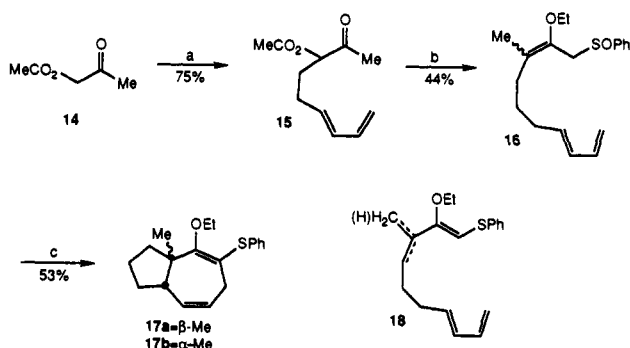


Scheme III^a

^a(a) (1) NaH, THF. (2) (*E*)-6-Iodo-1,3-hexadiene, reflux. (b) (1) LiCl, DMF/H₂O, heat. (2) (Ethoxyvinyl)lithium, THF. (3) *n*-BuLi, then PhSPh, THF, -78 °C. (c) Tf₂O (1 equiv), 2,6-di-*tert*-butylpyridine (2 equiv), CH₂Cl₂, 25 °C.

epimers. Normal addition either destroyed (*E*)-7 or resulted in the recovery of starting material. Fortunately, (*Z*)-7 reacted smoothly under the same reaction conditions to give a 67% yield of 9 as a mixture of isomers. On the basis of these results, we speculate that (*E*)-7 can serve as a bidentate ligand for TiCl₄ to produce a chelate which is unreactive with respect to ionization to alkoxyvinyl thionium ion 8 and subsequent cycloaddition (Figure 1).^{11,12} The stereochemistry of the cycloadduct 9 with respect to the angular positions was assigned in accordance with stereochemical assignments made on related cycloadducts.¹ It was clear from the NMR spectrum of 9 that the isomers arose from epimerization at carbon 7 (azulenone numbering).

In order to address the difficulties associated with the cyclization of (*E*)-7, we considered other means of generating 8 and concluded that the Pummerer rearrangement of alkoxyallylic sulfoxides offered one of the best options.^{12,13} The substrate needed to examine this idea was prepared as shown in Scheme II. Treatment of 2-(3-chloropropyl)furan¹⁴ with magnesium and quenching the resulting Grignard reagent with excess acetic anhydride gave ketone 11 in 72% yield.¹⁵ Condensation of 11 with (ethoxyvinyl)lithium¹⁶ and treatment with phenylsulfenyl chloride gave sulfoxide 12 as a 1:1 *E/Z* mixture.¹⁷

After some experimentation we found that the best conditions for 4 + 3 cycloaddition consisted of treatment of a 0.017 M CH₂Cl₂ solution of 12 with Tf₂O and 2 equiv of 2,6-lutidine at room temperature. This gave enol ether 13 in exceptionally high yield. The stereochemical assignment was made on the basis of aforementioned considerations.¹

A substrate containing a free diene was tested as well (Scheme III). Alkylation of the sodium enolate¹⁸ of 14 with 6-iodo-1,3-hexadiene¹⁹ gave keto ester 15 in good yield. Krapcho decar-

boxylation²⁰ and straightforward manipulations gave 16 as a 1:1 mixture of isomers. Considerable difficulties were associated with attempts to induce cycloaddition using protocols successful with 12. Elimination to form 18 as a mixture of regioisomers competed effectively with cycloaddition over a wide range of conditions. Eventually we found that treatment of a 0.015 M CH₂Cl₂ solution of 16 with Tf₂O in the presence of 2 equiv of 2,6-di-*tert*-butylpyridine at room temperature gave cycloadduct 17 as a 1:1 mixture of isomers in 53% isolated yield. Apparently, a combination of the decreased nucleophilicity and conformational mobility of the diene in 16 relative to the furan in 12 is detrimental to the cycloaddition process.²¹

In summary, we have invented two convenient means of generating alkoxyvinyl thionium ions for use in the intramolecular 4 + 3 cycloaddition reaction to form functionalized, fused 5,7 carbocyclic systems. Work continues on improving the stereoselectivity of these reactions, applying the methodology to synthetic targets, and expanding the reaction profile of these unique intermediates.

