generated quantitatively in its triplet state, as seems to be the case, a trapping efficiency of only ca. 4% was achieved, and **2** is trapped with very much lower efficiency than triplet 1,3-biradicals.[2] In fact under similar conditions triplet 1,3-cyclopentadiyl (**1b**) is trapped with >99% efficiency.[13]

Theoretical work[14] predicts a triplet ground state for trimethylene 1,3-biradical with its terminal methylene groups in a coplanar conformation. The facts that 1,3-cyclopentadiyl (**1b**) can be detected by ESR spectroscopy[15] and trapped efficiently by triplet oxygen[13] confirm the triplet ground state character and indicate an appreciable lifetime for this species. On the other hand, analogous to the tetramethylene 1,4-biradical for which a singlet ground state with a small singlet-triplet energy gap (ca. 1.6 kcal/mol) has been determined theoretically,[16] we expect the triplet 1,4-cyclohexadiyl (**2**) to be a short-lived species. Consequently, the oxygen-trapping efficiency of ca. 4% for triplet **2** vs. ca. >99% for triplet **1b** nicely corroborates this expectation. On the basis of these results, we estimate[17] lifetimes of ca. 0.1 ns for the triplet 1,4-biradical **2** at −20 °C and ca. 900 ns for the triplet 1,3-biradical **1b** at 7 °C.

Finally, of particular interest is the unusually high proportion of hydroperoxide formation in this system. The hydroperoxide and its decomposition products predominate over the endoperoxide **3** in a ratio of ca. 9:1.[18] It is interesting to note that if the nitrogen extrusion occurs with the more or less concerted breakage of both carbon–nitrogen bonds,[19] the triplet biradical **2** will be born in a boatlike conformation **9** (eq 2). With use of cyclohexane as

$$(2)$$
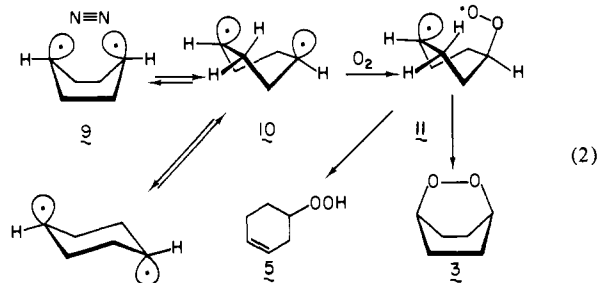
a model, **9** would be expected to immediately relax to a twist-boat conformation **10**, which should be ca. 1.6 kcal/mol more stable than **9**.[20] This twist-boat conformation **10** might be transformed

into other members of the twist-boat family of conformers. The lifetime of this initial twist-boat conformer **10** should be ca. 5 × 10^{-10} s at −20 °C, or significantly longer than the lifetime of the biradical itself. In contrast isomerization from the twist-boat manifold of conformers to a chair conformation should have an activation energy of ca. 5.3 kcal/mol.[21] Consequently, the twist-boat family of conformers should have a lifetime of ca. 7 × 10^{-9} s at −20 °C or much longer than that of the triplet biradical species **2**. These considerations indicate that the biradical being trapped has a twist-boat conformation and quite possibly is the initially formed twist-boat conformer **10**. The corresponding conformation of the resulting hydroperoxy biradical **11**[22] has a geometry that should favor hydrogen abstraction to form the hydroperoxide **5** over collapse to the endoperoxide **3** as indicated in eq 2. Related conformational memory effects have been proposed to account for the chemistry of other 1,4-biradicals.[23]

In conclusion, the oxygen trapping of triplet 1,4-cyclohexadiyl (**2**) establishes this laser photochemical technique as a useful method for the study of previously inaccessible, short-lived biradicals. Furthermore, the characterization of the trapping products provides valuable insight into the chemistry of the intermediary biradicals.

