

A report on the Discussion Meeting on organic synthesis and catalysis via metalloorganics

The chemistry of organometallic compounds or *metalloorganics* has emerged as a field with enormous potential for application in organic synthesis and catalysis. Even bio-organic chemistry and material science stand to gain from its advances. In India, research in metalloorganic chemistry has begun only recently. The difficulty lies in the multi-disciplinary nature of this area and the lacuna of an adequate curriculum in postgraduate courses. The experimentation usually demands stringent inert atmosphere techniques and modern spectroscopic analyses, which are often beyond the reach of average University faculty. However, a Discussion Meeting on 'Organic synthesis and catalysis via metalloorganics' held at the National Chemical Laboratory, Pune, on 23 and 24 September 1993, under the auspices of the Indian Academy of Sciences, Bangalore, concluded on an encouraging note.

The meeting was the first of its kind in India. The main objective was to provide a forum for the exchange of ideas amongst organometallic chemists, to create an awareness of international research in various directions, and, to assess and promote the research currently being conducted in India. The presentations revealed that a large number of groups are actively engaged in research in this area. While the interests were widely varied, ranging from clusters to cobaloximes, the seriousness of their pursuit was evident. It was also heartening to note that the average age of participants was around thirty.

Unprecedented stereo- and regio-control in complex metal-mediated transformations immensely enriched the arsenal of organic synthetic chemists. The special lecture of S. Chandrasekaran (IISc) illustrated this with impressive examples of new and useful reactions and their application in the synthesis of complex targets, natural and non-natural. T. K. Sarkar (IIT/Kharagpur) described a judicious use of silicon in his synthesis of (\pm)-cucurbitic acid and (\pm)-methyl epijasmone. A. Sarkar (NCL) presented an account of remote stereocontrol on arenechromium templates where the metal fragment acts as a stereodirecting group. The new

half-sandwich arene-ruthenium complex characterized by Z. Shirin and R. N. Mukherjee (IIT/Kanpur) promises rich chemistry waiting to be synthetically exploited.

