CH_3, $R^3 = R^4 = H$, $R_2 = (C_6H_5)_2$), 82798-08-1; (*E*)-II (R^1 = 2,6,6-trimethyl-1-cyclohexen-1-yl, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_2 = (C_6H_5)_2$), 82798-10-5; (*E*)-II (R^1 = 2,6,6-trimethyl-1-cyclohexen-1-yl, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_2 = (C_2H_5)_2$), 82798-11-6; II (R^1 = 2,6,6-trimethyl-2-cyclohexen-1-yl, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_2 = (C_6H_5)_2$), 82798-15-0; II ($R^1 = C_6H_5$, $R^2 = R^3 = H$, $R^4 = CH_3$, $R_2 = (C_6H_5)_2$), 82798-33-2; II ($R^1 = C_6H_5$, $R^2 = R^3 = R^4 = H$, $R_2 = (C_6H_5)_2$), 82798-34-3; $(Ph_3P)_3RhCl$, 14694-95-2; $EtMe_2SiH$, 758-21-4; $PhMe_2SiH$, 766-77-8; $PhMeSiH_2$, 766-08-5; Ph_2SiH_2, 775-12-2; $PhSiH_3$, 694-53-1; Et_3SiH, 617-86-7; $i\text{-}Pr_2SiH_2$, 18209-66-0; Et_2SiH_2, 542-91-6; piperitol, 491-04-3; 4-methyl-2-pentanone, 108-10-1; 4-methyl-3-penten-2-ol, 4325-82-0; citronellal, 106-23-0; geraniol, 106-24-1; dihydro-β-ionol, 3293-47-8; *trans*-β-ionol, 472-80-0; dihydro-α-ionol, 13720-37-1; α-ionol, 25312-34-9; 2-methylcyclohexanone, 583-60-8; 2-methyl-2-cyclohexen-1-ol, 20461-30-7; 3-methylcyclohexanone, 591-24-2; 3-methyl-2-cyclohexen-1-ol, 21378-21-2; 2-octalone, 4832-17-1; $\Delta^{1,9}$-2-octalol, 39879-90-8; 2-isopropyl-5-methylcyclohexanone, 10458-14-7; 2-isopropylidene-5-methylcyclohexanol, 529-02-2; cyclohexyl methyl ketone, 823-76-7; 1-(1-cyclohexen-1-yl)ethanol, 18325-75-2; dihydrochalcone, 1083-30-3; butyrophenone, 495-40-9; 4-phenyl-2-butanone, 2550-26-7; hydrocinnamaldehyde, 104-53-0; 4-phenyl-3-buten-2-ol, 17488-65-2; cinnamyl alcohol, 104-54-1; (*E*)-1-[3-(dimethylphenylsiloxy)but-1-ene]-2,6,6-trimethyl-1-cyclohexene, 82798-12-7; (*E*)-1-[3-(triethylsiloxy)but-1-ene]-2,6,6-trimethyl-1-cyclohexene, 82798-14-9; 1-(dimethylethylsiloxy)-2-methyl-1-cyclohexene, 82798-16-1; 1-(diphenylsiloxy)-2-methyl-2-cyclohexene, 82798-17-2; 1-(triethylsiloxy)-3-methyl-1-cyclohexene, 18407-91-5; 1-(diphenylsiloxy)-3-methyl-2-cyclohexene, 82798-18-3; 2-(triethylsiloxy)-$\Delta^{1,2}$-octalin, 57137-82-3; 2-(diethylsiloxy)-$\Delta^{1,9}$-octalin, 82798-19-4; 1-(dimethylethylsiloxy)-2-isopropyl-5-methyl-1-cyclohexene, 82798-20-7; 1-(diphenylsiloxy)-2-isopropylidene-5-methylcyclohexane, 82798-21-8; 1-(diethylsiloxy)-2-isopropylidene-5-methylcyclohexane, 82798-22-9; 3-(diphenylsiloxy)-4-isopropyl-1-methyl-1-cyclohexene, 82798-23-0; 3-(diethylsiloxy)-4-isopropyl-1-methyl-1-cyclohexene, 82798-24-1; 1-cyclohexylidene-1-(triethylsiloxy)ethane, 82798-25-2; 1-(cyclohex-1-en-1-yl)-1-(triethylsiloxy)ethane, 82798-26-3; 1-(cyclohex-1-en-1-yl)-1-(diphenylsiloxy)ethane, 82798-27-4; nitrosodurene, 38899-21-7; triethyldeuteriosilane, 1631-33-0; (*E*)-1-(triethylsiloxy)-3,7-dimethylocta-1,6-diene-*3-d*, 82798-37-6; citronellal-*3-d*, 82798-38-7; diphenyldideuteriosilane, 17950-94-6; (*E*)-1-(diphenyldeuteriosiloxy)-3,7-dimethylocta-2,6-diene-*1-d*, 82798-39-8; geraniol-*1-d*, 82863-21-6; (*Z*)-1-(triethylsiloxy)-3,7-dimethylocta-1,6-diene-*3-d*, 82798-47-8; 4-phenyl-2-(triethylsiloxy)-3-butene, 82798-48-9.

