3 H; CH_2CH_3), 1.21 (t, $^3J(H,H) = 6.8$ Hz, 3 H; CH_2CH_3), 1.51 (s, 3 H; $=CCH_3$), 1.86 (s, 3 H; $=CCH_3$), 3.08 (q, $^3J(H,H) = 6.8$ Hz, 2 H; CH_2CH_3), 3.76 (q, $^3J(H,H) = 6.8$ Hz, 2 H; CH_2CH_3), 5.88 ppm (s, 1 H; =CH); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 18 °C): $\delta = 12.90$ (s; CH_2CH_3), 13.78 (s; CH_2CH_3), 17.33 (s; $=CCH_3$), 20.60 (s; $=CCH_3$), 45.91 (s; CH_2CH_3), 47.02 (s; CH_2CH_3), 121.07 (s; C_β), 126.98–143.33 (m; C_{arom}, $=CCH_3$, $=CPh_2$), 132.41 (s; =CH), 156.21 (s; $C_\gamma N$), 202.21 ppm (t, $^2J(C,P) = 21.2$ Hz; $Ru = C_\alpha$). **10:** Yield: 0.14 g, 45 %, IR (KBr): $\tilde{\nu} =$ 1990 (C=C=C) cm^{-1}; $^{31}P\{^1H\}$ NMR (121.44 MHz, $CDCl_3$, 18 °C): $\delta =$ 49.59 ppm (s); ^1H NMR (300 MHz, $CDCl_3$, 18 °C): $\delta = 1.26$ (t, $^3J(H,H) = 7.4$ Hz, 3 H; CH_2CH_3), 1.31 (t, $^3J(H,H) = 7.4$ Hz, 3 H; CH_2CH_3), 1.49, 1.65 (s, 3 H; $=CCH_3$), 1.88 (s, 3 H; $=CCH_3$), 3.54 (q, $^3J(H,H) = 7.4$ Hz, 2 H; CH_2CH_3), 3.88 (q, $^3J(H,H) = 7.4$ Hz, 2 H; CH_2CH_3), 5.50 (s, 1 H; =CH), 5.97 ppm (s, 1 H; =CH); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 18 °C): $\delta = 13.02$ and 13.76 (s; CH_2CH_3), 16.78 (s; $=CCH_3$), 18.22 (s; $=CCH_3$), 21.09 (s; $=CCH_3$), 46.40 (s; CH_2CH_3), 47.55 (s; CH_2CH_3), 121.14 (s; C_β), 126.60–143.18 (m; Ph, $=CCH_3$, $=CPh_2$, =CH), 157.11 (s; $C_\gamma N$), 202.61 ppm (t, $^2J(C,P) = 21.5$ Hz; $Ru{=}C_\alpha$).

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[8] $^{13}C\{^1H\}$ NMR (RuC_α) $\delta = 199.39$ (**3**) versus 295.05 ppm (**6**) and $\tilde{\nu}$(C=C=C) 1989 (**3**) versus 1932 cm^{-1} (**6**).

[9] Data for the X-ray structure analysis for **7:** Crystal from MeOH/CH_2Cl_2/pentane, $C_{70}H_{64}F_6NP_3Ru$ ($M_r = 1227.20$); crystal size $0.37 \times 0.27 \times 0.20$ mm^3; orthorhombic, space group $P2_12_12_1$ $a = 14.41810(10)$, $b = 14.57510(10)$, $c = 28.23070(10)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $Z = 4$, $V = 5932.55(6)$ Å^3, $\rho = 1.374$ g cm^{-3}; $T = 200(2)$ K; $2\Theta_{max.} = 68.2°$; 95 891 reflections measured, 10 850 unique ($R_{int.} = 0.000$), and 9859 observed ($I > 2\sigma(I)$); Nonius KAPPA-CCD diffractometer, $Cu_{K\alpha}$ radiation ($\lambda = 1.54184$ Å), graphite monochromator; multiscan absorption corrections (Ψ scan, min. transmission 79.67 %). The structure was solved by DIRDIF and refined with the full-matrix, least-squares method; $R_1 = 0.00397$, $wR_2 = 0.0999$ (for 9859 reflections with $I > 2\sigma(I)$), $R_1 = 0.0437$, $wR_2 = 0.1035$ (for all data); residual electron density $+0.678/-0.759$ e Å^{-3}. CCDC-179713 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[10] Interatomic distances and angles of the cumulene moiety, as well as those of the rest of the unsaturated chain, are usual for this type of carbon–carbon connectivity (see ref. [1]).