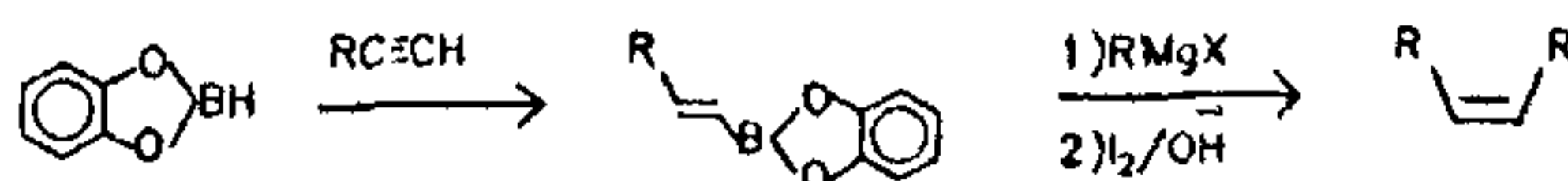
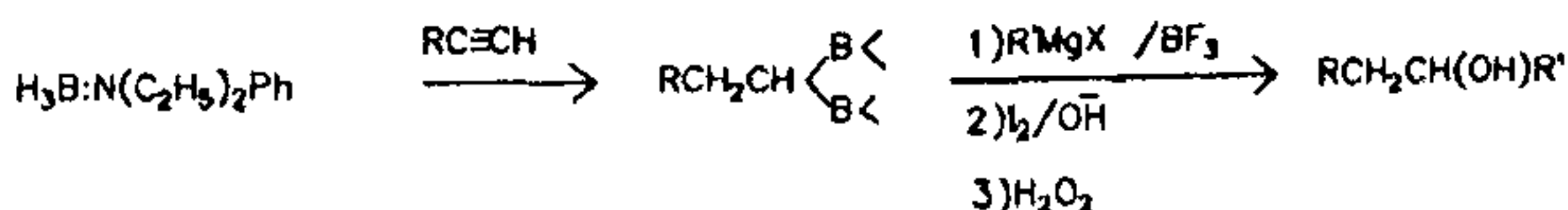
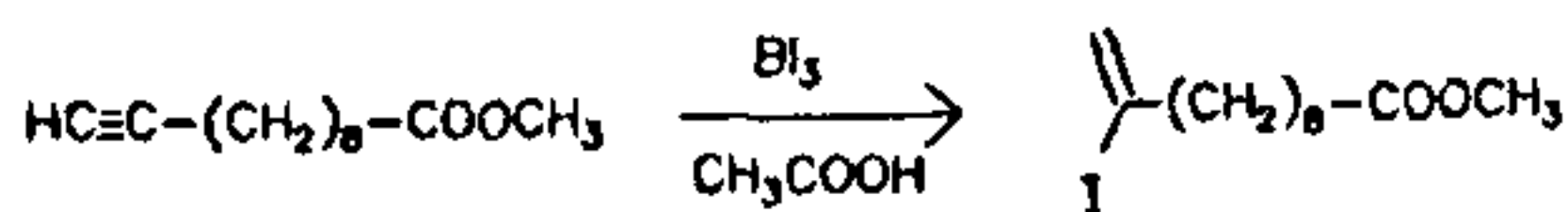
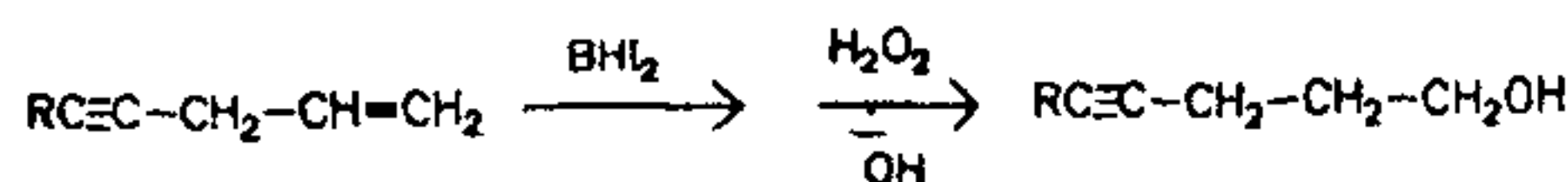
New reagents are sometimes developed by modifying existing reagents to attain improved selectivity and efficiency. Such modifications must originate from an intuitive understanding of chemistry guided by imagination. M. Periasamy (Univ. of Hyderabad) described systematic development of a number of new reagents derived from boron, aminoboranes and NaBH_4/I_2 in particular, and those derived from transition metals to effect selective transformations (scheme 1). S. K. Nayak (BARC) discussed novel synthetic transformations induced by low-valent titanium complexes while A. G. Samuelson (IISc) presented activation of allylic substrates promoted by copper(I). In their poster, D. Jayaprakash and Samuelson displayed an interesting zinc-mediated allyl transfer in aqueous medium. Unexpected ring opening of THF in organometallic reaction medium, as observed by S. Bhar and B. C. Ranu (IACS), questioned the suitability of this solvent in many such reactions.

