Radical cage effects. Effect of radical mass and bond energies on cage recombination efficiencies for photochemical cage pair intermediates of $[Mo_2(CO)_6[(\eta^5\text{-}C_5H_4CH_2CH_2OSiMe_3)_2]$, $[Mo_2(CO)_6(\eta^5\text{-}C_5H_4Me)]$ and $[W_2(CO)_6(\eta^5\text{-}C_5H_4Me)]$

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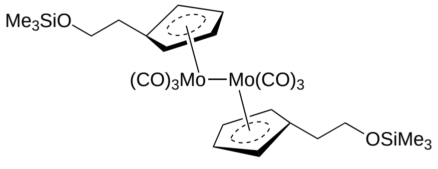
The cage recombination efficiency of the $[(\eta^5\text{-}C_5H_4Me)(CO)_3W\cdot, \cdot W(CO)_3(\eta^5\text{-}C_5H_4Me)]$ radical cage pair in hydrocarbon solvent systems is higher than that of the analogous, but less massive, $[(\eta^5\text{-}C_5H_4Me)(CO)_3Mo\cdot, \cdot Mo(CO)_3(\eta^5\text{-}C_5H_4Me)]$ cage pair; the difference is shown to be attributable not to differences in the radical masses but to differences in the metal–metal bond energies or in the spin–orbit coupling.

Radical cage effects[1–4] have an enormous impact on chemical reactivity in solution and they are necessary to explain some of the most fundamental physical reaction phenomena.[5–7] Despite the recognition that cage effects can be important, virtually nothing systematic or quantitative is known about how changes in radical mass affect the cage effect.‡ In a prior study, we showed that the cage effect for the photogenerated $[(\eta^5\text{-}C_5H_4Me)(CO)_3Mo\cdot, \cdot Mo(CO)_3(\eta^5\text{-}C_5\text{-}H_4Me)]$ radical pair was smaller than that for the similarly sized but more massive W analogue, $[(\eta^5\text{-}C_5H_4Me)(CO)_3W\cdot, \cdot W(CO)_3(\eta^5\text{-}C_5H_4Me)]$.[8] As tempting as it was to attribute the difference to a change in the mass of the radical fragments, the difference may instead be attributable to differences in the M–M bond energies or to differences in spin–orbit coupling.‡ In order to separate changes caused by differences in radical mass from changes caused by bond energies or spin orbit coupling, we synthesized and studied **1**.



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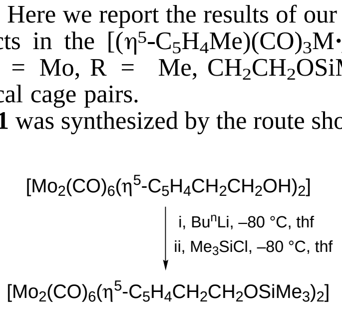
This molecule was chosen because its constituent radicals have about the same mass (361.3) as the $W(CO)_3(\eta^5\text{-}C_5H_4Me)$ radicals (347.0), yet it has a Mo–Mo bond. A comparison of **1** with $[Mo_2(CO)_6(\eta^5\text{-}C_5H_4Me)_2]$ **2** (259.1 for the radical) will therefore allow us to eliminate the influence of different M–M bond energies. Here we report the results of our comparison of the cage effects in the $[(\eta^5\text{-}C_5H_4Me)(CO)_3M\cdot, \cdot M(CO)_3(\eta^5\text{-}C_5H_4Me)]$ (M = Mo, R = Me, $CH_2CH_2OSiMe_3$; M = W, R = Me) radical cage pairs.

Compound **1** was synthesized by the route shown in Scheme 1.§



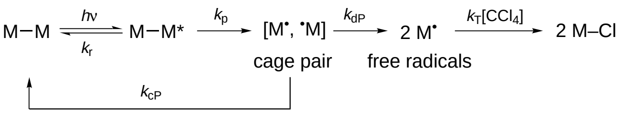
Scheme 1

The electronic spectra of **1** and **2** are virtually identical, a feature that suggests the Mo–Mo bond is not significantly perturbed by the changes in the side-chain and that therefore the Mo–Mo bond energies are essentially the same in each molecule.¶,‖

As previously reported,[8] the cage effect is measured by analyzing the quantum yields for disappearance of the dimer as a function of viscosity when the dimers are irradiated in the presence of a radical trap.** The radical trap used in these experiments was CCl_4 [eqn. (1), Scheme 2].[8]

$$[M_2(\eta^5\text{-}C_5H_4R)_2(CO)_6] \xrightarrow[\text{CCl}_4\text{, hexane–paraffin oil}]{h\nu\ (540\ \text{nm})} 2[M(\eta^5\text{-}C_5H_4R)(CO)_3Cl] \quad (1)$$

There is no back-reaction of the free radicals under the reaction conditions because the concentration of CCl_4 (2 M) is high enough to trap every free radical.†† The quantum yields for eqn. (1) were measured in hexane solution, and paraffin oil was used to increase the viscosity. (Paraffin oil was used to increase the viscosity since it is a straight-chain hydrocarbon; thus, we sought to avoid preferential solvation in the hexane solvent.[8]) Fig. 1 shows the quantum yields for the reactions of the two Mo dimers and $[W_2(CO)_6(\eta^5\text{-}C_5H_4Me)_2]$ **3** with CCl_4 as a function of viscosity.