Acknowledgment. We are grateful to the National Science Foundation for support of this work (CHE-8912190) and for partial support of the NMR (PCM-8115599) and MS (PCM-88117116) facilities at the University of Missouri—Columbia. Thanks to Dr. Charles L. Barnes for acquisition of X-ray data on 6 and 17a.

Supplementary Material Available: Experimental procedures and spectral data for compounds 5–7, 11–13, and 15–17 and tables of bond lengths, bond angles, and dihedral angles for 6 and 17a (21 pages). Ordering information is given on any current masthead page.

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Intrinsic Barriers to Atom Transfer (Abstraction) Processes. Self-Exchange Rates for Cp(CO)₃M^{*} Radical/Cp(CO)₃M-X Halogen Couples

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The significant role played by radical pathways is now widely recognized^{1,2} for organometallic reagents once believed to undergo even-electron changes exclusively. These pathways are evident in reactions as diverse as olefin hydrogenation by metal hydrides³ and radical-chain substitution⁴ of metal halide complexes. The reactivities of both metal hydrides^{3,5} and halides^{4,6} with respect to atom transfer (abstraction) are now being systematically addressed. However, the self-exchange process itself has not received attention. Here we apply "isotopically labeled" materials and a

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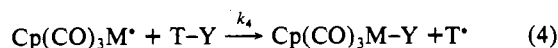
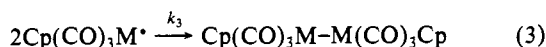
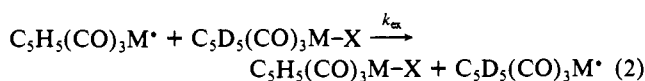
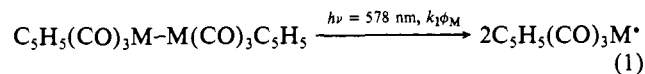
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photochemical method to the direct determination of self-exchange rates for the $\text{CpM}(\text{CO})_3$ ($\text{Cp} = \text{C}_5\text{H}_5$, cyclopentadienide) molybdenum and tungsten complexes for which we⁷ recently examined two-electron or X^+ self-exchange processes. We find that, in contrast to our results for the X^+ exchanges which spanned 6 orders of magnitude, the X^+ self-exchanges fall in the narrow range 10^5 ($\text{X} = \text{Cl}$) to 10^8 ($\text{X} = \text{I}$) $\text{M}^{-1} \text{s}^{-1}$ at 25 °C. The intrinsic free-energy barriers $\Delta G_{\text{ex}}^{\ddagger}$ are $\leq 15\%$ of the $\text{M}-\text{X}$ bond dissociation energies. While intrinsic barriers to atom abstraction processes have been inferred from analyses of the free-energy dependence of the rates,^{6,8,9} to our knowledge, this is the first direct determination.

The metal radicals were generated by long-wavelength^{10,11} irradiation¹¹⁻¹⁴ (eq 1) of 1×10^{-3} M CD_3CN solutions of the appropriate metal dimer containing the C_5H_5 ligand. Self-exchange (eq 2) between the metal radical and the $(0.5$ to $5) \times 10^{-3}$ M halo complex containing C_5D_5 (Cp^{D}) took place in competition with metal-radical recombination (eq 3) or trapping (eq 4) by CCl_4 , CH_2I_2 , or CBr_4 . The samples (total 3 mL, 0.24 mL



irradiated volume, contained in 10-mm NMR tubes) were irradiated 10 to 120 s ($\leq 10\%$ conversion) with 578-nm excitation rates (k_1)¹⁵ of $(0.02$ to $2) \times 10^{-4}$ einstein $\text{L}^{-1} \text{s}^{-1}$, and the distribution of the C_5H_5 label was determined by ^1H NMR.¹⁶

For the $\text{W}-\text{Cl}$ self-exchange, the quantum yield ϕ_{ex} was both light intensity and $[\text{W}-\text{Cl}]$ dependent. A plot of $(\phi_{\text{M}} - \phi_{\text{ex}})^{1/2}/\phi_{\text{ex}}$ vs $k_1^{1/2}/[\text{W}-\text{Cl}]$ was linear, with a slope $(=2k_3/k_4^2)^{1/2}$ of $(0.6 \pm 0.2) \text{M}^{1/2} \text{s}^{1/2}$, which, with $k_3 = 5 \times 10^9 \text{M}^{-1} \text{s}^{-1}$,^{11,12} and ϕ_{M}