Several posters were presented on the involvement of organometallic reagents

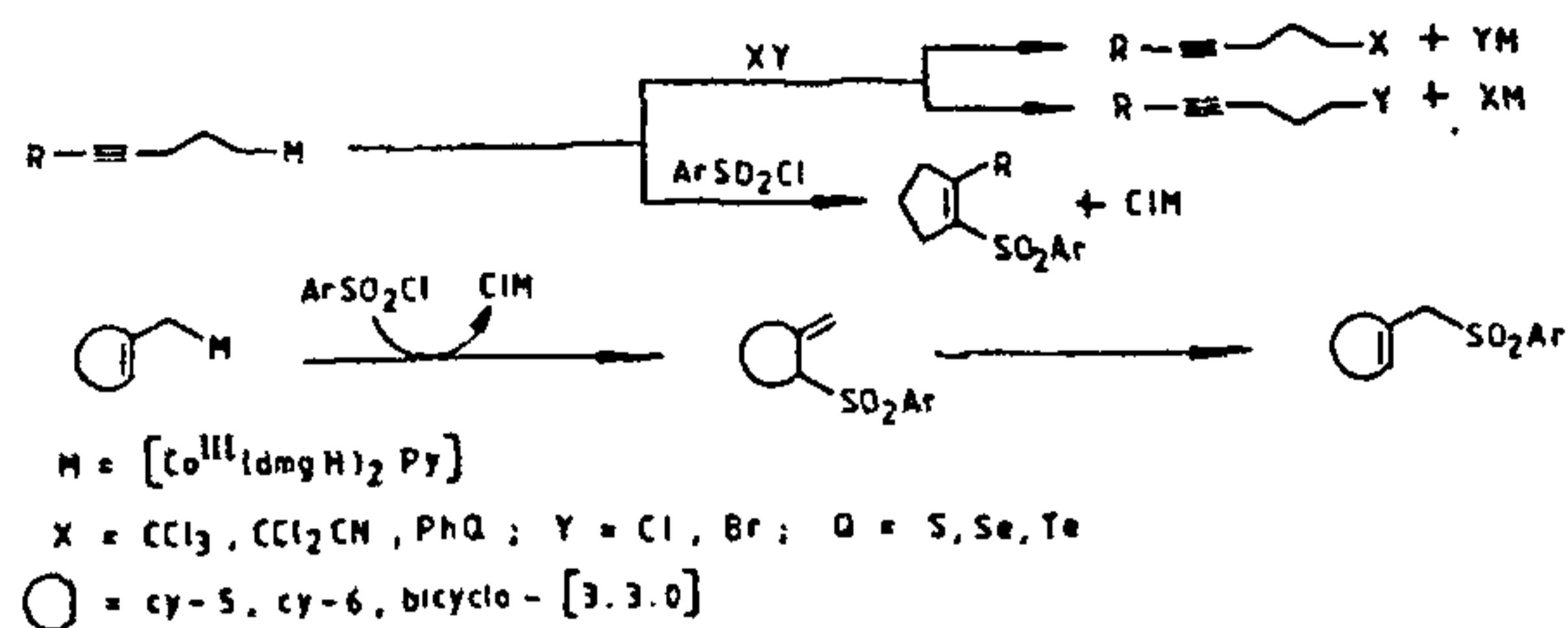
in group transfer reactions. B. G. Hazra (NCL) described selective *trans* dichlorination and dibromination mediated by manganese. E. Nandanam and B. B. Lohray (NCL) proposed a new transition state model for the enantioselective dihydroxylation of unfunctionalized alkenes catalysed by OsO_4 . D. Chatterjee (CSMCRI) presented a study on the epoxidation of olefins by Ru(V) oxo complexes.

Organometallic complexes are also synonymous with catalysis. Some of the major uses of cobalt as an oxygenation catalyst was discussed by J. Iqbal (IIT/Kanpur). His associate Beena Bhatia presented illustrations of a host of other organic transformations effected by cobalt catalysis. Construction of asymmetric quaternary carbon centres through a catalytic pathway was discussed in detail by A. K. Sarkar (Presidency College, Calcutta). S. Sengupta (Jadavpur Univ.) disclosed the preliminary results of palladium catalysed reactions being developed to construct biaryl-derived targets. The use of phase-transfer catalysis in organometallic chemistry was illustrated by S. Vancheesan (IIT/Madras).