C_8K-Promoted Self-Condensation and Self-Condensation-Cycloisomerization Reactions of *α,β*-Unsaturated Fischer Carbene Complexes[**]

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Mar Gómez-Gallego, Tore Lejon, and
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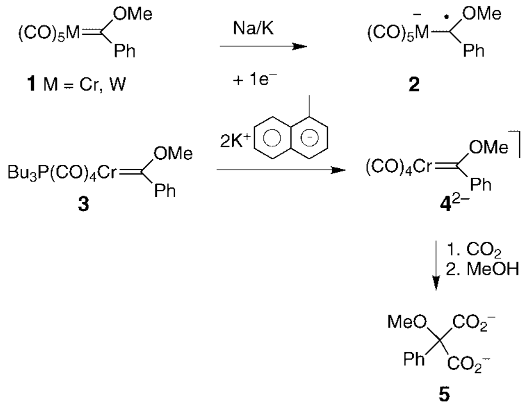
Dedicated to Professor William M. Horspool

The chemistry of stabilized Group 6 metal carbene complexes (Fischer carbenes) has reached a high level of maturity and carbenes have become very valuable building blocks in organic synthesis.[1] In spite of this, the reactivity of highly reduced Fischer carbene complexes has been somewhat neglected. The one-electron reduction of the Group 6 alkoxyaryl carbene complexes **1** by Na/K alloy was originally reported by Casey.[2] In this case, radical anion species **2** stable in diluted THF/hexamethyl phosphoramide (HMPA) solutions were detected by ESR spectroscopy. Further, Cooper and Lee[3] reported the reaction of [$Bu_3P(CO)_4CrC(OMe)Ph$] (**3**), with potassium 1-methylnaphthalenide to yield the highly reduced carbene complex **4**$^{2-}$ (Scheme 1). This species **4**$^{2-}$ shows the expected umpolung at the carbene carbon atom (which becomes a nucleophile as a result of the increased



Scheme 1.

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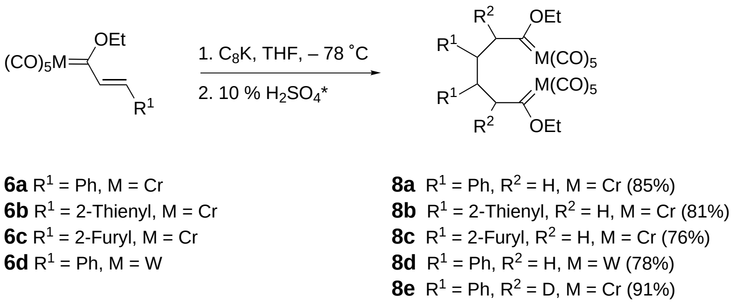
metal back donation) and reacts with CO_2 as electrophile to yield malonic acid derivative **5** (Scheme 1). Recently, Iwasawa and Fuchibe [4] used SmI_2 to effect the one-electron reduction of alkoxyaryl chromium(0) and tungsten(0)carbene complexes. The anion radical species generated from these complexes give reactions such as carbene-ligand dimerization, carbonyl insertion, and insertion into α,β-unsaturated esters.

