acta*, 1975, **14**, 25; 1975, **15**, 137; R. A. Love, T. F. Koetzle, G. J. B. William, L. C. Andrews, and R. Bau, *Inorg. Chem.*, 1975, **14**, 2653.
- 5 S. G. Davies, M. L. H. Green, and D. M. P. Mingos, *Tetrahedron*, 1978, **34**, 3047 and references therein; H. Werner, R. Feser, and R. Werner, *J. Organomet. Chem.*, 1979, **181**, C7; L. Cosslett and L. A. P. Kane-Maguire, *ibid.*, 1978, **178**, C17; P. J. Lennon, A. Rosan, M. Rosenblum, J. Tancrede, and P. Waterman, *J. Am. Chem. Soc.*, 1980, **102**, 7033 and references therein; T. Bodnar, S. J. La Croce, and A. R. Cutler, *ibid.*, 1980, **102**, 3292; H. Werner and R. Werner, *J. Organomet. Chem.*, 1979, **174**, C63; M. L. H. Green, *Pure Appl. Chem.*, 1978, **50**, 27; H. Kurosawa, T. Majima, and N. Asada, *J. Am. Chem. Soc.*, 1980, **102**, 6996.
- 6 P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Am. Chem. Soc.*, 1968, **90**, 4175; R. Palumbo, A. De Renzi, A. Panunzi, and G. Paiaro, *ibid.*, 1969, **91**, 3879; A. Panunzi, A. De Renzi, and G. Paiaro, *ibid.*, 1970, **92**, 3488; D. Hollings, M. Green, and D. V. Claridge, *J. Organomet. Chem.*, 1973, **54**, 399; G. Natile, L. Maresca, and L. Cattalini, *J. Chem. Soc., Dalton Trans.*, 1977, 651; G. Natile, *J. Chem. Soc., Chem. Commun.*, 1978, 654; I. M. Al-Najjar and M. Green, *ibid.*, 1977, 926; *J. Chem. Soc., Dalton Trans.*, 1979, 1651.