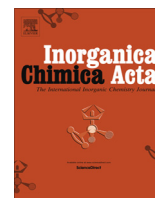




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Review

Primary photochemical dynamics of metal carbonyl dimers and clusters in solution: Insights into the results of metal–metal bond cleavage from ultrafast spectroscopic studies



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ABSTRACT

Metal carbonyl dimers and clusters constitute a diverse class of organometallic reagents and catalysts. The photochemistry of these complexes is a topic of significant and long-standing interest, as preparative-scale photolyses constitute many of the most synthetically powerful reactions in organometallic chemistry. The metal–metal bonding present in dimers and clusters is varied and significantly influences their overall reactivity. In this review we discuss the primary photochemical dynamics of transition metal carbonyl metal dimers and clusters, with a focus on the changes in metal–metal bonding that occur upon visible and/or ultraviolet photochemical excitation. The bulk of the results discussed here were obtained using ultrafast time-resolved infrared spectroscopy, a technique with high structural sensitivity afforded by the carbonyl reporter ligands of the complexes studied. Picosecond time resolution allows detailed monitoring of the photochemical reaction dynamics, including observation of initially excited complexes and short-lived transient metal–metal bond cleavage intermediates, as well as formation of the longer-lived, yet reactive, intermediates responsible for reactivity occurring on diffusion-limited time scales and beyond.

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Justin P. Lomont is a 5th year graduate student in Physical Chemistry at the University of California, Berkeley under the direction of Charles B. Harris. He is the recipient of several awards including an NSF Graduate Research Fellowship, an NSF-EAPSI Research Fellowship, and the K. Patricia Cross Future Leaders Award. Justin recently co-authored a book targeted at introducing chemistry to a general audience, and in the future he hopes to become a faculty member at an academic research institution. Upon completing his PhD he has plans to work as postdoctoral fellow with Professor Long Cai at the California Institute of Technology.

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Charles B. Harris received his PhD in Chemistry from the Massachusetts Institute of Technology in 1966 under the direction of Albert F. Cotton. After completing a post-doctoral fellowship in Physics from the Atomic Energy Commission at MIT, he joined the faculty at the University of California, Berkeley, in 1967. He currently holds appointments as a Professor of Chemistry at UC-Berkeley and as a Principle Investigator in the Chemical Sciences Division at Lawrence Berkeley National Laboratory. In addition to his work studying organometallic reaction dynamics using ultrafast infrared spectroscopy, his research also focuses on ultrafast electron dynamics at surfaces and interfaces. He is the recipient of numerous prestigious awards including, most recently, the Ahmed Zewail Award in Ultrafast Science and Technology.

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1. Introduction

The chemistry of transition metal carbonyl dimers and clusters is a subject of significant and long-standing interest. This is due to their numerous and varied applications in catalysis and as building blocks in the syntheses of organometallic complexes, along with the fact that their chemical reactivity and fluxional rearrangement patterns serve as models for the chemistry of other transition metal cluster complexes [1–3]. Preparative-scale photolyses are among the most synthetically useful reactions in all of organometallic chemistry, and as such a mechanistic understanding of the elementary steps of the photochemistry behind these reactions carries broad relevance.

The metal–metal (M–M) bonding in these complexes, and in particular the changes in M–M bonding that occur upon photoexcitation, play a crucial role in dictating the photochemical reactivity of these species in the solution phase. The 1960s represented a renaissance in the theory and experimental observation of M–M bonding, with double [4], triple [5], and quadruple [6–9] bonds all being discovered within the span of just a few short years. At the center of these numerous and rapid discoveries was Albert F. Cotton, to whose fruitful life and career this special issue is dedicated. In addition to his work discovering new types of M–M bonding, Cotton was at the forefront of the initial structural characterizations of many of the complexes studied in this article,

laying the foundation for subsequent explorations, such as those described here.

In this article we describe a series of ultrafast investigations into the solution-phase photochemistry of metal carbonyl dimers and clusters, with a focus on the primary photochemical processes involving cleavage of M–M bonds. The photochemistry of these complexes is diverse, with excited state lifetimes ranging from femtosecond to millisecond time scales, along with the possibility for charge transfer, ligand dissociation, transient M–M bond cleavage, or fragmentation pathways, depending on the identity of the complex and the excitation wavelength used. Initial photochemical cleavage of a M–M bond may result in the formation of long-lived photoproducts that go on to react on diffusion-limited time scales in solution. Alternatively, M–M bond cleavage may only result in transiently lived intermediates (in which the M–M bond is rapidly reformed), whose short lifetimes preclude their involvement in reactivity occurring on diffusion-limited time scales. In such cases, pathways involving dissociation of a CO ligand are more likely to dictate the bulk solution-phase photochemistry of these dimers and clusters. Knowledge of the solution-phase photochemical behavior of these complexes is quite useful toward reaching a meaningful level of mechanistic understanding of the photochemistry of these dimers and clusters, which can be applied to better understand and predict their synthetic applications.

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