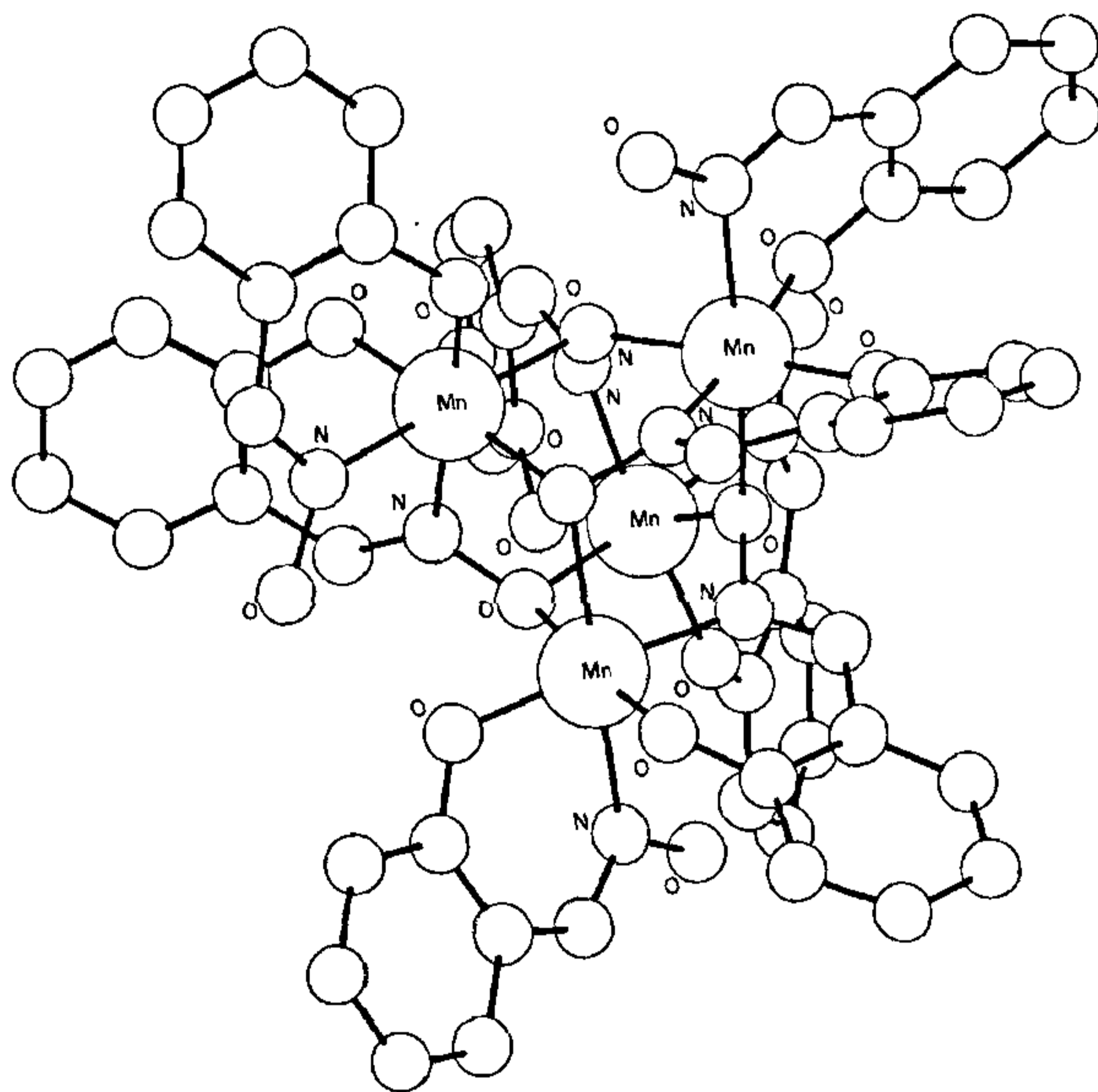
Metal clusters bridge the span between homogeneous and heterogeneous catalysis. S. Bhaduri (Alchemie) forwarded arguments as well



New boron reagents.



Cobaloximes in synthesis.



X-ray structure of tetramanganese cluster.

as evidence to refute the notion that catalysis through cluster compounds usually involves breaking down of the cluster to provide active mononuclear species. He also pointed out that clusters can be tailored to provide highly selective catalytic species. Activation of phenylacetylene in butterfly clusters of iron and facile C-C bond cleavage were highlighted by P. Mathur (IIT/Bombay). An interesting poster on cluster chemistry by S. K. Bhar and R. L. Dey (Jadavpur Univ.) featured synthesis and characterization of

new R-P bridged clusters of iron and cobalt.

One of the most important aspects of organometallic chemistry is the study of their structures. The chance observation of an unusual product by S. K. Chandra and A. Chakravorti (IACS) raised an intricate mechanistic question concerning cobalt/organic ligand interaction. S. K. Chowdhury and A. Sarkar (NCL) presented evidence in support of an unusual affinity of a phenyl ring for a proximal methyl group, relevant to the existence of a CH/ π stabilizing interac-

tion. S. Bhattacharya and V. D. Gupta (BIU) displayed structural studies on cyclopentadienylzirconium(IV) complexes while M. V. Gururaj and B. S. Chandrasekhar (Gulbarga Univ.) disclosed structural characterization of mixed polypyrazolyl borate complexes of Zr, V, Mo, Ni, and Cu. Structural studies were also carried out by A. S. Kumbhar and S. B. Padhye (Poona Univ.) on *cis*-dicarbonyltetraiodoiridium(III), an intermediate in the catalytic cycle of oxycarbonylation promoted by iodide. S. S. Tavale and V. G. Puranik (NCL) presented X-ray structure determination of a giant tetrameric manganese complex with greater than ninety atoms (scheme 2). C. Gopinathan (NCL) and his group displayed a poster depicting insertion reactions in selected organoruthenium complexes.