Communications

Thermally Induced Reductive Ligand Coupling in Chromium π Complexes of Aromatic Ketones[1]

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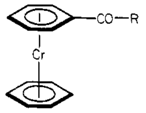
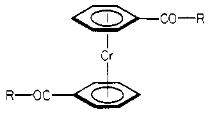
Summary: Thermolysis below or at the melting point of crystalline samples of bis(η^6-acylbenzene)chromium(0) complexes yields ethene derivatives as main products. An intramolecular mechanism of ligand coupling is ruled out as the result of cross thermolysis experiments. Evidence for the intermediacy of arylcarbenes, formed via deoxygenation of the π-bonded aromatic ketones by Cr(0), is provided by the minor products of the thermolysis.

Deoxygenative coupling of carbonyl compounds to symmetrical alkenes can be effected in a variety of ways,[2] employing low-valent transition-metal compounds[3,4] or even metal(0) slurries.[5]

In this communication we present a reductive coupling reaction which is autogenic in that the carbonyl components are present as ligands in a bis(η^6-arene)chromium(0) complex and the role of the coupling agent is played by the central metal atom. This work was triggered by the observation that the mass spectra of a series of new acyl derivatives **6–10** of bis(η^6-benzene)chromium (Table I), which we had prepared to study spin delocalization in the corresponding ketyl radical complexes,[6] displayed high intensity peaks from tetraarylethene molecular ions.[7]

Table I. Bis(η^6-benzene)chromium Complexes Studied in Thermolysis Reactions

R		
H	1	6 (135)[a]
C_6H_5	2	7 (150)
$4\text{-}C_6H_4CH_3$	3	8 (150)
$4\text{-}C_6H_4CF_3$	4	9 (162)
$4\text{-}C_5H_4N$	5	10 (205)

[a] Temperature (°C) of decomposition of neat sample.

These signals were absent in the mass spectra of the monoacyl derivatives **1–5**. It was soon realized that deoxygenative ligand dimerization is a thermally induced reaction of the neutral complexes rather than a reaction of the parent ion generated in the mass spectrometer and we therefore studied more thoroughly the thermolysis of complexes **6–10** in the crystalline state as well as in solution.

When samples of **6–10** are heated in a nitrogen atmosphere, vigorous reaction occurs at temperatures characteristic for the respective complex. The product distribution from thermolysis reactions of complexes **6** and **7**

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[1] Metal π Complexes of Benzene Derivatives. 18. Part 17: Ch. Elschenbroich and J. Koch, *J. Organomet. Chem.*, **229**, 139 (1982).

[2] Tse-Lok Ho, *Synthesis*, 1 (1979) for leading references.