(13) Wilson, R. M.; Adam, W.; Hannemann, K., unpublished results.
(14) (a) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284. (b) Doubleday, C., Jr.; McIver, J. W.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533.
(15) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857.
(16) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 5409.
(17) This value has been estimated by using modified Stern–Volmer kinetics in which the bimolecular diffusion-controlled rate constant for the oxygen quenching of the biradical was taken to be $k = 2.4 \times 10^9$ M⁻¹ s⁻¹ (personal communication of J. Wirz, to whom we are most grateful for providing us with this value) and an experimentally determined value for the oxygen concentration in CFCl₃ at 10 atm of 0.24 M. In the case of the 1,4-biradical **2**, a lifetime of 7.2 × 10⁻¹¹ s is obtained if oxygen-catalyzed intersystem crossing is neglected. If one assumes equal contributions to biradical quenching from trapping and catalyzed intersystem crossing, a lifetime of 1.4 × 10⁻¹⁰ s is obtained. In the case of the 1,3-biradical **1b**, it is known that oxygen-catalyzed intersystem crossing is negligible, since virtually all hydrocarbon formation is suppressed (<1% hydrocarbon formation) at oxygen pressures greater than about 2 atm. At this time it is not clear why oxygen-catalyzed intersystem crossing of the simple triplet biradical **1b** does not appear to be an important process. It has been reported to be the major oxygen-quenching route with much more complex, delocalized 1,4-biradicals (Caldwell, R. A.; Creed, D. *J. Phys. Chem.* **1978**, *82*, 2644. Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4512). More quantitative work is being done in an effort to evaluate the factors that influence the partitioning between oxygen-catalyzed intersystem crossing and oxygen trapping.
(18) Since the enone **6** (0.8%) is a secondary product derived from the hydroperoxide **5** (2.8%), the total relative yield of **5** is 3.6% and the ratio of **5/3** is 3.6%:0.4%, or about 9:1.
(19) As yet there is no experimental evidence that photochemical nitrogen extrusion from symmetrical azo alkanes such as **4** is a stepwise process. In the case of 1,3-cyclopentadiyl (**1b**), it is known that the species being trapped has lost the nitrogen, as trapping occurs with equal efficiency from both faces of the biradical: Adam, W.; Hannemann, K.; Oppenländer, T., unpublished results.

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(21) Squillacote, M.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *J. Am. Chem. Soc.* **1975**, *97*, 3244.
(22) The hydroperoxy biradical **11** also must be very short lived, since no products that might arise from the trapping of **11** by a second oxygen molecule were detected.
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Conversion of Cyclohexenes into π-Complexed Arenes

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We have had a continuing interest in the reactions of metal atoms with unsaturated substrates to form organometallic species.[1] The conventional route to bis(arene)chromium compounds involves cocondensation of chromium atoms and arenes. This procedure is of little value for the synthesis of chromium π-complexes with nonvolatile ligands which are not amenable to cocondensation reactions. We have sought to develop a new route to bis(arene)chromium(0) compounds by the generation of reactive intermediates that on addition of a suitable arene will yield the desired organometallic complex. Several examples of our proposed strategy which employ iron and nickel atoms have been reported recently.[2-4]

Cocondensation of chromium atoms with 1-butene has been shown by Skell[5] to result in isomerization of the olefin; however,

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Table I. Products Formed from the Reaction of Chromium/Alkene Matrices with Selected Arenes

cycloalkene/Cr matrix	arene	products obsd	
		organometallic	hydrocarbon[a]
cyclohexene (25 mL, 0.25 mol)/Cr(1.10 g, 21 mmol)	none	no isolable products	benzene (3%), cyclohexane (5%), bicyclohexyl (1%), cyclohexylcyclohexene (1%)
cyclohexene (0.69 mol)/Cr (1.00 g, 19.2 mmol)	toluene (60 mL, 0.57 mol)	total yield = 20 mg, bis(toluene)chromium(0), bis(benzene)chromium(0), (benzene)(toluene)chromium(0)	total yield, 6.0 mL, bicyclohexyl (30%), cyclohexylcyclohexene[b] (70%), cyclohexylbenzene[d]
4-methylcyclohex-1-ene (25 mL, 0.21 mol)/Cr (0.69 g, 13 mmol)	benzene (50 mL, 0.56 mol)	traces of bis(toluene)chromium(0)	total yield, 12.7 mL, methylcyclohexane (7%), toluene (15%), methylcyclohexene[c] (28%)
4-methylcyclohex-1-ene (25 mL, 0.21 mol)/Cr (1.41 g, 27 mmol)	33% benzene in THF solution	total yield = 20 mg, bis(toluene)chromium(0)	total yield, 6.0 mL methylcyclohexane (4%), toluene (4%), methylcyclohexene[c] (5%), di(methylcyclohexyl),[d] methylcyclohexylmethylcyclohexene[d]
4-methylcyclohex-1-ene (25 mL, 0.21 mol)/Cr (1.48 g, 28 mmol)	ethylbenzene (30 mL, 0.25 mol)	total yield = 180 mg, bis(toluene)chromium(0), bis(ethylbenzene)chromium(0), (ethylbenzene)(toluene)chromium(0)	total yield, 11.7 mL, methylcyclohexane (9.5%), toluene (16%), methylcyclohexene[c] (28.5%), di(methylcyclohexyl),[d] methylcyclohexylmethylcyclohexene,[d] di(methylcyclohexene),[d] methylcyclohexyltoluene[d]

[a] Percent of total mass indicated in parentheses. [b] Two isomers present (54.3% and 45.7% of the total isomer mass). [c] Two isomers present. [d] Compounds detected by mass spectroscopy, but not quantified.

no isolable organometallic products were reported. It was suggested that a "chromium–olefin" complex forms, which decomposes on warming the matrix. The possible formation of weak solvates with alkenes suggested to us a new synthetic route to bis(arene)chromium(0) species, as illustrated by eq 1.

$$Cr(atoms) + alkene \rightarrow [Cr(alkene)_n\ intermediate] \xrightarrow{\text{arene}} bis(arene)Cr(0)\ \ (1)$$
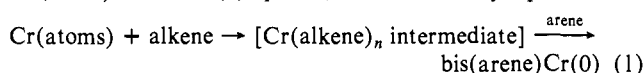
We report in this communication our results of the reaction of chromium atoms with cyclohexenes; the resulting reaction mixture was treated with an arene at low temperatures to test for the presence of reactive intermediates. Initially we chose cyclohexene to interact with chromium atoms because we anticipated that it would have very little tendency to oligomerize and isomerization processes would not produce products that would obscure our analysis of the reaction mixture.

In a typical reaction, 1.00 g of chromium (19.2 mmol) was condensed with 70 mL of cyclohexene (0.69 mol).[6] After the matrix formed, 60 mL of toluene (0.567 mol) were added to the melting matrix. Working up the reaction mixture resulted in a mixture of several products. Predominant among the organometallic products (20 mg) was the mixed sandwich compound $(C_6H_6)(CH_3C_6H_5)Cr(0)$. The original target compound $(CH_3-C_6H_5)_2Cr(0)$ was present in small amounts as was $(C_6H_6)_2Cr(0)$. Included among the hydrocarbon products (total amount ≈ 6 mL) are bicyclohexyl and two isomers of cyclohexylcyclohexene in the ratio 30:38:32. The surprising presence of π-C_6H_6-bound chromium species among the products can only result from the dehydrogenation of cyclohexene.

Prompted by this observation, similar reactions were carried out with methylcyclohexene as the initial alkene "solvating agent" and various arene substrates. A control reaction using cyclohexene with no added arene was also performed. The results of these

(5) Skell, P. S.; Williams-Smith, D. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 3337.
(6) In all of the reactions reported here, chromium was cocondensed with cyclohexene or methylcyclohexene at liquid nitrogen temperature by using procedures reported previously.[1] The reaction flask was vented with dry and deoxygenated argon, and the arene was added to the still cold reaction mixture as the neat liquid or diluted with an inert solvent. In some cases, the arene was flash distilled onto the still frozen chromium atom/alkene matrix. Standard vacuum line oriented methods, as well as sublimation, were used to separate the reaction mixture into its components. Identification was effected by a combination of high- and low-resolution mass spectroscopy and gas chromatography/mass spectroscopy. In general, two kinds of new products were present in the resulting mixture, organometallic species and various hydrocarbons.

experiments are summarized in Table I.

Although definitive statements concerning the mechanism of the reaction described here cannot be made at this point in time, the results of our experiments summarized in Table I suggest the general nature of some of the intermediates that are probably involved. It is highly likely that the initially formed alkene/chromium atom matrix contains loosely bound alkene–chromium complexes as Skell[5] previously suggested. Our results also indicate that the complexed alkene undergoes isomerization, as well as dehydrogenation, to the extent that the end product of the latter process—an arene—is found ultimately complexed to the chromium center. The organometallic product distribution also indicates that the alkene bonded to chromium atoms in the matrix can be either completely displaced by arenes to produce the corresponding bis(arene)chromium(0) compound, our original objective, or partially displaced (and the remainder dehydrogenated but still bound to chromium) to form the mixed-arene complexes.

All of the products identified, with two exceptions, are species resulting from either a dehydrogenation or hydrogenation of the cycloalkene. The two exceptions are the isomerized cycloalkene and the sandwich compound derived from the added arene (e.g., bis(ethylbenzene)chromium(0)). This observation indicates that hydrogen transfer is the major course of the metal–olefin interaction. The products formed when a cyclohexene matrix is allowed to warm (without added arene) indicate that the hydrogen-transfer reaction can occur in the original weakly complexed cyclohexene–chromium "solvate"; the absence of any organometallic species (e.g., bis(benzene)chromium(0)) in the control reaction is an interesting contrast to one observation that a π-complexed benzene molecule is observed when an arene is added to the mixture. Although the original object compounds, the organometallics, are formed in low yields relative to more conventional synthetic methods, they are still present in significant quantities. Moreover, the process also produces mixed-arene–chromium complexes in reasonable yield; up to now, such species have been difficult to obtain by conventional methods of synthesis.

The details of the hydrogen-transfer portion of the reaction sequence are obscure at this point. However, the hydrocarbon distribution provides some useful insight into this process. That it probably involves radicals is supported by the occurrence of products that are structurally derived from dimerized cycloalkenes or their hydrogenation products. The products which are arenes substituted by the cycloalkenes, the lack of saturated derivatives of the arenes, and the isomerization of the cycloalkene all suggest that the primary source of the hydrogen-transfer species is

probably one of the alkene–chromium species described above. This argument suggests an intermediate chromium–hydrogen system possibly containing a π-allyl moiety. The activation of the C–H bond is apparently related to the resonance stabilization gained upon formation of the arene and the further stabilization from the tendency of chromium to form strong π bonds with arene ligands. This unusual nature of our chromium–cyclohexene reaction system is further demonstrated by the absence of the oligomerization products observed when 1-butene is cocondensed with chromium atoms as reported by Skell;[5] the addition of D_2O is necessary to generate oligomeric products in the case of 1-propene, but we observed oligomerization in the absence of a proton source.

We are currently attempting to further elucidate the mechanistic details of the process involved in this reaction, as well as optimizing the process as a synthetic method for the convenient preparation of mixed, π-complexed arene chromium compounds.

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Reaction of Diene Group 4 Metallocene Complexes with Metal Carbonyls: A Novel Entry to Fischer-Type Carbene Complexes

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Transition-metal carbene complexes are among the most important organometallic substrates involved in stoichiometric as well as catalytic reaction sequences for the transformation of organic compounds.[1] Surprisingly, most presently employed synthetic routes for the conversion of a metal carbonyl to a transition-metal carbene moiety are basically variations of E. O. Fischer's original method,[2] published back in 1964, which is characterized by a nucleophile initially attacking the carbonyl carbon atom. Limitations of this route[3] have been circumvented by using carbene precursors other than coordinated carbon monoxide.[1] However, a general mechanistic alternative to Fischer's procedure for the MC≡O → M=CR(OR′) conversion seems still to be lacking.

We have recently observed two competing reactions taking place upon exposure of the unique (s-cis-/s-trans-η⁴-conjugated diene)metallocene system **1** ⇌ **3**[4] to ketones and aldehydes. Metallacyclic σ²,π-type structured **3** reacts by a usual carbonyl addition reaction.[5,6] Under equilibrium conditions, the reactivity of the s-trans isomer **1** is much higher, however. Its reactions with ketones is believed to proceed through a coordinatively unsaturated
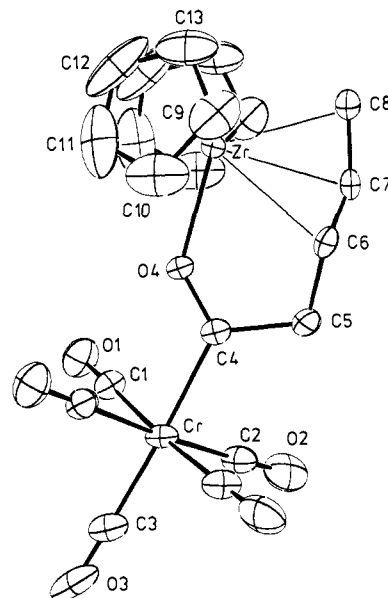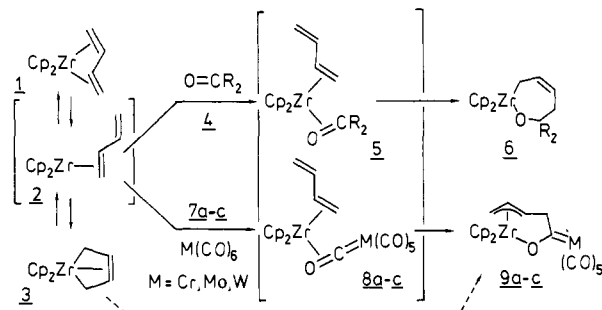

Figure 1. Perspective view of the molecular structure of **9a** with atom numbering scheme.

Scheme I

(η²-diene)MCp₂ intermediate **2**. It has been suggested that CC coupling takes place during a (probably concerted) electrocyclic ring-closure reaction of **5** to produce a metallacyclic σ-allyl complex **6**.[6,7] Replacement of the organic carbonyl compound **4** in this reaction sequence (Scheme I) by its inorganic analogue, a transition-metal carbonyl, should lead to a Fischer-type carbene complex, formed from coordinated carbon monoxide by electrocyclic CC coupling.

In fact, the (s-cis-/s-trans-η⁴-butadiene)zirconocene equilibrium mixture (**1** ⇌ **3**)[4] slowly reacts at room temperature with $Cr(CO)_6$ (equimolar, 2% in benzene, 12 h) to yield the (zirconoxycarbene)Cr(CO)₅ complex[8] **9a**. (Yellow crystals from benzene, 51% isolated yield. Anal. Calcd for $C_{20}H_{16}O_6CrZr$: C, 48.47; H, 3.25. Found: C, 48.59; H, 3.13. IR[9] (C_6D_6) ν_{CO} = 2048 (m), 1994 (s), 1920 (vs) cm⁻¹.) The NMR spectra of **9a** indicate the presence of a syn-substituted π-allyl unit[7b,10] $(C_6D_6$ solution,

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