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Reactions of Novel Reactive Species Generated by Samarium(II)-Mediated One-Electron Reduction of Fischer-Type Carbene Complexes

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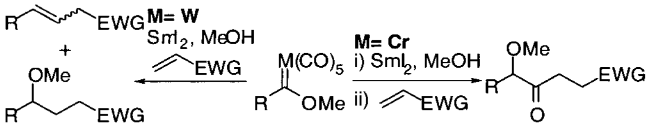
ABSTRACT

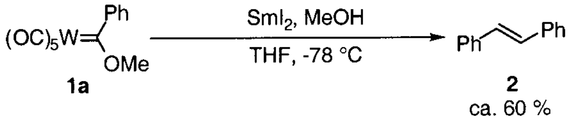


Two types of novel reactive species were generated by one-electron reductions of Fischer-type carbene complexes. In the case of tungsten complexes, one-electron reductions generated anion radical species, which added to electron-deficient olefins to give addition products. In the case of chromium complexes, carbonyl insertion occurred to give acyl chromate complexes, which underwent 1,4-addition to various electron-deficient olefins.

It is well-known that the pentacarbonyl metal moiety of the Fischer-type carbene complexes of group 6 metals acts as a strongly electron-withdrawing group and that the carbon−metal double bond of the complexes behaves like a carbonyl group.[1] One would therefore expect that one-electron reduction of the Fischer-type carbene complexes would generate metal-containing anion radical species, which could be employed for further carbon−carbon bond formations. In fact, on one-electron reduction of a chromium phenyl carbene complex with Na/K, Casey et al. observed by ESR an anion radical species, which was stable at −78 °C in a highly diluted solution.[2] This species, however, has not been employed in further carbon−carbon bond-forming reactions. In this Letter, we report the reactions of two types of reactive species generated by samarium(II)-mediated reduction of Fischer-type carbene complexes of group 6 metals.

First, one-electron reduction of the tungsten phenyl carbene complex **1a** was examined. When a THF solution of complex **1a** was treated with 2.5 molar amounts of samarium diiodide[3] in the presence of methanol at −78 °C, *trans*-stilbene **2** was obtained in about 60% yield (Scheme 1).

Scheme 1



When the same reaction was carried out in the presence of ethyl acrylate, methyl ether **3** and olefin **4** were obtained

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[1] (a) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (b) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5, p 1065. (c) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, A. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12, p 469.

[2] Krusic, P. J.; Klabunde, U.; Casey, C. P.; Block, T. F. *J. Am. Chem. Soc.* **1976**, *98*, 2015.

[3] (a) Namy, J. L.; Girard, P.; Kagan, H. B. *Nouv. J. Chim.* **1977**, *1*, 5. (b) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307.

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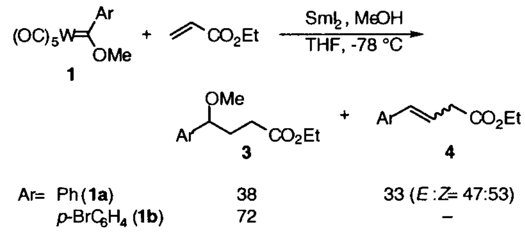
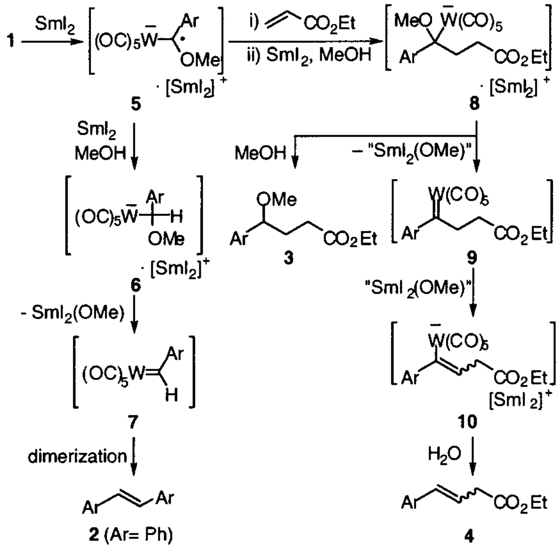
in 38% and 33% yields, respectively.[4] *p*-Bromophenyl carbene complex **1b** could also be employed in this reaction (Scheme 2).[5]

Scheme 2



Our proposed reaction mechanism is shown in Scheme 3: One-electron reduction of the complex **1** gives the expected anion radical species **5**. In the absence of ethyl acrylate, the anion radical **5** is converted to anionic species **6** by protonation and further one-electron reduction. Elimination of samarium methoxide from the anionic species **6** gives unstable carbene complex **7**, which dimerizes to give *trans*-stilbene **2**.[6,7]

Scheme 3



In the presence of ethyl acrylate, the anion radical species **5** undergoes radical addition to the acceptor to give, after one-electron reduction and protonation, alkyl tungsten species **8**. Protonolysis of the carbon−tungsten bond of **8** by methanol gives methyl ether **3**.[8] On the other hand, elimination of samarium methoxide from **8** gives unstable carbene complex **9**, which is deprotonated by the eliminated samarium methoxide to give alkenyl tungsten species **10**. Protonation of **10** on quenching gives olefin **4**.[9]

Next, one-electron reduction of the chromium phenyl carbene complex **11** was examined. When **11** was treated with samarium diiodide in the presence of ethyl acrylate and methanol, carbonyl-inserted product **12** was obtained in 8% yield, along with the methyl ether **3** and olefin **4** in 10% and 60% yields, respectively (Scheme 4, Table 1). Furthermore, the yield of ketone **12** increased to 41% when ethyl acrylate was added after the treatment of carbene complex **11** with samarium diiodide.

Scheme 4

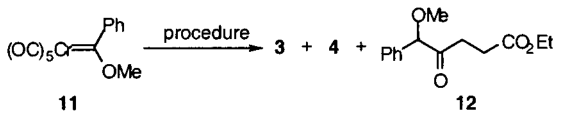
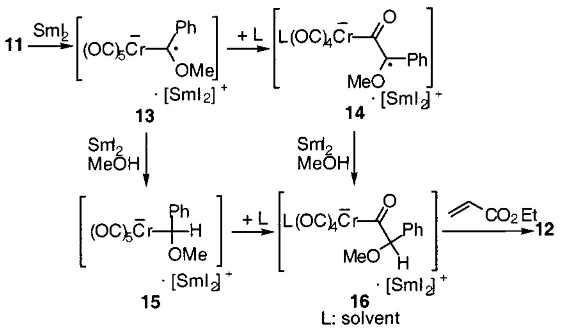


Table 1. Reduction of Chromium Phenyl Carbene Complex

procedure	3/%	4/%	12/%
i)  CO$_2$Et , -78 °C ii) SmI$_2$, -78 °C ~ rt, 2h	10	60	8
i) SmI$_2$, -78 °C, overnight ii)  CO$_2$Et , -78 °C ~ rt, 2h	5	26	41

We propose ketone **12** to be derived from acyl chromate complex **16** (Scheme 5): One-electron reduction of carbene complex **11** gives anion radical species **13**. Because of the weaker bond energy of the carbon−chromium bond compared to the carbon−tungsten bond, carbonyl insertion takes place at the stage of the anion radical species **13** or its one-electron reduced and protonated species **15** to give acyl chromate complex **16**.[10] The resulting acyl chromate complex

Scheme 5



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(4) When ethyl acrylate was added after the treatment of carbene complex **1a** with samarium diiodide, *trans*-stilbene **2** was obtained in about 60% yield. This indicates that the anion radical species **5** is short-lived.

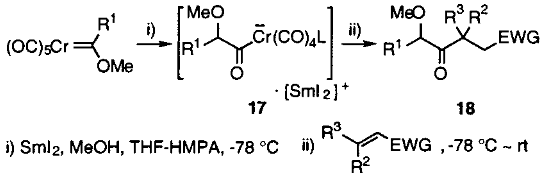
(5) When the tungsten butyl carbene complex and ethyl acrylate were treated in the same manner as for the phenyl carbene complex, no reaction took place at −78 °C. When the mixture was slowly warmed to rt, reduction of ethyl acrylate took place while the carbene complex remained intact.

(6) Generation of *trans*-stilbene **2** from the tungsten benzylidene complex is described in the following paper: Fischer, H.; Zeuner, S.; Ackermann, K. *J. Chem. Soc., Chem. Commun.* **1984**, 684.

16 undergoes 1,4-addition to the electron-deficient olefin to give ketone **12**.[11]

The reaction was further examined by employing several chromium alkyl carbene complexes (Scheme 6, Table 2).

Scheme 6



Although one-electron reduction of the alkyl carbene complexes did not proceed with samarium diiodide alone, the samarium diiodide−HMPA complex was found to reduce them at −78 °C.[12] As summarized in Table 2, the reaction of *n*-butyl, *s*-butyl, and methyl carbene complexes with various electron-deficient olefins proceeded to give the corresponding addition products in moderate to good yields.

Söderberg et al. reported that acyl(pentacarbonyl)−chromate complexes react with electron-deficient olefins in a 1,4-manner under thermal (refluxing in THF) or photochemical conditions.[11] It is believed that liberation of one carbonyl ligand from the complex is necessary for olefin coordination. On the other hand, our reaction proceeded between −78 °C and rt. This is probably due to the facile coordination of electron-deficient olefins to chromium enabled by carbonyl insertion generating a coordinatively unsaturated species.

Table 2. 1,4-Addition of Acyl Chromate Complexes to Electron-Deficient Olefins

R^1	EWG	R^2	R^3	**18**/% (diastereomer ratio)[a]
n-Bu	CO$_2$Et	H	H	85
n-Bu	CN	H	H	69
n-Bu	CO$_2$Me	H	Me	46 (81:19)
n-Bu	C(O)(CH$_2$)$_2$ (cyclopentenone)		H	51 (50:50)
n-Bu	CO$_2$Me	H	CO$_2$Me	61 (53:47)
s-Bu	CO$_2$Et	H	H	65 (55:45)
s-Bu	CN	H	H	56 (56:44)
Me	CO$_2$(CH$_2$)$_2$Ph	H	H	55

[a] Determined by integration of ^{1}H NMR. Relative stereochemistry was not determined.

In summary, the Fischer-type carbene complexes of group 6 metals were reduced with samarium(II) diiodide to give two types of reactive species depending on the metal center of the carbene complexes. In the case of the aryl tungsten complexes, an anion radical species was generated by one electron-reduction, and this underwent radical addition to an electron-deficient olefin. In the case of the chromium complexes, carbonyl insertion took place within the reduced species to give acyl chromate complexes, which underwent 1,4-addition to electron-deficient olefins.

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Supporting Information Available: General procedures for the samarium(II)-mediated reactions and the spectroscopic data of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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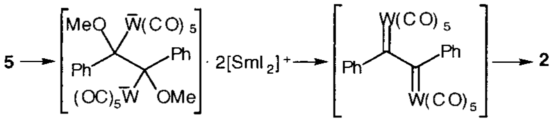
[7] It is also possible that dimerization of anion radical species **5** occurs first, and that subsequent elimination of a methoxy samarium species gives dinuclear carbene complex **19**. One-electron reduction of each carbene moiety followed by protonation could give *trans*-stilbene **2**.



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[8] When methanol-d_4 was employed, the position α to the methoxy group of **3** was 79% deuterated.

[9] When methanol-d_4 was employed, the position α to the phenyl group of **4** was not deuterated. However, when the reaction was quenched with D_2O, the position was 76% and 70% deuterated for the *E*- and *Z*- isomers, respectively. These results suggest that **10** was not protonated by methanol in the reaction mixture.

[10] (a) Lee, I.; Cooper, N. J. *J. Am. Chem. Soc.* **1993**, *115*, 4389. (b) Rudler, H.: Parlier, A.; D.-Réville, T.; M.-Vaca, B.; Audouin, M.; Garrier, E.; Certal, V.; Vaissermann, J. *Tetrahedron* **2000**, *56*, 5001.

[11] (a) Söderberg, B. C.; York, D. C.; Hoye, T. R.; Rehberg, G. M.; Suriano, J. A. *Organometallics* **1994**, *13*, 4501. (b) Söderberg, B. C.; York, D. C.; Harriston, E. A.; Caprara, H. J.; Flurry, A. H. *Organometallics* **1995**, *14*, 3712. See also: (c) Barluenga, J.; Rodríguez, F.; Fanãnás, F. J. *Chem. Eur. J.* **2000**, *6*, 1930. (d) Sakurai, H.; Narasaka, K. *Chem. Lett.* **1994**, 2017, and ref 10b.

[12] A total of 2.8 equiv of HMPA based on samarium diiodide was employed. Use of more or less HMPA resulted in a decrease of the yields of the products. Concerning the effect of HMPA, see: Inanaga, J.; Ishikawa, M.; Yamaguchi, M. *Chem. Lett.* **1987**, 1485. Shabangi, M.; Flowers, R. A., II. *Tetrahedron Lett.* **1997**, *38*, 1137.