[3] J. E. McMurry, *Acc. Chem. Res.*, **7**, 281 (1974).

[4] H. Leddon, I. Tkatchenko, and D. Young, *Tetrahedron Lett.*, 173 (1979).

[5] (a) J. E. McMurry and M. P. Fleming, *J. Org. Chem.*, 41, 896 (1976); (b) J. E. McMurry and L. R. Krepski, *ibid.*, 41, 3929 (1976); (c) J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *ibid.*, **43**, 3255 (1978).

[6] Ch. Elschenbroich, J. Heck, and F. Stohler, *Chem. Ber.*, to be submitted for publication.

[7] In the mass spectra of 1,1′-diacylferrocenes there are no indications for interligand coupling.

[8] The residue of the toluene extraction process analyzes to a composition of 25.45% C, 2.35% H, 36.6% Cr, and 34.6% O (difference to 100%) which leads to a ratio of Cr/O ≈ 1:3, implying that, apart from Cr_2O_3 or CrO_2, some oxygen must be present in insoluble organic material.

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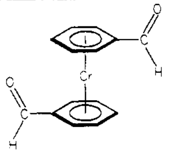
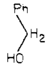
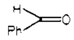
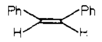
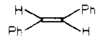
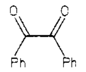
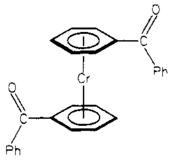
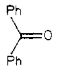
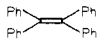
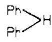
Table II. Thermolysis of the Complexes 6 and 7

complex	products,[a] %		
		neat sample[b]	soln[c]
 **6**			0.6
		trace	
		12.7	2.4
		42.0	7.5
	Ph—≡—Ph	6.3	
			2.5
	insoluble residue		
 **7**		40.3	
		37.6	
		15.6	
	insoluble residue		

[a] The products were extracted with toluene and identified by gas chromatography/mass spectrometry (6) and NMR (7). The yields refer to starting materials 6 and 7, respectively. [b] Reaction temperature: 135 °C (6), and 150 °C (7). [c] Solvent: methylcyclohexane; sealed tube; 135 °C; 3 h.

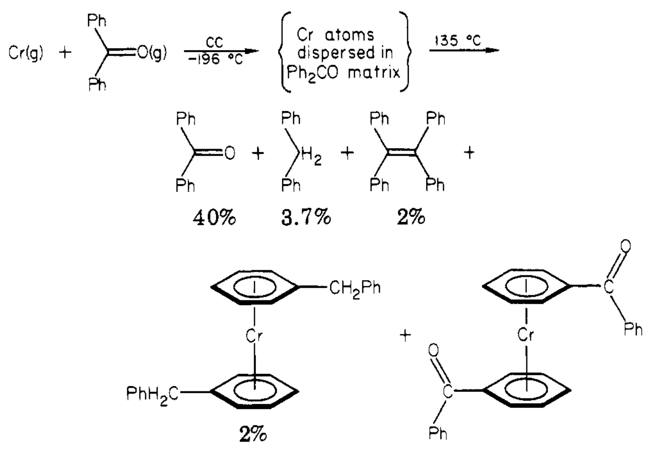
is listed in Table II. As a generalization, it may be stated that with increasing electron affinity of the R group an increase in the reaction temperature and the free ligand to coupling product ratio is observed. If the thermolysis of **6** is carried out in solution (methylcyclohexane) rather than in the crystalline state, the reaction only proceeds sluggishly and even after 3 h at 135 °C, the yield of organic thermolysis products is much lower as compared to the solid-state reaction. However, the cis to trans ratio of the ethene derivatives isolated is the same.

Turning now to the course of this reductive ligand coupling, three alternatives are conceivable: (A) an intramolecular concerted process where CrO_2 is eliminated and two ligands of one individual complex molecule are converted into an ethene derivative; (B) an intermolecular concerted reaction where via CrO_2 elimination two carbene molecules form which react not only with each other but also with adjacent complex units and/or species derived therefrom; (C) an intermolecular consecutive path where cleavage of the sandwich complex precedes reaction of the chromium atoms, thereby generated, with ligand molecules which may or may not stem from the original complex unit.

