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Book review

Electron Spin Resonance Vol. 6. Ed. P.B. Ayscough, The Royal Society of Chemistry, London, 1981, £49.00 (non-members), £29.00 (members).

In 1842 Bunsen tried to make $Me_2As\cdot$ radicals from dimethylchloroarsine and zinc. Ever since, the development of the chemistry of organometallic compounds has been remarkably closely involved with that of free radicals, and Frankland's work on the reaction of alkyl iodides with zinc, Gomberg's studies of the similar reaction of triphenylmethyl chloride, and Paneth's pyrolysis of organolead compounds, are important land-marks in both histories. The more recent development of the organic chemistry of transition metals has of course given many paramagnetic complexes.

Organometallic chemists may therefore be surprised how much they will find to interest them in this review of work reported on electron spin resonance between June 1978 and November 1979. ESR spectroscopy is the most powerful technique for studying paramagnetic species, and in appropriate cases it can detect and identify the radical, determine its electronic configuration and its conformation, monitor its reactions, and measure its concentration and its reaction kinetics.

This book contains twelve chapters, each contributed by an expert in the field. The two chapters most relevant to organometallic chemistry are those by A.L. Porte on transition metal ions, and by M.C.R. Symons on inorganic and organometallic radicals, but examples of homolytic organometallic chemistry occur throughout the book. The following few examples may help to whet the appetite.

Decamethylcyclopentasilane can be reduced to a radical anion, $Me_{10}Si_5\cdot^-$, which shows an ESR spectrum consisting of a 31-peak multiplet arising from hyperfine interaction with ten equivalent methyl groups. The unpaired electron is believed to occupy π-type orbital which is formed by the overlap of $3d$ or $4p$ orbitals on the silicon atoms. Some arylated examples (e.g. $Me_9PhSi_5\cdot^-$ and $Ph_8Si_4\cdot^-$ have now been prepared).

Resonance stabilization of the $C_5H_5\cdot$ radical causes the cyclopentadienyl—metal bond in many compounds C_5H_5—MX_n to be photolabile, providing a source of a variety of metal-centred radicals, $\cdot MX_n$.

Aluminium atoms will add to the double bond of ethylene to give a complex with a structure which can be represented on the Chatt-Dewar-Duncanson model: the π-bond of the alkene donates electrons into a vacant sp_y hybrid orbital on aluminium, and the semifilled p_x orbital on aluminium back-donates into the vacant antibonding orbital of the alkene. A similar benzene complex has now been prepared; the aluminium atom interacts with only one C=C unit of the ring.

Phosphorus(III) compounds react with radicals to form trigonal bipyramidal phosphorus(IV) (phophiranyl) radicals whose ESR spectra show fascinating temperature effects as the axial and equatorial ligands change places.

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