

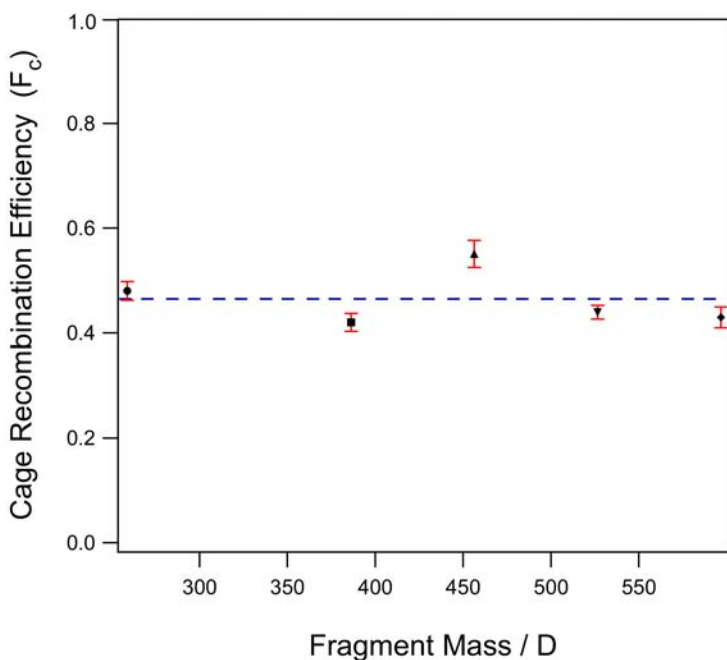
## Supplementary Information

Solvent Cage Effects: The Influence of Radical Mass and Volume on the Recombination Dynamics of Radical Cage Pairs Generated by Photolysis of  $[\text{CpCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{C}(\text{O})(\text{CH}_2)_n\text{CH}_3\text{Mo}(\text{CO})_3]_2$  ( $n = 3, 8, 13, 18$ ) ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_4$ ) Complexes.

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**Table S1** Kinetic parameters for the photolysis and geminate recombination of substituted molybdenum dimers

Compound	$\tau_2$ / ps	$F_c$	$k_c/10^{10} \text{ s}^{-1}$	$k_d/10^{10} \text{ s}^{-1}$
$[\text{Cp}'\text{Mo}(\text{CO})_3]_2$	$190 \pm 15$	$0.48 \pm 0.01$	$8.1 \pm 0.6$	$8.1 \pm 0.9$
<b>5</b>	$100 \pm 15$	$0.42 \pm 0.02$	$13 \pm 2$	$18 \pm 3$
<b>6</b>	$100 \pm 10$	$0.55 \pm 0.03$	$13 \pm 2$	$11 \pm 1$
<b>7</b>	$75 \pm 10$	$0.44 \pm 0.01$	$13 \pm 1$	$17 \pm 1$
<b>8</b>	$60 \pm 10$	$0.43 \pm 0.02$	$11 \pm 1$	



**Fig. S1** A comparison of the caging efficiency ( $F_{cP}$ ) vs. mass for the radical fragments created by photolysis of dimers **5** – **8** and  $[\text{Cp}'\text{Mo}(\text{CO})_3]_2$  in cyclohexane:  $\bullet$  =  $[\text{Cp}'\text{Mo}(\text{CO})_3]_2$ ,  $\blacksquare$  = **5**,  $\blacktriangle$  = **6**,  $\blacktriangledown$  = **7**,  $\blacklozenge$  = **8**. The error bars represent one standard deviation as determined from propagating the error generated from the least-squares non-linear regression fit of the kinetic traces (eqs 1 and 2). The dashed-blue line represents the mean value of the five data points,  $F_{cP} = 0.46$ .