

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 $\text{Cr}(\text{CO})_5$ – 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 $\text{Cr}(\text{CO})_5$ 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 $\text{Fe}(\text{CO})_5$. Although there is a high quantum yield for double substitution by phosphites, and $\text{Fe}(\text{CO})_3[\text{P}(\text{OR}_3)_2]$ 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 $\text{M}_3(\text{CO})_{12}$, photosubstitution of Group 6 hexacarbonyls by alkenes, photocatalytic hydrogenation and hydrosilylation of norbornadiene.

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.* $\text{Cr}(\text{CO})_6$ 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.* $(\text{OC})_5\text{Mn}-\text{Mn}(\text{CO})_5$, $\text{H}-\text{Co}(\text{CO})_4$).

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 $(\text{OC})_5\text{Mn}-\text{Mn}(\text{CO})_3(\alpha\text{-diimine})$ and $(\text{OC})_3\text{Mn}(\alpha\text{-diimine})\text{X}$ 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 YO1 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 litera-