In spite of the plethora of versatile processes involving α,β-unsaturated Group 6 carbene complexes,[5] the behavior of this class of compounds towards simple reducing agents has only recently been reported by us,[6] and others.[7] These processes are considerably more complex than the expected hydride addition reaction and they involve the metal center in many cases.[6] In this context, α,β-unsaturated chromium(0) or tungsten(0)carbene complexes are ideal substrates to effect one-electron reactions, since the hypothetical radical anions formed would be multidentate intermediates which may react in diverse ways. Therefore, we decided to study the reactivity of complexes **6** and **7** towards potassium graphite (C_8K). This reducing agent is easily prepared by heating metallic potassium and graphite at 150–160 °C for a short time under argon and it is recognized as an exceptional heterogeneous reducing reagent.[8] Nevertheless, its use in organometallic chemistry has been somewhat neglected and, to our knowledge, it has not been used in metal-carbene chemistry. The exception is the preparation of $[Cr(CO)_5]^{2-}$ from $[Cr(CO)_6]$ in the Hegedus synthesis of aminochromiumcarbene complexes.[9]

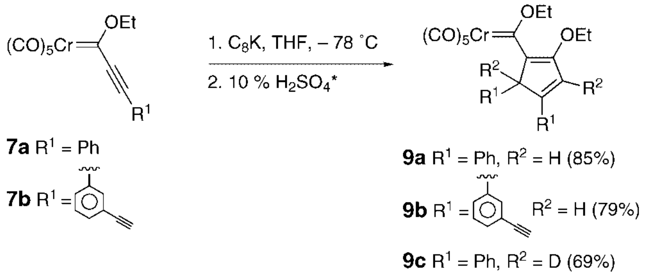
First, we checked the reaction between complex **6a** and C_8K in THF at −78 °C. After quenching with water, a new chromium-containing product was isolated in very low yields. Several experiments were then carried out varying both the temperature and the reaction times without significant improvement in the yields. The spectroscopic data of the new compound were fully consistent with an equimolecular mixture of diastereomeric complexes **8a** (see Scheme 2). We thought at this point that, perhaps, the quenching agent was not electrophilic enough to effectively protonate the expected intermediate dianions (see below), allowing for the decomposition of these materials during workup and hence for the low yields obtained. Based on these premises, the reaction between complex **6a** and C_8K was effected at −78 °C in THF and quenched with 10% H_2SO_4 at this temperature. Under these conditions an 85% yield of the inseparable (65:35) diastereomeric mixture of compounds **8a** was obtained by adsorption of the crude on neutral Al_2O_3, followed by filtration of the resulting material through a short path of silica gel with CH_2Cl_2. Having optimized the reaction conditions, the procedure was applied to α,β-unsaturated carbene complexes **6b** and **6c**. Dimers **8b** and **8c** were obtained in both cases as a (60:40) diastereomeric mixture in yields over 75%. Tungsten carbene complex **6d** also reacted efficiently with C_8K, yielding tungsten(0) biscarbene complex **8d** in 78% yield (Scheme 2). It is remarkable that complexes **6** exclusively dimerize in a tail-to-tail fashion.

Alkynyl chromium(0)carbene complex **7a** was also employed and again a new carbene complex was obtained. However, and in contrast with the results obtained for the alkenyl carbene complexes **6**, this new complex was not a biscarbene but a monocarbene derivative, albeit it incorporated two units of the starting complex. The structure of this product could not be unambiguously established by means of a combination of 1D and 2D NMR spectroscopic techniques. Therefore, a single crystal of this compound was submitted to X-ray diffraction analysis and its structure was unambiguously established as the cyclopentadienylchromium(0)carbene **9a**.[10] Complex **7b**, bearing an additional triple bond, formed cyclopentadienylchromium(0)carbene **9b** in 79% yield (Scheme 3). It has been reported that mixtures of dimerization products are mainly obtained with C_8K and α,β-unsaturated esters.[11]



*D_2SO_4/D_2O (10 %) in the deuteration experiment

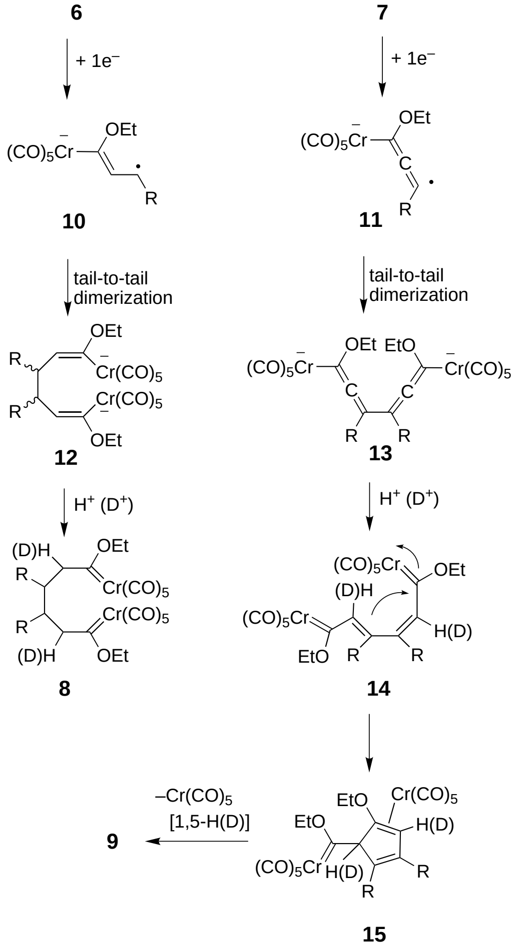
Scheme 2.



*D_2SO_4/D_2O (10 %) in the deuteration experiment

Scheme 3.

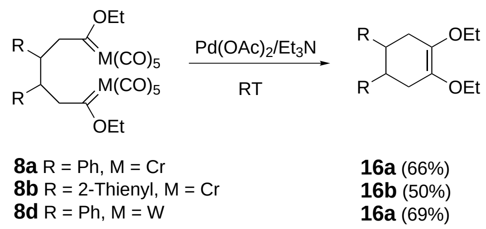
To shed light into the mechanism of these processes, the reactions of complexes **6a** and **7a** were repeated as above but using D_2SO_4 (10% in D_2O) as the quenching agent. Dideuterated complexes **8e** and **9c** were obtained in these cases in 91% and 69% yields, respectively (Scheme 2 and 3). The deuteration positions were unambiguously determined by ^1H and ^{13}C NMR spectroscopy.[12] From the results of these deuteration experiments we could propose that the first step of these reactions is the single-electron addition to the starting α,β-unsaturated complexes to form the radical anions **10** and **11** (see Scheme 4). The next step is the dimerization of these intermediates to form biscarbene anions **12** and **13**, respectively. The reaction pathways diverge at this point. Thus, biscarbene anion **12** would survive until acid quenching, and protonation (deuteration) at both α positions accounts for the observed products **8**.[13] The situation with bisallenyl-intermediate **13** is different. Once the quenching agent is added, protonated (deuterated) 1,8-dichroma-1,3,5,7-tetraene complexes **14** are formed. These intermediates undergo a fast cyclization reaction to produce new complexes **15**, that loose one chromium moiety to yield the final products **9** after a 1,5-H (D) shift. Within this proposal, the deuterated positions may be defined in the conversion of **13** into **14** and therefore they are fully compatible with the experimental results (Scheme 4).[14,15]



Scheme 4.

The efficient entry into symmetrical biscarbene complexes **8** developed above offered an opportunity to combine these results with our recently developed palladium chemistry.[16] In fact, the Pd-induced dimerization of complexes **8** yields the dimethoxycyclohexenes **16** in 50–70 % yields (Scheme 5).[17] Therefore, the sequential C_8K intermolecular dimerization of α,β-unsaturated carbene complexes, followed by Pd-catalyzed intramolecular dimerization of the resulting biscarbene complexes, is a new two-step entry to six-membered rings.

In conclusion, the reaction of α,β-unsaturated chromium(o) or tungsten(o)carbene complexes and C_8K occurs through one-electron transfer, from the interstitial potassium to the organochromium complex, to generate intermediate radical anions. These intermediates undergo a tail-to-tail dimerization to form biscarbene anions, which upon protonation with a strong acid produce complexes **8** or 1,8-dichroma-1,3,5,7-tetraene complexes **14** which convert in situ into cyclopentadienylchromium(o)carbenes **9**.[18] This mechanistic proposal is supported by deuteration experiments. Complexes **8** may in turn be transformed into functionalized cyclohexenes by Pd-catalyzed ring closure.



Scheme 5.

Experimental Section

General Procedure for the reaction of complexes **6** and **7** with potassium–graphite (C_8K) laminate. In a two-neck round-bottom flask equipped with reflux condenser and magnetic stirring bar, graphite (17.6 equiv) was heated (while stirred) under argon, for 15 min at 150–160 °C. Potassium (2.2 equiv) was added under argon, and the mixture was kept at 160 °C with careful stirring until the laminate had formed (10–15 min). The material was highly pyrophoric, necessitating cautious handling in thoroughly dried solvents. The distinctive bronze color of the mixture indicates that C_8K is formed, this is then suspended in anhydrous THF and cooled to −78 °C. To this suspension was added by syringe, a solution of the corresponding complex[19] (1.0 equiv) in THF at −78 °C over a period of 10 min. This solution was allowed to stir until the starting material was consumed (checked by TLC). The reaction was quenched with H_2SO_4 (10 %) at −78 °C and then was warmed to 25 °C for 30 min. The crude was adsorbed on neutral Al_2O_3, and the solvent carefully removed under reduced pressure. The resulting dry powder was filtered through a short pad of SiO_2 with CH_2Cl_2 as eluent, to obtain the corresponding complex as the only reaction product. For the deuterium experiments the same procedure was followed using D_2SO_4/D_2O (10 %) as quencher.

8a: 85 % (65:35 mixture of diastereoisomers). Major isomer: ^1H NMR (300 mHz, $COCl_3$): $\delta = 1.23$ (t, $J = 7.1$ Hz, 6 H), 3.27–3.31 (m, 2 H), 3.58 (dd, $J_1 = 16.2$ Hz, $J_2 = 3.5$ Hz, 2 H), 3.95 (dd, $J_1 = 16.2$ Hz, $J_2 = 9.6$ Hz, 2 H), 4.75 (q, $J = 7.1$ Hz, 4 H), 6.74–7.03 ppm (m, 10 H); ^{13}C NMR (75.43 mHz, $COCl_3$): $\delta = 357.9$, 222.7, 216.0, 141.4, 128.5, 127.8, 127.0, 78.0, 67.4, 48.3, 14.5; IR (film): $\tilde{\nu} = 2060$, 1942 cm^{-1}. Minor isomer (from an enriched mixture): ^1H NMR: $\delta = 1.32$ (t, $J = 7.1$ Hz, 6 H), 2.93 (dd, $J_1 = 16.4$ Hz, $J_2 = 2.7$ Hz, 2 H), 3.16–3.21 (m, 2 H), 3.76–3.92 (m, 2 H), 4.67–4.80 (m, 4 H), 7.11–7.28 ppm (m, 10 H); ^{13}C NMR: $\delta = 356.7$, 222.6, 216.1, 140.5, 128.3, 127.7, 126.3, 77.8, 66.1, 47.8, 14.3 ppm.

9a: Yield 85 %; ^1H NMR: $\delta = 1.24$ (t, $J = 7.0$ Hz, 3 H), 1.62 (t, $J = 7.1$ Hz, 3 H), 4.40–4.54 (m, 3 H), 4.74 (dq, $J_1 = 10.4$ Hz, $J_2 = 7.1$ Hz, 1 H), 4.97 (s, 1 H), 6.90 (s, 1 H), 6.97–7.40 ppm (m, 10 H). ^{13}C NMR: $\delta = 304.9$, 225.0, 217.9, 174.8, 160.9, 138.9, 138.5, 133.0, 129.6, 128.6, 128.2, 127.8, 127.4, 126.4, 120.1, 74.0, 68.4, 54.8, 15.3, 14.7 ppm; IR (film): $\tilde{\nu} = 2048$, 1978, 1931 cm^{-1}.

General procedure for the reaction of complexes **8** with $Pd(OAc)_2/Et_3N$: A mixture of the corresponding complex (1.0 equiv) and $Pd(OAc)_2$ (0.1 equiv) in anhydrous THF at room temperature, was placed in a flame-dried airless flask containing a magnetic stirring bar, degassed by evacuation/back fill with argon (3 ×). Then, Et_3N (1.1 equiv) was added by syringe at room temperature and the mixture was stirred at this temperature until complete disappearance of the starting material (checked by TLC). Finally, the reaction was concentrated under vacuum, diluted with AcOEt and filtered through Celite. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel.

16a: 66 % (65:35 mixture of diastereoisomers) ^1H NMR (for the mixture of diastereoisomers): $\delta = 1.20$ (t, $J = 7.0$ Hz, 3.9 H), 1.25 (t, $J = 7.0$ Hz, 2.1 H), 2.31–2.50 (m, 4 H), 3.06–3.09 (m, 0.7 H), 3.24 (t, $J = 4.7$ Hz, 1.3 H), 3.79 (q, $J = 7.0$ Hz, 2.6 H), 3.90 (q, $J = 7.0$ Hz, 1.4 H), 6.72–7.13 ppm (m, 10 H); ^{13}C NMR: $\delta = 144.0$, 142.1, 137.2, 136.7, 128.6, 128.5, 127.9, 127.8, 126.4, 126.1, 65.2, 65.1, 46.4, 44.7, 35.9, 30.2, 16.0, 15.9 ppm; IR (film): $\tilde{\nu} = 1655$, 1215 cm^{-1}. Compound **16a** was unstable and correct analytical data could not be obtained.

Further experimental details can be found in the Supporting Information.

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Revised: June 6, 2002 [Z18826]

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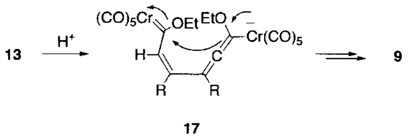
[15] A reviewer has suggested an alternate mechanism. Monoprotonation of **13** would give intermediate **17** which by cyclization by the addition of the enolate anion of one carbene complex to the other neutral carbene would yield the final product **9**.



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[17] Compounds **16** were unstable products and considerable loss of material was observed upon chromatographic purification.

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[19] Complexes **6** and **7** were prepared by procedures previously described in the literature. a) **6a–d**: R. Aumann, H. Heinen, *Chem. Ber.* **1987**, *120*, 537; b) **7a**: R. Aumann, P. Hinterding, *Chem. Ber.* **1993**, *126*, 421; c) **7b**: I. Fernández, M. A. Sierra, M. J. Mancheño, M. Gómez-Gallego, S. Ricart, *Organometallics* **2001**, *20*, 4304.

Probing Fast Facilitated Ion Transfer across an Externally Polarized Liquid–Liquid Interface by Scanning Electrochemical Microscopy**

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Ion transfer reactions at a liquid–liquid interface or an interface between two immiscible electrolyte solutions are essential for many biological and chemical processes, such as transmembrane signaling, drug delivery, and phase-transfer catalysis.[1–3] Over the last three decades, the thermodynamics and kinetics of such processes have been extensively studied using electrochemical methods. Several groups have tried to measure the rate constant using transient techniques,[4] but met with limited success. This is mainly because the ion transfer is often very fast and therefore the transfer rate is difficult to measure.[4]

Recently we obtained the rate constant of potassium ion transfer from water to 1,2-dichloroethane facilitated by dibenzo[18]crown-6 (DB18C6) using nanopipet voltamme-

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