To address contemporary research efforts in synthetic polymeric materials and advances in polymerization catalysts, S. Sivaram (NCL) provided an excellent overview of the field. He illustrated, with specific examples, the unprecedented control of reactivity, regioselectivity, stereoselectivity and enantioface selectivity possible during polymer synthesis using organotransition metal catalysts. Involvement of metal-carbene intermediates in polyacetylene synthesis was explored by B. Gita and G. Sundararajan (IIT/Madras). H. B. Singh (IIT/Bombay) presented his work on the synthesis of some novel organotelluriums of potential synthetic interest and material application.

E. D. Jemmis (Univ. of Hyderabad) elucidated the theoretical framework for organometallic chemistry and illustrated how the isolobal concept simplified descriptions of FMOs of M_n fragments. The application of theory to understand structure and reactivity of the carbyne ligand was based on his own work.

The latest development in the area of metalloorganics is their application in biological systems. S. B. Padhye (Poona Univ.) presented an account of current research efforts in metalloimmunoassay where organometallic complexes are used as labels for studying enzyme-substrate, hormone-receptor and antigen-antibody reactions. His work on bioorganometallics involved the design, synthesis and structural characterization of a tetrameric manganese cluster for the photoreactivation of manganese depleted spinach PS II particles. Two consecutive presentations of the same

session concerned synthetic exploits of cobaloxime chemistry discussed by B. D. Gupta (IIT/Kanpur) and S. Roy (IICT) (scheme 3). A related facet of this chemistry was presented by K. Qanungo and B. D. Gupta in a poster.

In the concluding session of panel discussion, it was unanimously agreed that a serious beginning in organometallic research has been made despite

all the limitations of an Indian laboratory. It was suggested that training programmes like summer/winter schools and workshops should be organized as a national initiative to sustain the growth of this discipline. To foster closer interaction with practising chemists of this area, such small and intensive meetings could be organized periodically at various parts of the country.

S. Rajappa, Chairman of the Organizing Committee, gratefully acknowledged the sponsorship of the Indian Academy of Sciences, Bangalore, for this timely and stimulating scientific event.

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RESEARCH NEWS

Should entropy always drive a system to disorder?

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It is one of the accepted tenets of physics that entropy is intimately associated with the degree of disorder present in a system. Therefore it follows that an increase in entropy in any given system should lead to an increase in disorder. This has become an important topic for discussion in recent times. Surprisingly, theorists and experimentalists have come up with systems that behave very differently. In these systems an increase in entropy drives them from a state of positional disorder to a state of positional order. There is also one other possibility of going to a relatively ordered state. For example a homogeneous mixture of two components may also be driven, by entropy, to a state in which the two components get separated spatially resulting in a phase separation. In fact, it was this problem that first attracted the attention of theorists.

The early work of Labowitz and Rowlinson¹ on multicomponent hard sphere fluids indicated that in the Percus-Yevick (PY) approximation a complete miscibility results between the various components. There were no indications whatever of a phase separation at all concentrations and particle size ratios. This led to the generally accepted idea that binary hard-sphere fluids never phase-separate. It is in this context, that the work of Biben and Hansen² acquires a lot of significance. They studied a binary mixture of large (*A*) and small (*B*) hard spheres having diameter ratios $(\sigma_A/\sigma_B) \gg 1$, on the basis of Rogers and Young³ and Ballone *et al.*⁴ theories, which differ from that of

PY. They found the interesting result that the mixture phase separates at packing fractions typical of liquids. This is very important in view of the fact that there are no real attractive interactions between the components of the fluid. The effect is entirely due to an increase in the entropy of the phase-separated system relative to that of the homogeneous binary mixture. These authors attribute this feature to an effective 'attraction' between the large spheres *A*. This attraction which is entropic in origin leads to an aggregation of large spheres *A* in a solvent of small spheres *B*.