$M = M(CO)_3(\eta^5\text{-}C_5H_4R)$; $F_{cP} = k_{cP}/(k_{cP} + k_{dP})$

Scheme 2 Reaction scheme for metal–metal bond photolysis

Plots of the cage effect (F_{cP}) *vs.* viscosity for the three dimers are shown in Fig. 2. Note that at any viscosity, the cage effects increase in the order $Mo(CO)_3(\eta^5\text{-}C_5H_4Me) \approx Mo(CO)_3(\eta^5\text{-}C_5H_4CH_2CH_2OSiMe_3) << W(CO)_3(\eta^5\text{-}C_5H_4Me)$. The large difference in F_{cP} between the $[(\eta^5\text{-}C_5H_4Me)(CO)_3W\cdot,$

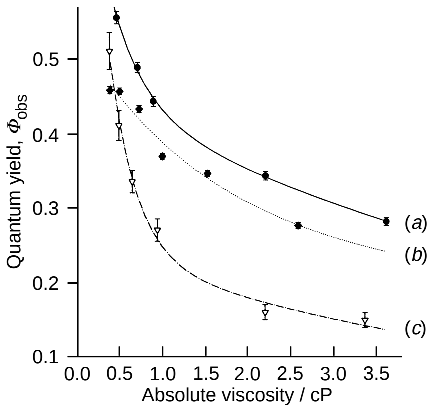


Fig. 1 Plot of Φ_{obs} *vs.* viscosity for the photochemical reactions (λ = 540 nm) of **1** (*a*), **2** (*b*) and **3** (*c*) with CCl_4 (2 M) in hexane–paraffin oil at 23 ± 1 °C. All error bars represent $\pm 1\sigma$.

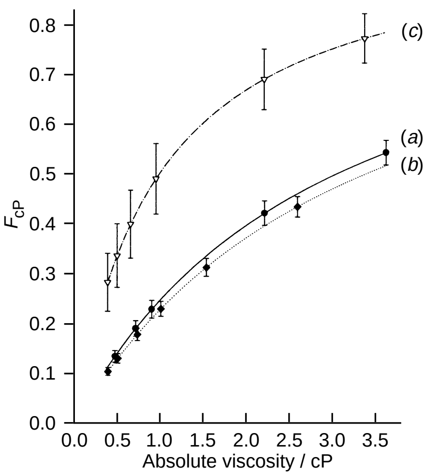


Fig. 2 Plot of F_{cP} *vs.* viscosity for **1** (*a*), **2** (*b*) and **3** (*c*) at 23 ± 1 °C in hexane–paraffin oil solutions. All error bars represent ±1σ.

$\cdot W(CO)_3(\eta^5\text{-}C_5H_4Me)$] and [$(\eta^5\text{-}C_5H_4CH_2CH_2OSiMe_3)(CO)_3Mo\cdot$, $\cdot Mo(CO)_3(\eta^5\text{-}C_5H_4CH_2CH_2OSiMe_3)$] cage pairs (which have about the same mass) and the similarity in the cage effects for the $Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ and $Mo(CO)_3(\eta^5\text{-}C_5H_4CH_2CH_2OSiMe_3)$ cage pairs shows that a mass effect is not responsible for the difference reported earlier between [$(\eta^5\text{-}C_5H_4Me)(CO)_3Mo\cdot$, $\cdot Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$] and [$(\eta^5\text{-}C_5H_4Me)(CO)_3W\cdot$, $\cdot W(CO)_3(\eta^5\text{-}C_5H_4Me)$]. The difference may be attributed to several factors. One possible factor is the smaller difference between the bond dissociation energy and the photochemical excitation energy for **2** compared to **3**.‡ The excess photonic energy for Mo may lead to an increase in translational energy in the photogenerated radicals and a consequent decrease in the cage effect. Alternatively, the larger cage effect for the W radical pair may reflect the increased driving force (and consequently lower activation barrier) for the recombination of the two W radicals compared to the Mo radicals. A third explanation is the increase in spin–orbit coupling for W compared to Mo. The increase will facilitate intersystem crossing, which may be important if there is a spin barrier to recombination of the cage pair.

It might be argued that the difference in cage effects between the $W(CO)_3(\eta^5\text{-}C_5H_4Me)$ and $Mo(CO)_3(\eta^5\text{-}C_5H_4MeCH_2CH_2OSiMe_3)$ radical pairs depicted in Fig. 2 is attributable to a size effect.‡‡ This alternative explanation is unlikely for two reasons. First, in his mathematical description of the cage effect,[3] Noyes predicted that sterically larger radicals will have larger cage effects than smaller radical cage pairs. Second, our experiments with the $\eta^5\text{-}C_5H_4CH_2CH_2OSiR_3$ (R = Pr^n, Pr^i, $n\text{-}C_6H_{13}$) analogues of compound **1** show that, as the R group gets bigger, the cage effect increases.[11] Thus, our experiments confirm Noyes's prediction that bigger cage pairs will have larger cage effects. It is concluded therefore that the difference in cage effects between the $W(CO)_3(\eta^5\text{-}C_5H_4Me)$ and $Mo(CO)_3(\eta^5\text{-}C_5H_4CH_2CH_2OSiMe_3)$ radical pairs is not attributable to a size effect.

Two fundamental conclusions result from this study. First, the effects of radical mass on the cage effect are not nearly as pronounced as suggested by the previously reported data for the [$(\eta^5\text{-}C_5H_4Me)(CO)_3Mo\cdot$, $\cdot Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$] and [$(\eta^5\text{-}C_5H_4Me)(CO)_3W\cdot$, $\cdot W(CO)_3(\eta^5\text{-}C_5H_4Me)$] cage pairs. Secondly, differences in bond energies may influence the cage effect, and it is important therefore to always compare systems with similar bond energies. We are continuing to investigate molecular parameters that influence the magnitude of the cage effect.

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Footnotes and References

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† Some incidental data are available, but no systematic studies have been done. See ref. 2(*a*), p. 174.

‡ D_{W-W} ≈ 56 kcal mol^{-1}; D_{Mo-Mo} ≈ 32 kcal mol^{-1} [9] $h\nu$ = 52 kcal mol^{-1}.

§ The molecule was synthesized under nitrogen as follows: To a −80 °C (dry ice/acetone) solution of [$Mo_2(CO)_6(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2$] in thf was added 2.2 equiv. of Bu^nLi dropwise over 20 min. After 1 h of reaction time, a brick-red solid was allowed to settle. The supernatant was removed with a cannula and the solid was washed twice with thf at −80 °C (20 ml). Tetrahydrofuran (25 ml) was again added and the mixture was cooled to −80 °C. To the mixture was added 2 equiv. of Me_3SiCl. The reaction was allowed to proceed until the solution became clear and deep burgundy. After removal of thf *in vacuo*, hexanes were added and the resulting cloudy burgundy solution was filtered through a fine frit. The product was eluted with hexanes through a short, basic alumina column prior to crystallization from hexanes.

¶ The molecule has an intense band at 393 nm (ε ≈ 20 000 dm^3 mol^{-1} cm^{-1}), assigned to the $\sigma \rightarrow \sigma^*$ transition, and a weaker band at 512 (ε ≈ 2000), assigned to a $d_\pi \rightarrow \sigma^*$ transition.

‖ By having a $-CH_2CH_2-$ spacer, we also sought to minimize the difference in the electronic structures of the molecules. For an example of a similar strategy, see ref. 10.

** The cage effect is denoted by F_{cP} and is defined as the ratio of the rate constant for cage recombination to the sum of the rate constants for all cage processes. The procedure for obtaining F_{cP} is to plot $1/\Phi_{obs}$ *vs.* viscosity. The plots are linear with a *y* intercept equal to $1/\Phi_{pair}$, the quantum yield for the formation of the cage pair species. This value of Φ_{pair} is then used in the equation $1/\Phi_{obs} = [1/\Phi_{pair}][1 + k_{cP}/k_{dP}]$, and the value of F_{cP} is calculated by rewriting k_{cP}/k_{dP}. Complete details are found in ref. 8 and 11. The Φ_{pair} values were: 0.51 ± 0.01 (**2**), 0.61 ± 0.02 (**1**), 0.58 ± 0.09 (**3**).

†† The quantum yields increased with increasing concentration of CCl_4 up to *ca.* 0.1 M, at which point saturation was achieved.

‡‡ The static molecular volumes of $W(CO)_3(\eta^5\text{-}C_5H_4Me)$ and $Mo(CO)_3(\eta^5\text{-}C_5H_4CH_2CH_2OSiMe_3)$ were calculated as 107 and 185 Å^3, respectively, by using the computer program Steric (written by B. Craig Taverner, Department of Chemistry, Witwatersrand, Private Bag 3, WITS 2050, Johannesburg, South Africa).

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