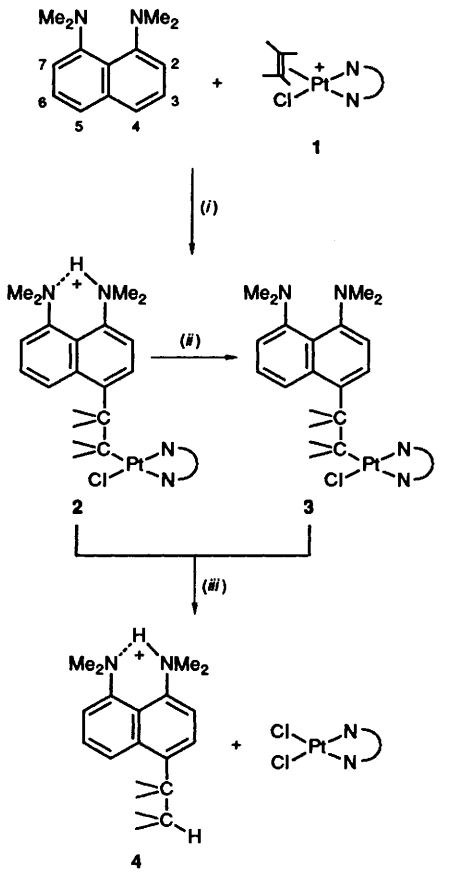
On the Carbon Nucleophilicity of Proton Sponge

Luciana Maresca,* Giovanni Natile and Francesco P. Fanizzi
Dipartimento Farmaco-Chimico, Università di Bari, via G. Amendola 173, 70126 Bari, Italy

Proton sponge [1,8-bis(dimethylamino)naphthalene] acts as a carbon nucleophile towards co-ordinated alkenes in $[Pt(\eta^2\text{-alkene})Cl(Me_2NCH_2CH_2NMe_2)]^+$ (alkene = ethylene, propene or styrene), the resulting Pt–C σ bond being cleaved by acids to afford the 4-alkyl-substituted base.

1,8-Bis(dimethylamino)naphthalene, widely known as proton sponge (a trade-mark of Aldrich), being a very strong base but a very poor nucleophile,[1] is largely employed in many processes where proton removal can be achieved excluding side reactions with the base.[2] Recently, however, there have been some reports of the reactivity of proton sponge itself or of some of its derivatives,[3–5] *e.g.* hydrogen loss from one methyl group and formation of 2,3-dihydro-1,1,3-trimethylpyrimidinium cation promoted by rhodium(III) complexes,[3] or substitution of one *para*-hydrogen by a heteroaromatic super electrophile such as 4,6-dinitrobenzofurazan 1-oxide or 4,6-dinitrobenzofurazan.[4]

We now report on a new reaction of this base, that is nucleophilic addition to co-ordinated alkenes. The complexes $[Pt(\eta^2\text{-alkene})Cl(tmen)]^+$ (tmen = *N,N,N′,N′*-tetramethylethane-1,2-diamine; alkene = ethylene **1a**,[6] propene **1b** or styrene **1c**) react smoothly with proton sponge in dry chlorinated solvents to give an addition product **2** in which a platinum alkyl moiety has replaced a proton in the *para* position and this has been taken up by the amino groups (Scheme 1). Treatment of the cationic species **2** with a base removes the proton yielding the corresponding neutral complex **3**. Acids do not reverse the carbon-to-carbon coupling but cleave quantitatively the Pt–C bond yielding the corresponding alkylated proton sponge **4**.[†]



Scheme 1 (*i*), Dry CH_2Cl_2 or $CHCl_3$; (*ii*), KOH, CH_2Cl_2 or $CHCl_3$; (*iii*) gaseous HCl, CH_2Cl_2 or $CHCl_3$

The addition reaction is rapid in the case of ethylene, slower in the cases of propene and styrene (the presence of a substituent, either for electronic or steric reasons, resulting in a reduced electrophilicity).[‡] In a protic medium such as water or alcohol the above reaction does not take place but the proton sponge mediates the simple addition of OH^- or OR^- to the platinum substrates.[8]

Aromatic amines have the tendency to behave as weak carbon bases since the strong resonance interaction between the amino group and the aromatic ring makes the lone pair of electrons partially available to the *ortho*- and *para*-carbon atoms.[9] This resonance should be considerably reduced in 1,8-bis(dimethylamino)naphthalene owing to steric reasons which

---

[†] The GC-MS spectra of deprotonated compounds **4a** and **4b** gave rise to a single peak with *m*/*z* 242 and 256 respectively; in the case of **4c** the presence of two peaks of different intensity at *m*/*z* 318 stems from the presence of a certain amount of the anti-Markovnikov addition product.[7]

[‡] The NMR assignments (atom numbering as in Scheme 1) were based on ^1H and double-resonance experiments. ^1H NMR (300 MHz, CD_2Cl_2, standard $SiMe_4$): **2a**, δ 1.63 [m, 2 H, $PtCH_2CH_2N$, $J(PtH)$ = 85], 2.76 (s, 6 H, NMe_2 of tmen), 2.87 (s, 6 H, NMe_2 of tmen), 3.11 (m, $PtCH_2CH_2$), 3.20 [d, 6 H, NMe_2 of proton sponge, $J(H^+\text{–}NMe_2)$ = 2.5], 3.23 [d, 6 H, NMe_2 of proton sponge, $J(H^+\text{–}NMe_2)$ = 2.9], 7.57 (d, 1 H, H^3), 7.69 [d, 1 H, H^2, $J(H^2H^3)$ = 7.7], 7.72 [dd, 1 H, H^6, $J(H^6H^7)$ = 7.6], 8.67 [dd, 1 H, H^5, $J(H^5H^6)$ = 7.4, $J(H^5H^7)$ = 2.3], 19.35 (s, br, 1 H, NH); **3a**, 1.61 [m, 2 H, $PtCH_2CH_2N$, $J(PtH$ = 88], 2.76 (s, 6 H, NMe_2 of tmen), 2.77 (s, 12 H, NMe_2 of proton sponge), 2.80 (s, 6 H, NMe_2 of tmen), 2.95 (m, $PtCH_2CH_2N$), 6.88 [d, 1 H, H^2, $J(H^2H^3)$ = 7.7], 6.95 (d, 1 H, H^7), 7.25 (d, 1 H, H^3), 7.34 [dd, 1 H, H^6, $J(H^6H^7)$ = 7.3] and 7.93 [d, 1 H, H^5, $J(H^5H^6)$ = 7.6]; **4a** (in its deprotonated form), 1.36 (t, 3 H, CH_2CH_3), 2.79 (s, 6 H, NMe_2), 2.83 (s, 6 H, NMe_2), 3.01 (q, 2 H CH_2CH_3), 6.91 [d, 1 H, H^2, $J(H^2H^3)$ = 7.8], 7.00 (dd, 1 H, H^7), 7.36 [dd, 1 H, H^6, $J(H^6H^7)$ = 6.7], 7.59 [dd, 1 H, H^5, $J(H^5H^6)$ = 8.4, $J(H^5H^7)$ = 1.1 Hz]. For **2a** and **3a** the assignments of H^5 and H^7 could also be reversed. The corresponding series of compounds **2b**–**4b** and **2c**–**4c** exhibit a general broadening of the NMR signals as a consequence of restricted rotation about the newly formed C–C bond; a temperature-dependent NMR study is in progress.

prevent the dimethylamino groups from becoming coplanar with the aromatic rings;[10] still proton sponge can act as a carbon nucleophile towards olefins co-ordinated to a metal centre in a cationic substrate.

We suggest that proton sponge may exist, at least in aprotic solvents, in equilibrium with a zwitterionic form having a proton shared by the two amino functions and a naked carbanion in *para* position. Although the concentration of such a zwitterion should not have analytical relevance, it could account for the observed reactivity. The other possibility would be a direct nucleophilic attack of proton sponge in its usual form on the co-ordinated olefin, which would lead to a quinoid type of intermediate (or transition state) in which one *para*-carbon carries the platinumalkyl moiety in addition to the hydrogen and the corresponding amino group shares its lone pair of electrons with the ring carbon. Such an intermediate is surely disfavoured both on electronic and steric grounds, and implies loss of aromaticity and, furthermore, coplanarity of a NMe_2 function with the ring system which is sterically hindered.

In conclusion the reaction described has evidenced a potent reactivity of proton sponge and allows a metal-co-ordinated olefin in a cationic substrate to be classified as an extremely good electrophile.

Acknowledgements

This work was supported by the Consiglio Nazionale delle Ricerche and Ministero della Università e della Ricerca Scientifica e Tecnologica.

References

1 R. W. Alder, P. Bowman, W. R. S. Steele and D. R. Winterman, *Chem. Commun.*, 1968, 723; R. W. Alder and J. E. Anderson, *J. Chem. Soc., Perkin Trans. 2*, 1973, 2086; A. Awwal and F. Hibbert, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1589; R. W. Alder, M. R. Bryce and N. C. Goode, *J. Chem. Soc., Perkin Trans. 2*, 1982, 477.

2 See, for example, J. L. Sessler, T. Murai, V. Lynch and M. Cyr, *J. Am. Chem. Soc.*, 1988, **110**, 5586; K. E. Garrett, J. B. Sheridan, D. B. Pourreau, W. Changfeng, G. L. Geoffroy, D. L. Staley and A. L. Rheingold, *J. Am. Chem. Soc.*, 1989, **111**, 8383.

3 S. N. Gamage, R. H. Morris, S. J. Rettig, D. C. Thackray, I. S. Thorburn and B. R. James, *J. Chem. Soc., Chem. Commun.*, 1987, 894.

4 F. Terrier, J. C. Halle, N. J. Pouet and M. P. Simonnin, *J. Org. Chem.*, 1986, **51**, 409; N. P. Simonnin, J. C. Halle, M. J. Pouet and F. Terrier, *Can. J. Chem.*, 1987, **65**, 404.

5 N. V. Vistorobskii, A. F. Pozharskii, S. V. Shorshnev and A. I. Chernyshev, *Mendeleev Commun.*, 1991, 10.

6 L. Maresca, G. Natile and G. Rizzardi, *Inorg. Chim. Acta*, 1980, **30**, 53; G. Gervasio, S. A. Mason, L. Maresca and G. Natile, *Inorg. Chem.*, 1986, **25**, 2207.

7 M. K. Cooper, P. J. Guerny, J. H. Ling and R. S. Nyholm, *J. Organomet. Chem.*, 1975, **91**, 117; R. Palumbo, A. de Renzi, A. Panunzi and G. Paiaro, *J. Am. Chem. Soc.*, 1969, **91**, 3874.

8 F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile and F. Gasparrini, *J. Chem. Soc., Dalton Trans.*, 1990, 1019.

9 M. J. Strauss, R. A. Renfrow and E. Buncel, *J. Am. Chem. Soc.*, 1983, **105**, 2473; R. J. Spear, W. P. Norris and R. W. Read, *Tetrahedron Lett.*, 1983, **24**, 1555.

10 H. Einspahr, J. B. Robert, R. E. Marsh and J. D. Roberts, *Acta Crystallogr., Sect. B*, 1973, **29**, 1611.

Received 3rd *February* 1992; *Communication* 2/00586G