Supporting Information

19-electron Intermediates and Cage-effects in the Photochemical Disproportionation of $[CpW(CO)_3]_2$ with Lewis Bases

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Geminate Recombination Dynamics

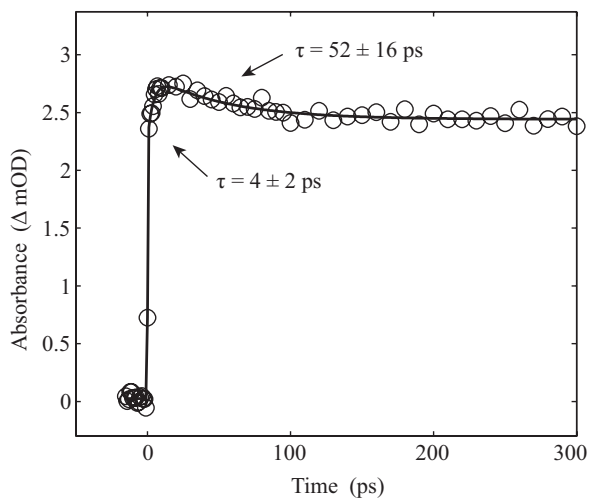

Figure 1. Kinetic plot for the 17-electron radical $CpW(CO)_3^{\bullet}$ in neat CH_2Cl_2

In the initial tens of picoseconds after laser photolysis of $[CpW(CO)_3]_2$ in neat CH_2Cl_2, the nascent 17-electron radicals $CpW(CO)_3^{\bullet}$ exhibit two dynamics, vibrational cooling and geminate recombination to reform the parent dimer. Figure 1 shows a kinetic plot of the 17-electron radical kinetics from spectral data in the range of 1970 to 2005 cm^{-1}. A wide spectral range is used to capture the absorption of both the vibrationally excited and cooled 17-electron radicals and hence limit the effect of vibrational cooling on the kinetics. Nevertheless, the dynamics of vibrational cooling and geminate recombination are difficult to separate and exponential fits to the data yield a rise time of 4 ± 2 ps and decay time of 52 ± 16 ps. The exponential rise is attributed to vibrational cooling and exponential decay to both vibrational cooling and geminate recombination of the radicals. The kinetics thus indicate that both processes are complete within ca. 50 ps in neat CH_2Cl_2.

Photolysis of $[CpW(CO)_3]_2$ causes depletion of this molecule, resulting in negative absorption signals, or bleaches. Within the first 50 ps following laser photolysis, geminate recombination of the photo-generated 17-electron radicals, $CpW(CO)_3^{\bullet}$, regenerates the $[CpW(CO)_3]_2$ molecule, causing a recovery of the bleach signal. Figure 2 shows the kinetics of bleach recovery in neat CH_2Cl_2 and 1.6 M $P(OMe)_3$ with CH_2Cl_2. Single exponential fits to absorption data recorded at 1910 cm^{-1} yield recovery time constants of 36 ± 2 ps and 21 ± 2 ps for CH_2Cl_2 and $P(OMe)_3$ / CH_2Cl_2, respectively. Spectral overlap of the 17-electron radical absorption and the bleach, however, limits the reliability of these kinetic traces. The decay of 17-electron radicals and recovery of the bleach in neat CH_2Cl_2 are

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roughly correlated, with differences most likely due to spectral overlap and effects of vibrational cooling. Recovery of the bleach in $P(OMe)_3$ / CH_2Cl_2 gives a shorter time constant than in neat CH_2Cl_2 and suggests that geminate recombination occurs for a shorter time in the presence of $P(OMe)_3$. This difference may be attributed to the formation of 19-electron intermediates from the 17-electron radical in these solutions.

Disproportionation as a result of in-cage electron transfer between the 17-electron and 19-electron species occurs up to 140 ps after laser photolysis. Geminate recombination is also an in-cage process yet occurs on a time scale of ca. 50 ps. The disparity in time constants for the two processes suggests that geminate recombination of the 17-electron radicals is more sensitive to the distance between the radicals than in-cage electron transfer. Geminate recombination necessitates that the radicals are sufficiently close and properly oriented to reform the metal-metal bond. Disproportionation, on the other hand, only requires sufficient electronic coupling between the two radicals to allow electron transfer. Reorientation and separation of the radicals within the first 50 ps likely prevents formation of a metal-metal bond while electron transfer still remains a viable reaction pathway.

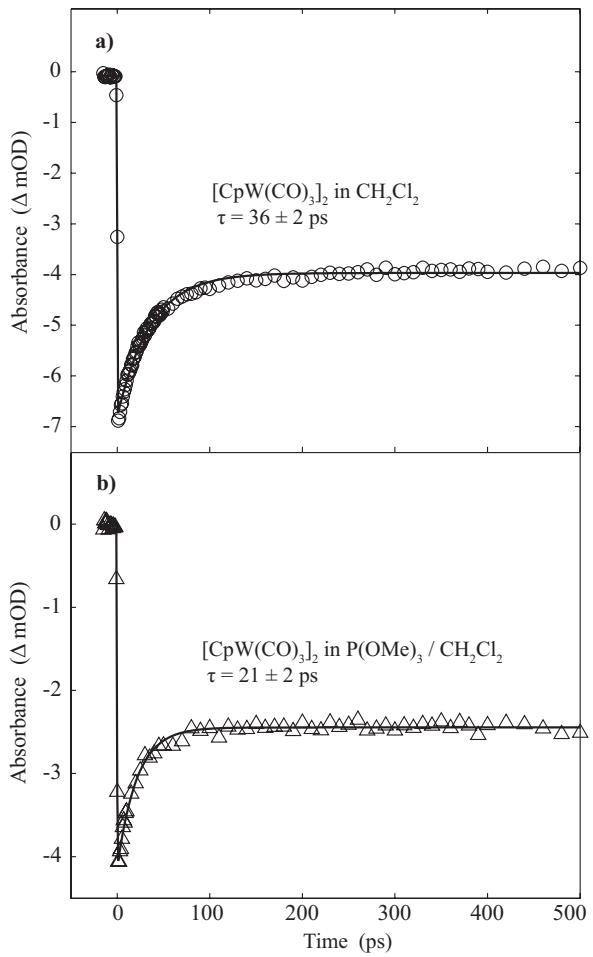

Figure 2. Kinetic plots for $[CpW(CO)_3]_2$ in a) neat CH_2Cl_2 and b) 1.6 M $P(OMe)_3$ with CH_2Cl_2

References

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