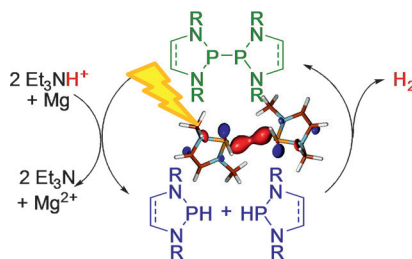


Photocatalysis

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Specific Photochemical Dehydrocoupling of N-Heterocyclic Phosphanes and Their Use in the Photocatalytic Generation of Dihydrogen



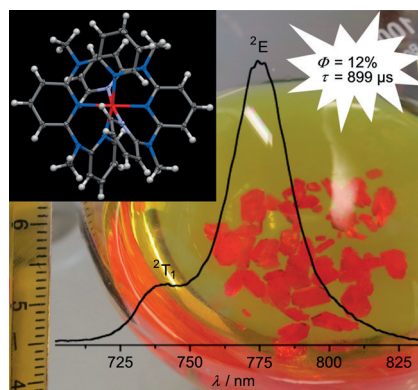
Hydrogen cycle: Highly selective photochemical dehydrocoupling converts N-heterocyclic phosphanes to diphosphanes and H₂, and is a key step in a reaction cycle enabling photocatalytic reductive generation of H₂ from Et₃NH⁺. Computational studies suggest that the reaction is initiated by the formation of dimeric molecular associates whose electronic excitation yields H₂ and two phosphanyl radicals.

Luminescent Complexes

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[Cr(ddpd)₂]³⁺: A Molecular, Water-Soluble, Highly NIR-Emissive Ruby Analogue



Strong, long-lived, and sharp NIR phosphorescence (775 nm, $\Phi = 12\%$, $\tau = 899 \mu\text{s}$) is achieved in the soluble chromium(III) complex [Cr(ddpd)₂]³⁺ (ddpd = *N,N'*-dimethyl-*N,N'*-dipyridin-2-ylpyridine-2,6-diamine) by ligand-field tuning through optimization of the ligand's bite angle and σ -donor strength. ³O₂ quenches the emission, allowing for optical oxygen sensing. The highly stable complex is easy to prepare in high yields from inexpensive starting materials.

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Flashback: 50 Years Ago ...

A range of reviews showed just how important various spectroscopic techniques had become. H. T. Witt et al. discussed the use of flashlight techniques in the analysis of photosynthetic processes by studying the time variation of the absorption spectra of chloroplasts after excitation. A. Almenningen et al. outlined the theory of electron diffraction for the study of gas-phase molecules, L. Vellutz and M. Legrand discussed progress in optical circular dichroism, and F. Schneider et al. summarized the use of electron paramagnetic resonance in organic chemistry.

The Communications section also contained contributions that featured spectroscopic techniques. T. Kruck and W. Lang reported on the synthesis of HIr(PF₃)₄ and on the NMR spectra of HM(PF₃)₄, where M = Co, Rh, Ir. Coupling with the ³¹P and ¹⁹F nuclei means that the proton signal should theoretically split into a multiplet containing 65 lines, although there was a degree of overlap of the signals. In another Communication, W. Lüttke and K. Wilhelm described how they used infrared spectroscopy to study methylenetriphenylphosphoranes. They concluded that the bond between the phosphorus and the

methylene carbon atom has only a slight double-bond character, which is useful to know for understanding Wittig reaction.

Angewandte Chemie has always published stimulating chemistry, not least the report by F. Korte et al. on the separation of hashish extract and the subsequent isolation and identification of tetrahydrocannabinolcarboxylic acid. At the time, this acid was regarded as the “missing link” in the biosynthetic pathway of the active principles of hashish.

Read more in Issue 10/1965.