The fact that no ligand dimerization products were observed in the thermolysis of the monosubstituted complexes **1**–**5** at first appeared to favor alternative A. However, in order to furnish unambiguous proof for the alleged intramolecular nature of the coupling process, we cocrystallized **7** with an equimolar amount of the perdeuterated derivative **7**-d_{20}, subjected the material to thermolysis, and determined the composition of the reaction product. The tetraphenylethene (**11**) ratio obtained was **11**/**11**-d_{10}/**11**-d_{20} = 1:2:1.[9]

The formation of the cross product **11**-d_{10} in an amount in accordance with statistical considerations strongly militates against an intramolecular mechanism of type A.[10]

Scheme I



Further corroborative evidence for an intermolecular pathway is provided by the low reaction rate in solution as compared to the solid state. It is more difficult to determine the sequence of events which distinguishes the alternatives B and C. In a crude attempt toward that goal we prepared a matrix of the approximate composition Cr/benzophenone (1:2) by condensing chromium atoms with benzophenone vapor at −196 °C, assuming that the material thereby obtained mimics the state of the thermolysis system **7** after metal–arene cleavage but before consecutive reactions.[11]

The low yield of dimerization product obtained in this experiment[12] appears to argue against alternative C, keeping in mind limitations in the analogy of the complex thermolysis and the cocondensation approach. Irrespective of whether sequence B or C obtains, the fate of the primary deoxygenation species and their conversion to the final products must be clarified, accommodating in the explanation the tendency of decreased coupling with an increase in the electron-withdrawing nature of R and the stilbene cis to trans ratio of 1:3 observed in the case of **6**.[13]

Carbonyl coupling through an intermediate pinacol dimerization, as demonstrated for the case of coupling by means of Ti(0),[5] may be ruled out since this mechanism is thought to proceed via ketyl radicals and should be favored for ketones with electron-withdrawing groups, whereas the opposite behavior is found in the series **6**–**10**. Furthermore, the aforementioned reaction yields *trans*-ethene derivatives exclusively,[5c] whereas ligand coupling

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[9] The organic product does not contain any species **11**-$d_{1-9,11-19}$ which might originate from H/D scrambling.

[10] A reviewer pointed out that the refutation of alternative A is questionable since intermolecular ligand exchange might precede intramolecular ligand coupling. We consider this path highly unlikely because ligand exchange between bis(arene)chromium complexes is known to occur only on the presence of a catalyst (e.g., $AlCl_3$): E. O. Fischer and J. Seeholzer, *Z. Anorg. Allg. Chem.*, **312**, 244 (1961). Furthermore, ligand exchange prior to ligand coupling should lead to the formation of tetraphenylethene derivatives in the case of the monosubstituted complexes **1**–**5** as well which is contrary to observation.

[11] This is a crude attempt since not all of the chromium which is condensed remains atomic but part of it may form chromium clusters in the liquid zone at the matrix surface before reaching the temperature (77 K) of the cooling bath. These chromium aggregates may react differently from isolated chromium atoms. Furthermore, it is practically impossible to guarantee a homogeneous distribution of Cr and $(C_6H_5)_2CO$ on the surface of the cocondensation vessel.

[12] The low yield of coupling product agrees with results of Gladysz et al., who, upon cocondensation of alicyclic ketones with chromium atoms, also obtained very small amounts of ethene derivatives. S. Togashi, J. G. Fulcher, B. R. Cho, M. Hasegawa, and J. A. Gladysz, *J. Org. Chem.*, **45**, 3044 (1980).

