

Ultrafast Dynamics of a Ferracyclobutadiene

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The photo-induced primary processes of a carbonyl-bearing ferracyclobutadiene are revealed by ultrafast time-resolved mid-infrared spectroscopy. Following optical excitation, a CO-dissociation occurs within several tens of picoseconds via barrier-crossing on the electronically excited state. Solvent binding by the vacancy of a coordinatively unsaturated intermediate is faster than the initial CO-loss.

Alkyne metathesis [1] is an important transformation in polymer chemistry. The reaction is transition-metal (TM) catalyzed and involves the intermediacy of metallacyclobutadienes (MCBD), i.e. four-membered heterocycles containing a TM as the heteroatom. MCBDs of groups 6, 7, and 9 TMs have been isolated and characterized in great detail [2]. However, MCBDs containing a group-8 TM have been entirely unknown until very recently, when the synthesis of a ferracyclobutadiene (FeCBD, species [A]) was reported (cf. Fig. 1a and Refs. [2, 3]). Compound [A] is dressed with three carbonyl (CO) ligands in addition to the bidentate didehydroallyl moiety that is common to all MCBDs. We have recently initiated an extensive research program aimed at exploring the photochemistry of such FeCBDs in an effort to access yet unknown ferracycles with light and to explore their catalytic activities for alkyne metathesis and similar chemical transformations [3].

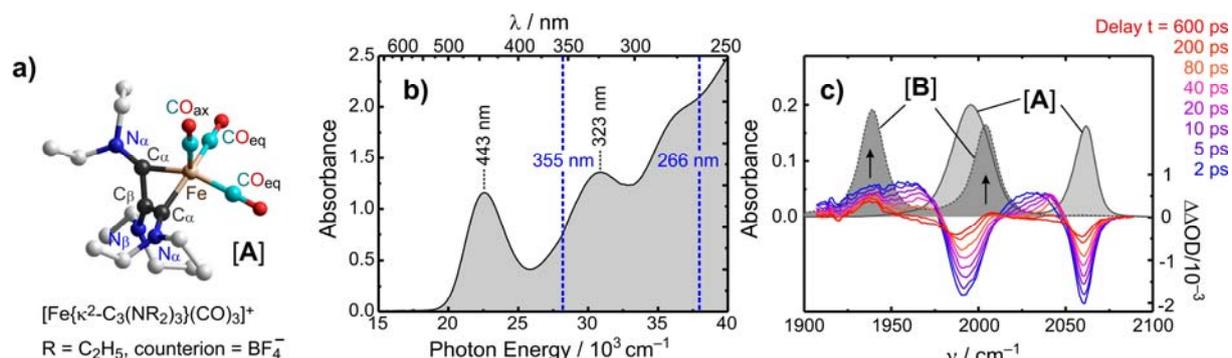


Fig.1 (a) Molecular structure of the FeCBD, [A] (all H-atoms hidden for clarity). The ferracycle is formed by the Fe-center, the two α -carbons (C_α) and the β -carbon (C_β). The metal center bears three CO-ligands, one of which occupies the axial (CO_{ax}), the other the two equatorial positions (CO_{eq}) of a square-pyramidal coordination sphere. (b) Experimental UV/Vis absorption spectrum of [A] in MeCN solution at 300 K. (c) Femtosecond MIR-spectra for various time delays (color-coded) and stationary FTIR spectra of [A], and its photoproduct, [B].

Using laser flash photolysis with step-scan Fourier-transform infrared (ss-FTIR) detection, we could show that in acetonitrile solution, [A] loses one of its two equatorial COs and that the vacancy, which is left behind by the departing ligand, is filled up by a solvent molecule thereby forming an acetonitrilo-ferracyclobutadiene dicarbonyl [B]. Since the time resolution of our ss-FTIR setup is limited to about 100 ns, we recorded the primary events following the initial absorption of the photolysis photon with femtosecond mid-infrared (MIR) spectroscopy (representative results, cf. Fig.1 c).

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