On the experimental side it is worth recalling the important results found in two totally different systems. It is quite well known⁵ that in a compound of sodium and zinc one can have a crystal with a complex structure AB_{13} with *A* representing Zn, the larger atom and *B* representing Na, the smaller of the two species. Interestingly an exactly similar structure has recently been seen by Bartlett *et al.*^{6,7} in a binary mixture of colloidal particles *A* and *B* in suspension with two different diameters σ_A and σ_B respectively ($\sigma_A > \sigma_B$). The structure AB_{13} is indeed very complex (Figure 1). It consists of a body-centred

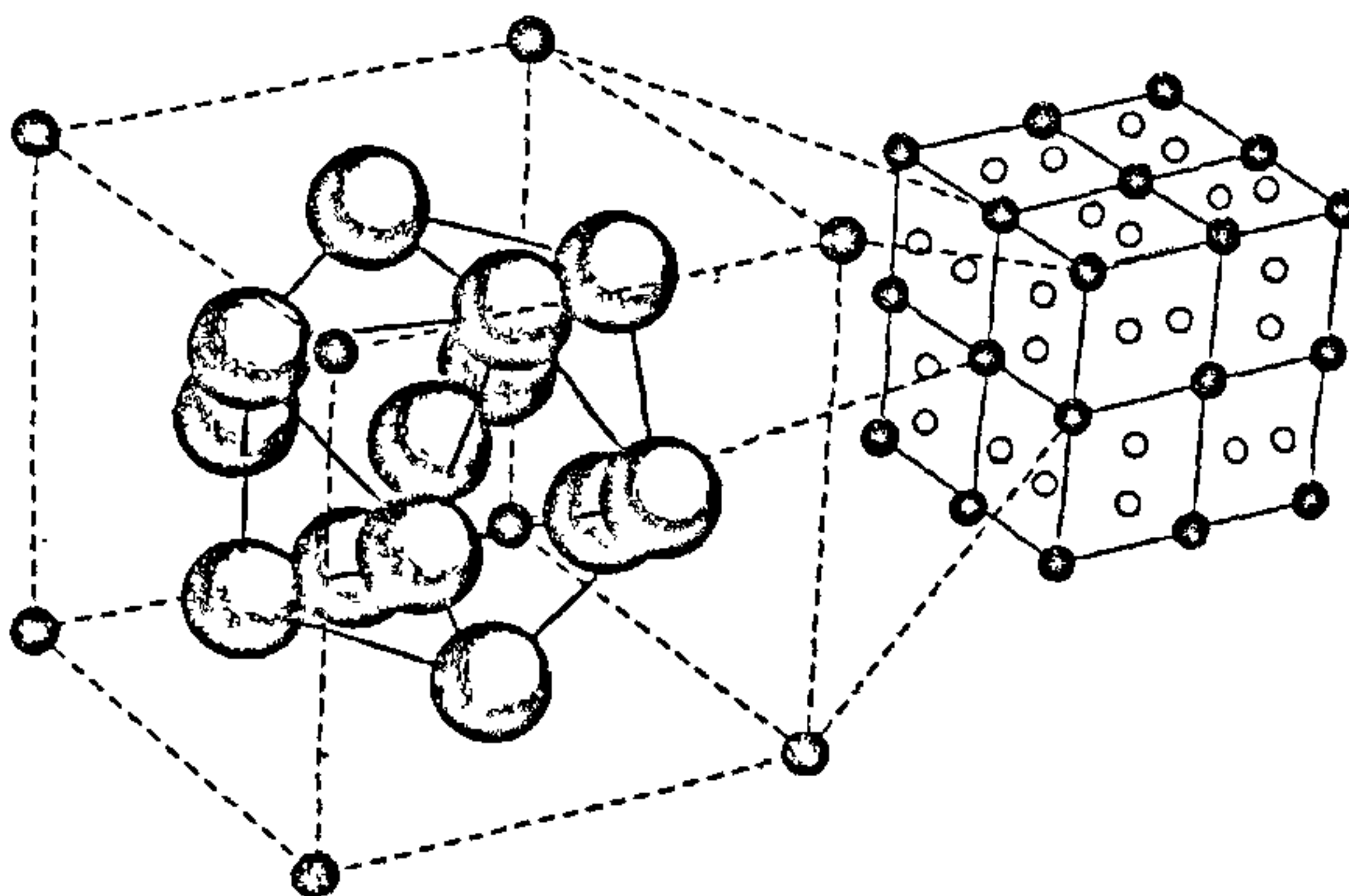


Figure 1. Schematic representation of AB_{13} structure. In the unit cell (right) 'closed' circles represent *A* and 'open' circles represent *B*. In the sub-cell (left), the small 'closed' circles represent *A* and the 'shaded' spheres represent *B* (After Eklridge *et al.*¹⁰).