[13] Reductive coupling of benzaldehyde by means of Ti(0) only yields *trans*-stilbene. J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *J. Org. Chem*, **43**, 3255 (1978).

of bis(η^6-acylbenzene)chromium complexes affords mixtures of cis and trans products. The increase of the ligand to dimer ratio with increasing electron affinity of R, i.e., with decreasing arene–metal bond strength, suggests that the aromatic ketone remains attached to the metal during the deoxygenation step (alternative B). The generation of carbenes by deoxygenation of carbonyl groups has only rarely been reported[14] and, to our knowledge, is without precedent for aromatic ketones. In the case of the complexes **6–10** however, favorable disposition of the carbonyl groups and the "coupling agent", Cr(0), is likely to assist such a process.

Due to the high reactivity of carbenes, formation of ethene derivatives via dimerization is unlikely in solution and the products are usually explained by an attack of one carbene on the carbene precursor and by addition and insertion reactions. In the case of the π complexes **6–10**, however, neat material reacts in the condensed state below or at the melting point, and the relative disposition of the ligands, as governed by the crystal lattice, may be of prime importance in determining the nature of the products. Since 1,1′ derivatives of bis(benzene)chromium usually adopt an anti conformation with regard to the ring–metal–ring axis,[17] carbenes formed via deoxygenation from ligands of neighboring complex units may be juxtaposed more favorably for dimerization than species stemming from the same complex unit. This notion rationalizes the result of the **7**/**7**-d_{20} cross thermolysis. Indications for the intermediacy of arylcarbenes may also be found among the minor products of the thermolysis. In the case of **6** we obtained via GC/MS the following distribution (m/e, formula, %): 106, PhCHO, 13.6; 168, Ph_2CH_2, 1.6; 178, Ph_2C_2, 14.6; 180, *cis*-$Ph_2C_2H_2$, 30.5; 180, *trans*-$Ph_2C_2H_2$, 100.0; 194, Ph_2C_2O, 5.8; 258, $Ph_3C_2H_3$, 0.5; 268, Ph_3C_3H, 1.3, 3.2; 270, $Ph_3C_3H_3$, 0.2, 0.8; 272, $Ph_3C_3H_5$, 2.8; 284, Ph_3C_3HO, 3.1.

Whereas the mode of formation of tolan (m/e 178) is not clear at present, the species m/e 270 and 268 probably represent cyclopropane and cyclopropene derivatives formed by addition of phenylcarbene to stilbene and tolan. One of the most characteristic differences between thermolysis of neat **6** and of its solution is the abundance of benzil among the solution thermolysis products. The latter compound may arise via dimerization of benzoyl radicals generated from benzaldehyde and chromium oxides.[18] Therefore, in addition to the carbene path, radical mechanisms have to be taken into account, at least for the thermolysis of (η^6-acylbenzene)chromium complexes in solution.

A more detailed discussion will be given in conjunction with the results of an X-ray structure determination for **6**.

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Registry No. 1, 1271-69-8; 2, 52445-45-1; 3, 82555-98-4; 4, 82571-34-4; 5, 82555-99-5; 6, 55140-34-6; 7, 82556-00-1; 8, 82571-35-5; 9, 82556-01-2; 10, 82556-02-3; Cr, 7440-47-3; benzophenone, 119-61-9.

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[14] Examples are the generation of carbenes from carbonyl compounds and carbon atoms[15] and the reaction of alicyclic ketones with magnesium atoms.[16]

[15] P. S. Skell and J. M. Plonka, *J. Am. Chem. Soc.*, **92**, 836 (1970).

[16] L. D. Wescott, Jr., C. Williford, F. Parks, M. Dowling, S. Sublett, and K. J. Klabunde, *J. Am. Chem. Soc.*, **98**, 7853 (1976).

[17] Examples include (Me-η^6-$C_6H_5)_2$CrI, O. V. Starovskii and Y. T. Struchkov, *Dokl. Chem.* (*Engl. Transl.*), **135**, 152 (1961); *J. Struct. Chem.* (*Engl. Transl.*) **2**, 152 (1961), and (Ph_2P-η^6-$C_6H_5)_2Cr^0$, B. Barnett, Ch. Elschenbroich, and F. Stohler, to be submitted for publication.

[18] The oxidation of aldehydes by metal complexes of Mn^{III}, Fe^{III}, and Co^{III} to yield acyl radicals is discussed in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, 1973, pp 656–660 and references therein.

Regio- and Stereoselective Addition of (Carbon disulfide)iron Complexes to α,β-Unsaturated Carbonyls in the Presence of Strong Acids

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Summary: The Fe(η^2-CS_2)(CO)$_2$(PR$_3$)$_2$ complexes add to α,β-unsaturated aldehydes, ketones, and esters in the presence of HPF_6 or HBF_4 to afford carbonyl derivatives having a bulky, cationic organometallic group at C-3. Cyclic substrates such as *l*-carvone and β-angelicalactone showed the stereoselectivity of the addition.

Electron transfer from a transition metal to an η^2-coordinated CS_2 molecule enhances the nucleophilicity of the uncoordinated sulfur atom and the dipolar character of the M–CS_2 moiety.[1] Such electronic changes might be expected to facilitate the incorporation of a metal–CS_2 fragment into an unsaturated substrate with potential implications for organic synthesis. Although electrophilic alkynes have been reported[2] to add smoothly to iron(0)–carbon disulfide complexes, cycloaddition was not observed with activated olefins. We now find that the readily available Fe(η^2-CS_2)(CO)$_2$(PR$_3$)$_2$[1] complexes can be incorporated into α,β-unsaturated carbonyls by regioselective addition, in the presence of a strong acid, to afford new cationic complexes having a bulky, sulfur-containing organometallic group linked to C-3 of the carbonyl substrate.

When 1.2 equiv of a strong acid such as $HPF_6\cdot Et_2O$ was added at 0 °C to the orange, ethereal solution of 1 equiv of complex **1** and 1.1 equiv of the α,β-unsaturated carbonyl compound **3** [such as acrolein (**3a**), methyl vinyl ketone (**3b**), chalcone (**3c**), and methyl acrylate (**3d**)], a yellow compound precipitated which was isolated by filtration, crystallized from dichloromethane–hexane mixtures, and identified, respectively, as the salts **4a** (32%), **4b** (71%), **4c** (98%), and **4d** (59%).[3] This reaction appears general for the cationic complexes since **5c** (88%) and **6c** (85%)[3] were obtained similarly from complex **2** and chalcone **3c**

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[1] Le Bozec, H.; Dixneuf, P. H.; Carty, A. J.; Taylor, N. J. *Inorg. Chem.* **1978**, *17*, 2568 and references cited therein.

[2] Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *Inorg. Chem.* **1981**, *20*, 2486.

[3] Melting points (°C): **4a**, 104–106; **4b**, 124–125; **4c**, 146–147; **4d**, 92–95; **5c**, 146–147; **6c**, 167–170. Anal. Calcd for **4a**: C, 39.66; H, 4.05; S, 9.63. Found: C, 39.82; H, 4.39; S, 9.96. Calcd for **4b**: C, 40.62; H, 4.26; S, 9.43. Found: C, 40.41; H, 4.21; S, 9.56. Calcd for **4c**: C, 49.88; H, 4.28. Found: C, 49.90; H, 4.30. Calcd for **4d**: C, 39.68; H, 4.26. Found: C, 39.61; H, 4.15. Calcd for **5c**: C, 60.82; H, 4.03. Found: C, 60.48; H, 4.28. Calcd for **6c**: C, 64.28; H, 4.27. Found: C, 64.34; H, 4.26. IR (Nujol; ν (cm^{-1})): **4a**, 2022, 1965, 1718; **4b**, 2020, 1972, 1715; **4c**, 2035, 1975, 1695; **4d**, 2027, 1985, 1732; **5c**, 2040, 1975, 1690; **6c**, 2035, 1970, 1682.

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