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(10) Although CO loss occurs with shorter wavelength irradiation,¹² long-wavelength and low-intensity yields $\text{M}-\text{M}$ bond scission exclusively for $\text{M} = \text{W}$.¹¹ For $\text{M} = \text{Mo}$, a small amount of photodecomposition ($< 5\%$) of the dimer does occur with 578-nm irradiation in the absence of $\text{T}-\text{Y}$ and the data have been corrected for this decomposition.

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(16) The total metal radical concentration at steady state is

$$[\text{M}^*_{\text{ss}}] = (-k_4[\text{T}-\text{Y}] + (k_4[\text{T}-\text{Y}]^2 + 8k_3k_1\phi_{\text{M}})^{1/2})/4k_3$$

k_1 is the dimer excitation rate: the number of photons incident upon the solution per second, divided by the volume of the solution irradiated, corrected by Beer's law for the fraction of the light not absorbed by the dimer. Self-exchange (eq 2) does not influence the M^* concentration at steady state, but it does determine the composition of the radical population: In the absence of self-exchange only the perproto radical is present; if self-exchange is infinitely rapid, only perdeuterio radical will be present (at negligible conversion of dimer starting material). The highest value ($[\text{T}-\text{Y}] = 0$) of $[\text{M}^*_{\text{ss}}]$ ($=k_1\phi_{\text{M}}/2k_3$)^{1/2} is 10^{-7} M at the highest intensities used, 2×10^{-4} einstein $\text{L}^{-1} \text{s}^{-1}$. For the intensity-dependent data the errors on the slopes are ca. $\pm 20\%$; however, systematic errors resulting from the modeling of the irradiated volume may be greater. The beam cross-section, imaged with photosensitive paper, is a rectangle of dimensions 3×8 mm. Since the solutions are relatively optically dilute ($A \leq 0.3$), the third dimension is 10 mm.

Table I. Rate Constants ($\text{M}^{-1} \text{s}^{-1}$) in CD_3CN at 25 °C^a

reactants		Mo	W	
$\text{Cp}(\text{CO})_3\text{M}^+$	+	$\text{Cp}^{\text{D}}(\text{CO})_3\text{M}-\text{Cl}$	0.8×10^6	2.4×10^5
		$\text{Cp}^{\text{D}}(\text{CO})_3\text{M}-\text{Br}$	1.0×10^7	4.2×10^6
		$\text{Cp}^{\text{D}}(\text{CO})_3\text{M}-\text{I}$	2.6×10^8	2.7×10^8
		$\text{Cp}^{\text{D}}(\text{CO})_3\text{M}^-$		$\geq 1 \times 10^6$
		$\text{Cp}^{\text{D}}(\text{CO})_3\text{M}-\text{H}$		$\geq 1 \times 10^6$
		$\text{Cp}^{\text{D}}(\text{CO})_3\text{M}-\text{CH}_3$		$\leq 5 \times 10^2$
		CCl_4^b	0.8×10^4	1.2×10^4
		CH_2I_2^c	6.4×10^5	2.8×10^6
$\text{Cp}^{\text{D}}(\text{CO})_3\text{M}^-$	+	$\text{Cp}(\text{CO})_3\text{M}-\text{Cl}^d$	9×10^{-2}	2.1×10^{-3}
	+	$\text{Cp}(\text{CO})_3\text{M}-\text{Br}^d$	16	2.8
$\text{Cp}(\text{CO})_3\text{M}^-$		$\text{Cp}(\text{CO})_3\text{M}-\text{I}^d$	1.5×10^4	4.5×10^3
		$\text{Cp}(\text{CO})_3\text{M}-\text{H}^e$	2.5×10^3	6.5×10^2

