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Electron Transfer Driven Reactions of Transition Metal π-Complexes: Hydrogenation of Styrene-$Cr(CO)_3$ Derivatives by Samarium(II)iodide in the Presence of Water

Hans-Günther Schmalz*, Stephan Siegel and Dirk Bernicke

Institut für Organische Chemie der Technischen Universität, Straße des 17. Juni 135, D-10623 Berlin, Germany

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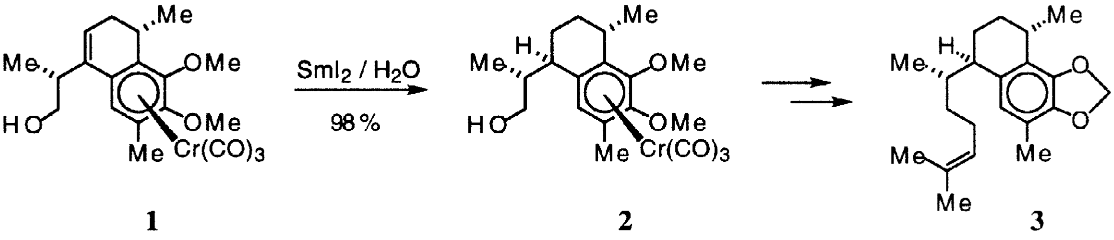
Abstract: The hydrogenation of the double bond of styrene-$Cr(CO)_3$ and some dihydronaphthalene-$Cr(CO)_3$ derivatives is achieved using samarium(II)iodide in the presence of water. 1,2-Dihydronaphthalene complexes carrying olefinic side chains in 4-position are reduced with virtually complete regio- and diastereocontrol leading to 1-*endo*-substituted tetralin complexes. The reactions seem to proceed via $Cr(CO)_3$ complexed benzylic radicals which are trapped by electron transfer to give the corresponding Cr-stabilized benzylic anions. © 1998 Elsevier Science Ltd. All rights reserved.

As part of our program on the use of chiral arene-$Cr(CO)_3$ complexes[1] as synthetic building blocks,[2] we recently achieved the diastereoselective conversion of the dihydronaphthalene complex **1** to the tetralin-$Cr(CO)_3$ derivative **2** in high yield employing samarium(II)iodide in the presence of water (Scheme 1).[3] This transformation, which represents a crucial step in the enantioselective total syntheses[3] of the bioactive sponge metabolites pseudopterosin A, *seco*-pseudopterosin A and helioporin D (**3**),[4] could not be achieved under normal catalytic hydrogenation conditions, possibly because of the strong steric hindrance of the triply substituted double bond in **1**.



Scheme 1

The idea to use SmI_2 for the conversion of **1** to **2** was based on our recent finding[5] that benzylic radicals, formed by (intramolecular) radical addition to styrene-$Cr(CO)_3$ derivatives, can be trapped with SmI_2 to give anionic intermediates ($Cr(CO)_3$-complexed benzylic anions) which are then protonated (see mechanism shown in Scheme 2). This reaction type is basically different to transformations involving SmI_2 generated ketyl- or aza-ketyl radicals in benzylic position of arene chromium complexes.[6] We here disclose new experiments which demonstrate the scope of the SmI_2 mediated hydrogenation of styrene-$Cr(CO)_3$ derivatives in a more general fashion.

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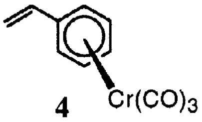
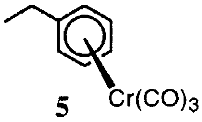
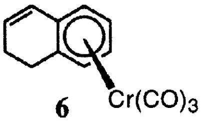
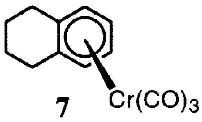
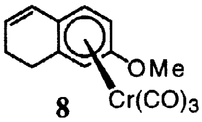
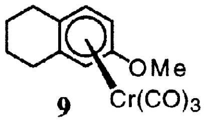
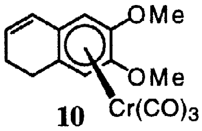
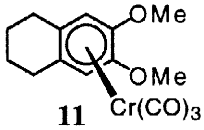
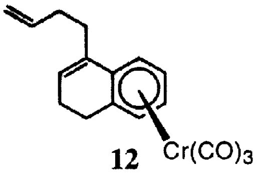
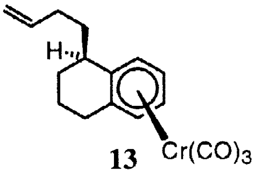
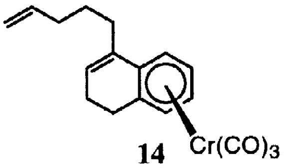
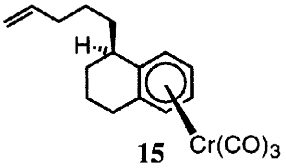
In addition to the parent styrene complex **4**, several dihydronaphthalene-$Cr(CO)_3$ complexes were investigated (see Table 1). Complexes *rac*-**6**, *rac*-**8** and *rac*-**10** were prepared from the corresponding racemic 1-tetralone-$Cr(CO)_3$ complexes[7] by reduction ($NaBH_4$) and subsequent elimination of water (p-TsOH/ SiO_2). In addition, complexes *rac*-**12** and *rac*-**14** were obtained from 1-tetralone-$Cr(CO)_3$ by introducing the olefinic side chain via the corresponding cerium organic reagent[8] followed by regioselective elimination of water.[5] The reduction experiments were performed under (optimized) standard conditions by adding a THF solution of the starting complex to an excess of SmI_2 in THF (freshly prepared solution) in the presence of HMPA and water.[9] The results of the various experiments are summarized in Table 1.

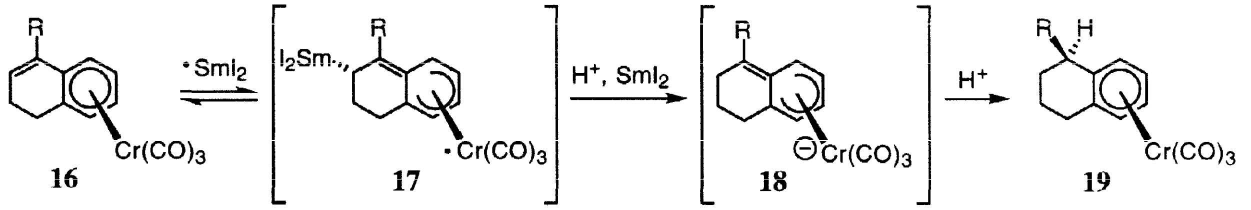
Table 1: Results of the hydrogenation experiments.

Entry	Starting Material[a)]	Product[b)]	Yield (%)[c)]
1	 **4**	 **5**	68
2	 **6**	 **7**	97
3	 **8**	 **9**	50[d)]
4	 **10**	 **11**	94
5	 **12**	 **13**	94
6	 **14**	 **15**	93

a) All chiral starting materials were employed as racemic mixtures; b) all products were fully characterized by spectroscopic methods; c) yields refer to isolated compounds after chromatographic purification; d) in this case, an inseparable 1:1 mixture of *rac*-**8** and *rac*-**9** was obtained in high yield.

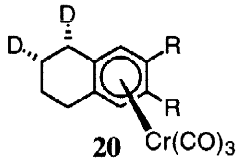
As Table 1 indicates, the reactions worked well with a variety of different substrates. In most cases, the hydrogenated product was obtained in essentially pure form. It proved to be important to use water as the *in situ* proton source. When water was replaced by *t*-butanol the reactions did not go to completion. In this case, substrate *rac*-**10**, for instance, only afforded a 1:1 mixture of *rac*-**10** and *rac*-**11**. It is important to note that in the case of substrates *rac*-**12** and *rac*-**14** the conjugated double bond was regioselectively hydrogenated without the double bond in the side chain being effected. Only the *endo*-configurated products *rac*-**13**[10] and *rac*-**15**,[11] respectively, were obtained and no by-products resulting from radical cyclization could be observed. The method seems not to be suitable for substrates carrying two substituents at the β-position of the double bond, as all attempts to reduce a 3-methyl-1,2-dihydronaphthalene complex failed.

A possible mechanism for these reactions is proposed in Scheme 2. In the first step, we assume SmI_2 adds (possibly reversible via a SET mechanism) across the electron deficient benzylic double bond[12,13] of the substrate (**16**) from the *exo*-face leading to a radical anion which is best represented through the resonance structure **17** (formally a 17 VE species).[14] This intermediate would then be converted to an anionic 18 VE complex of type **18** by single electron transfer (SET) and protonation. It is likely that the protonation preceeds the SET step, because the conversion is better in the presence of water as a stronger proton source. In the final step, **18** is trapped by benzylic protonation from the less hindered (*exo*) face to afford diastereoselectively an *endo*-substituted product of type **19**.



Scheme 2

Further evidence for this mechanism comes from the reduction of substrates *rac*-**6** and *rac*-**10** with SmI_2 in the presence of D_2O which afforded *cis*-dideuterated complexes of type *rac*-**20** in high yield.[15]



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In conclusion, we have demonstrated that the use of SmI_2 in the presence of water represents a mild and preparative attractive method for the regio- und stereoselective hydrogenation of a variety of styrene-$Cr(CO)_3$ derivatives. These transformations can be viewed as examples for *electron transfer driven transformations* involving the conversion of a 17 VE intermediate to a more favorable 18 VE species by single electron reduction.

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REFERENCES AND NOTES

1. For reviews on the use of arene-$Cr(CO)_3$ chemistry in synthesis, see, for instance: a) Hegedus, L.S. *Transition Metals in the Synthesis of Complex Organic Molecules*, University Science Books, Mill Valley, **1994**, chapter 10; b) Semmelhack, M.F. in *Comprehensive Organometallic Chemistry II, Vol. 12*, Abel, E.W.; Stone, F.G.A.; Wilkinson, G., Eds.; Pergamon: Oxford, 1995, pp. 979-1015; c) Semmelhack, M.F.,

ibid., pp. 1017-1038; d) Davies, S.G.; McCarthy, T.D.; *ibid.* pp. 1039-1070.

2. For some recent publications in this series, see: a) Majdalani, A.; Schmalz, H.-G. *Tetrahedron Lett.* **1997**, *38*, 4548; b) Geller, T; