Book Reviews

Photoprocesses in Transition Metal Complexes, Biosystems and Other Molecules. Experiment and Theory
E. Kochanski (ed.), NATO ASI Series C: Mathematical and Physical Sciences, Vol. 376, Kluwer Academic Publishers, Dordrecht, 1992, x + 449 pages. £97

This volume records the contributions to a NATO Advanced Institute held in Aussois, France in 1991. It includes 5 chapters of direct relevance to organometallic chemists and several more of considerable interest. For those of us who look in vain for a successor to Geoffroy and Wrighton's 1979 book on "Organometallic Photochemistry" in order to teach graduates, some of the material will be invaluable.

J.J. Turner's first chapter, entitled "Spectroscopic Techniques for Organometallic Intermediates" introduces matrix isolation, spectroscopy in liquid xenon, and time-resolved infrared (TRIR) spectroscopy (nano and picosecond timescales) as methods for reaction intermediates. He then shows how excited states can be probed by emission, excitation and resonance Raman spectroscopy in addition to TRIR. His second chapter "Photochemistry involving $Cr(CO)_5$ – still some puzzles" provides a timely review of this paradigm of metal carbonyl intermediates. Coming from the person who undoubtedly understands the story best, this review shows the contribution of the recent work especially on picosecond spectroscopy in the context of the earlier matrix and TRIR experiments. The new experiments provide direct evidence for the initial formation of $Cr(CO)_5$ in electronic and vibrational excited states, something which could only be deduced indirectly before spectroscopy stretched back to picoseconds.

Grevels' chapter on "Photochemistry of Organometal Carbonyls: Stereochemical and Catalytic Aspects" demonstrates the wealth of evidence to be garnered by conventional steady-state spectroscopy combined with preparative methods. He tackles first that most intractable of problems, the photosubstitution of $Fe(CO)_5$. Although there is a high quantum yield for double substitution by phosphites, and $Fe(CO)_3[P(OR_3)_2]$ is formed in a single flash, it does not follow that two carbonyl groups are expelled by one photon. Other topics covered are the photocatalytic isomerisation of alkenes, photosubstitution of $M_3(CO)_{12}$, photosubstitution of Group 6 hexacarbonyls by alkenes, photocatalytic hydrogenation and hydrosilylation of norbonadiene.

Veillard tackles theory in "Photochemistry of Organometallics: Quantum Chemical Approach". The theory of reaction pathways is of course particularly demanding. Veillard explains how the "Complete Active Space Self-Consistent Field" (CASSCF) can tackle the multitude of accessible states, many of which yield products via intersystem crossing and internal conversion. Ultimately, Veillard reduces the complexity to three situations: (i) one potential energy (PE) curve connects the excited state of reactant to the ground state of products (*e.g.* Cp_2MoH_2); (ii) one set of PE curves connect excited states of products (*e.g.* $Cr(CO)_6$ or *cis*-RuH_2L_4); (iii) excitation leads indirectly to population of a dissociative $^3(\sigma\sigma^*)$ PE curve leading to ground state radicals (*e.g.* $(OC)_5Mn–Mn(CO)_5$, $H–Co(CO)_4$).

D.J. Stufkens *et al.* provide a chapter summarising their work on "Photochemistry of Metal–metal Bonded Carbonyls and its relationship to Electron Transfer Chain Catalysis". They show how the photochemistry of $(OC)_5Mn–Mn(CO)_3(\alpha$-diimine) and $(OC)_3Mn(\alpha$-diimine)X depends on viscosity, temperature, the presence of donor solvent, the metal and the diimine – a complex, but intriguing story.

Other chapters of interest include that on "Theory of Electron Transfer Reactions and Comparison with Experiments" by Marcus and Siddarth; Peyerimhoff's account of "Relativistic Effects in Molecular Calculations," Balzani *et al.* on "Antenna Effect in Polynuclear Metal Complexes", and Scandola *et al.* on "Photophysics of Polynuclear Complexes, Intercomponent Energy and Electron Transfer Processes." The remainder of the book concentrates on long-range electron transfer in organic and biological contexts and on photosynthesis.

The book is produced from camera-ready copy, much of it of very high quality and includes a full index.

Robin N. Perutz
Department of Chemistry
University of York
Heslington, YORK Y01 5DD
UK

Metal Nitrosyls
G.B. Richter-Addo and P. Legzdins, Oxford University Press, Oxford, 1992, pp. 369 + xiv. £45.00
ISBN 0-19-506793-2

There was a time when metal nitrosyls were a topic of consuming interest to coordination chemists, but familiarity has perhaps made us too blasé about their challenge and significance. This book covers the literature to mid-to-late 1991, and it fills a void which has grown, rather unexpectedly, over the years. Although it is too early to deal in detail with the current excitement concerning NO as a biological signal, or the ideas about copper nitrosyls and their function in nitrite reductases, it is an endeavour entirely to be welcomed.

This book is aimed at beginning researchers or graduate students, and it is clearly written by authors who are teachers as well as investigators. It opens with a discussion of the electronic structures of NO and of its adducts and complexes. This is clear, fairly standard material, though I didn't know that NO^- is known as the nitroside anion. Unfortunately the authors do not avail themselves of IUPAC conventions and formalisms. The references for this one short chapter number 220.

The synthesis and characterisation of metal nitrosyls is dealt with next, and discusses subjects such as IR spectroscopy in the elucidation of terminal and bridging NO groups, the numbers of ν(NO) bands to be expected, and bent and linear nitrosyls. Again, a large number of references is adduced.

The next two chapters are highly condensed reviews on coordination compounds and organometallic compounds. These have a strong structural bias, and with over 900 references between them will serve as an invaluable guide to the original literature of the last 20 years. The chapter on organometallic compounds is one of the longest. The discussion is structure-based, in an arbitrary but useful fashion, and it complements the authors' own recent Chemical Review.

The next section deals with metal clusters (commencing with NO adsorption and extrapolating to molecular species) though there is no treatment of cluster electron counting. There is a short chapter on the bioinorganic chemistry of nitric oxide, which is principally concerned with haem derivatives, and the discussion of EDRF is understandably rather short. This is a pity, but is because the implication of the generation of NO in mammalian systems was not entirely clear when the book was written. Nevertheless, there are more than 280 references to this area.

Finally, there are chapters on the reactivity of metal nitrosyl complexes (this is a useful summary of the literature) and on nitric oxide and the environment.

In summary, this is an excellent book, which manages to present an enormous wealth of information in a digestible and accessible fashion. It covers the older chemistry and also indicates where the newer developments are coming. It fills a gap in the current literature, and should be available to any chemists with an interest in nitrogen(II) oxide.

G.J. Leigh
AFRC IPSR Nitrogen Fixation Laboratory
University of Sussex
Brighton BN1 9RQ
UK