^a $\text{Cp} = \text{C}_5\text{H}_5$ and $\text{Cp}^{\text{D}} = \text{C}_5\text{D}_5$. Based on competition studies with $\phi_{\text{M}} = 1.0$ (W) and 1.6 (Mo) determined here and $k_3 = 5 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ (W) and $3 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ (Mo),^{11,12} in CD_3CN solvent, except $\text{Cp}(\text{CO})_3\text{M}-\text{H}$ (C_6D_6). Estimated errors are $\pm 20\%$ of the rate constant. ^b Determined from the slopes $(=2k_3/k_4^2)^{1/2}$ of plots of $(\phi_{\text{M}} - \phi_{\text{MCl}})^{1/2}/\phi_{\text{MCl}}$ vs $k_1^{1/2}/[\text{CCl}_4]$; ϕ_{MCl} is the quantum yield for $\text{Cp}(\text{CO})_3\text{M}-\text{Cl}$ formation. ^c Determined via competition: for CH_2I_2 , with CCl_4 ; for CBr_4 with CH_2I_2 . ^d Schwarz, C. L.; Bullock, R. M.; Creutz, C. J. *Am. Chem. Soc.* **1991**, *113*, 1225-1236. ^e Eddin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945-3953.

$= 1.0$, yields $k_{\text{ex}} = 2.5 \times 10^5 \text{M}^{-1} \text{s}^{-1}$. For the bromo and iodo complexes under comparable conditions, ϕ_{ex} is independent of light intensity, indicating that self-exchange is too rapid for the metal-radical recombination (eq 3) to compete with the self-exchange. This was confirmed by use of the competition eq 4, with $\text{T}-\text{Y} = \text{CCl}_4$ ($k_4 = 1.2 \times 10^4 \text{M}^{-1} \text{s}^{-1}$, $\text{M} = \text{W}$ in CD_3CN ; lit. $1.3 \times 10^4 \text{M}^{-1} \text{s}^{-1}$ in THF,¹⁷ $2.2 \times 10^4 \text{M}^{-1} \text{s}^{-1}$ in benzene¹⁸) or CBr_4 for the iodo complexes and CH_2I_2 for the bromo complexes. The $\text{X} = \text{Cl}$ rate constants were also redetermined with CH_2I_2 . We attempted to evaluate rate constants for the metal-radical/metal-anion electron exchange and the metal-radical/metal-hydride H-atom exchange. Although no suitable trapping reagent could be found, these processes are quite rapid ($k \geq 10^6 \text{M}^{-1} \text{s}^{-1}$) based on the intensity independence of their quantum yields; by contrast, no exchange was detected for $\text{X} = \text{CH}_3$ ($\text{M} = \text{W}$) irradiated for 1 h ($k_{\text{ex}} \leq 5 \times 10^2 \text{M}^{-1} \text{s}^{-1}$). The rate constants are summarized in Table I.

The halo self-exchanges are indeed rapid as is required for the sustenance of chain reactions.⁴ The intrinsic free-energy barriers $\Delta G_{\text{ex}}^{\ddagger}$ lie in the range 8-11 kcal/mol—substantially greater than inferred by Lee and Brown⁶ for rhenium carbonyl systems. Bond dissociation energies for the molybdenum complexes are 72.4 (Cl), 60.5 (Br), and 51.8 (I) kcal/mol.¹⁹ Assuming ΔS^{\ddagger} values of -15 cal $\text{K}^{-1} \text{mol}^{-1}$, ΔH^{\ddagger} values for molybdenum are 5.5, 3.9, and 1.5 kcal/mol, respectively. Thus, although Brown⁶ has proposed that atom abstraction from alkyl and aromatic halides involves a substantial charge-transfer character, it is apparent that metal-halogen bond formation in a bridged $\text{M}-\text{X}-\text{M}$ transition state is extremely important in the self-exchange. (Marcus⁹ has proposed a barrier of the order of 5-10% of the bond energy.) The substitutional lability characteristic of metal radicals²⁰⁻²³ is undoubtedly critical to their high reactivity toward atom transfer. The best evidence is that, as is true for most carbon-centered radicals, the odd-electron exerts some steric significance in metal

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centered radicals of this type.²⁴

The intrinsic barriers for the analogous carbon-centered systems are also of considerable interest. Hiatt and Benson²⁵ have estimated activation energies for gas-phase halogen atom transfer of alkyl systems of ~ 10 (Cl), ~ 6 (Br), and 2-4 (I) kcal mol⁻¹. With X = I, the "self-exchange" process is sufficiently rapid in alcohol solvents to lead to epimerization of the norbornyl iodide starting material.²⁶ Studies of alkyl radical/alkyl halide transfer in benzene suggest transfer rates at zero driving force of ca. 10² (X = Cl), 10³ (X = Br), and 10⁵ (X = I) M⁻¹ s⁻¹ at 50 °C.²⁷ Since the Mo-Cl (72.4 ± 0.9 kcal/mol¹⁹) and CCl₃-Cl (68.9 ± 0.7 kcal/mol²⁸) bond energies are very similar, our data (Table I) implicate a greater intrinsic barrier for the Cl transfer to the Mo radical from CCl₄ than for the entirely metal-centered process.

Acknowledgment. We thank Drs. B. S. Brunshwig, H. A. Schwarz, and N. Sutin for invaluable discussions. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Note Added in Proof. In the broader context of multiequivalent atom transfer reactions, the extraordinarily facile transfer of nitride between Mn(V) and Mn(II) porphyrin centers, a three-electron transfer coupled to atom transfer, should be noted. (Woo, L. K.; Goll, J. G.; Czaplá, D. J.; Hays, J. A. *J. Am. Chem. Soc.* 1991, 113, 8478-8484 and references cited therein.)

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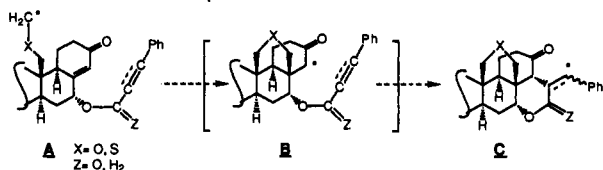
Intramolecular 1,4-Addition of α -Heteroatom-Substituted Radicals to β,β -Disubstituted Enones. Applications to Tandem Cyclizations

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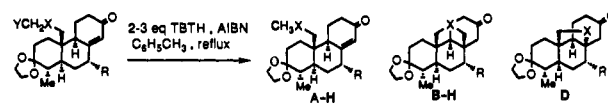
In conjunction with a synthetic problem in our laboratory, we elected to investigate a tandem cyclization (A \rightarrow B \rightarrow C) which is initiated by the intramolecular 1,4-addition reaction of α -heteroatom-substituted radical to a β,β -disubstituted enone (A \rightarrow B).



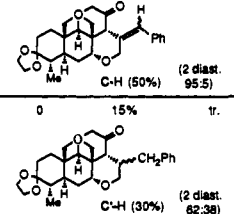
While the annulation chemistry of many types of carbon-centered radicals is now a standard synthetic protocol,¹ less attention

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Table I



Cmpd	Precursor			# of eq. TBTH	Addn. Time (hrs)	Product Yields ^a		
	X =	Y =	R =			A-H	B-H	D
4a	O	SePh	H	3.0	24	8	68	0
4b	O	SPh	H	2.4	14	5	0; recov 4b, 58	10
5	S	SePh	H	2.0-2.3	12-20	15	45	10
7	O	SePh	OH	2.5	14	tr	45	0
9a	O	SePh	OAc	2.5	12	0	70	0
9b	O	SePh	O ₂ CC ₆ H ₅	2.5	12	no products identified		
9c	O	SePh	OCH ₂ CH=CPh	2.4	11	0	0	15
9d	O	SePh	OCH ₂ CH=CPh (E)	2.3	14	0	15%	tr.



^aIn some instances the yield and product ratio was assigned after hydrolysis of the ketal moiety to facilitate separation.

has been paid to the synthetic applications of α -heteroatom-substituted radicals.² While this paper was under revision, Rawal reported the cyclization (principally 5-exo-trig) of a number of simple α -alkoxy radicals.³

Synthesis of the appropriate substrates began with the readily available⁴ tricyclics 1 and 2. Treatment of neopentyl alcohol 1 with α -halo sulfide, α -halo selenide, and diiodomethane did not provide the desired α -alkoxy derivatives 3a-c. However, alkylation with α -iodomethyl tributylstannane⁵ under these conditions produced 3d in 70% yield. Conversion of α -alkoxy stannane 3d to α -alkoxy organolithium 3e by treatment with *n*-BuLi in THF⁶ at -78 °C did not proceed in the absence of additives such as HMPA or TMEDA, even using 2 equiv of *n*-BuLi. When only

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