Electronic Structures of π-Complexes of Heteroaromatic Systems

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THE recent isolation of tricarbonyl-π-hexamethylborazinechromium[1] prompts us to report some simple molecular-orbital calculations of the delocalization energies of various arene- and borazine-chromium metal–ring bond strengths in π-complexes of a series of substituted borazines and benzenes and led one of us[2] to suggest that complexes of the former might occur.

The simple molecular-orbital theory of organometallic molecules has been reviewed recently,[2] so only the ring–metal delocalization energies are compared in the Table.[3] In all cases the chromium atom was assumed to lie on the 3 (or 6)-fold symmetry axis of the borazine or benzene and the Cr–ring atom distance was taken as 2·23 Å as observed in tricarbonyl-π-hexamethylbenzenechromium.[4] A B–N distance of 1·44 Å was assumed in all the borazines. The nature of substituent effects (methyl and chloro) in equivalently-substituted benzenes and borazines and the appropriate Coulomb terms (H_{ii}) required to calculate the π-electron energies of these molecules have recently been discussed by us.[5] In the present comparative calculations, approximation (1) of reference 5 was used; that is, the following δ values were used:

$$\delta_B = -0{\cdot}7989, \quad \delta_N = +0{\cdot}7989$$

$$\delta_{Me} = -0{\cdot}6800, \quad \delta_{Cl} = +0{\cdot}2271$$

where, for example, $H_{BB} = H_{CC} + \delta_B\beta_{CC}$.

The metal–ring interaction energies were then calculated with the usual assumption* that the resonance integral H_{ij} could be expressed as:

$$H_{ij} = kG_{ij}$$

where the group overlap integrals, G_{ij}, were calculated from the ring π-orbitals (calculated on the above approximation) and assuming Slater functions for the chromium(0) 3*d*, 4*s*, and 4*p* orbitals; this is a correct procedure for a comparative calculation of Cr–ring energies. The respective Coulomb terms of the ring orbitals were obtained by identifying the highest occupied π-orbital with

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* Rference 2 and references therein.

TABLE

Delocalization energies of the complexes (ev)

Complex	k = 3·0 ev	k = 5·0 ev	k = 7·0 ev	k = 9·0 ev
Benzene	1·72	4·30	7·50	11·23
Hexamethylbenzene	3·41	6·42	9·85	13·25
1,3,5-Trimethylbenzene	1·92	4·62	7·89	11·78
1,3,5-Trichlorobenzene	1·66	4·17	7·32	10·92
1,3,5-Trichloro-2,4,6-trimethylbenzene	1·75	4·32	7·49	11·21
Borazine	1·23	3·27	6·01	9·25
Hexamethylborazine	1·45	3·68	6·55	9·95
B-Trimethylborazine	1·09	2·90	5·38	8·36
B-Trichloroborazine	1·04	2·81	5·27	8·22
B-Trichloro-*N*-trimethylborazine	1·61	4·09	7·27	10·98
N-Trimethylborazine	1·56	3·98	7·09	10·72

the observed ionisation potential[5] and the metal-orbital energies from the observed ionisation potential of chromium(0) and the mean *d–p* and *d–s* separations as given in Moore's tables.[6]

The total π-electron energy of the ring-metal system was then calculated assuming a total of 12 π-electrons to be accommodated. The delocalization energy was obtained by subtracting from this figure the sum of the Cr^0 ($3d^44s^2$) orbital energies and the ring π-electron energy. The results are given in the Table for a reasonable variation in the proportionality constant, k.

In all cases the interaction energy of a borazine–chromium system is less than that of the corresponding benzene–chromium system so borazine complexes of either a "sandwich" or "half-sandwich" type might be expected to be the less stable. However, of the proposed borazine complexes, that formed by hexamethylborazine has a reasonably large delocalization energy and so its existence may be inferred. Our calculations also suggest that a number of other borazine complexes may also occur, notably from *N*-trimethylborazine and *B*-trichloro-*N*-trimethylborazine.

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[1] R. Prinz and H. Werner, *Angew. Chem. Internat. Edn.*, 1967, **6**, 91.

[2] D. A. Brown "Transition Metal Chemistry", Vol. III, Marcel Dekker Inc., New York.

[3] Full details are given in the thesis "Studies on Heteroaromatic Complexes", C. G. McCormack, National University of Ireland, 1966.

[4] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1298.

[5] D. A. Brown and C. G. McCormack, *Theor. Chim. Acta.*, 1966, **6**, 350.

[6] C. E. Moore, "Atomic Energy Levels", Nat. Bur. of Standards, Circular No. 467, Vol. III. U.S. Govt. Printing Office, Washington D.C. 1951.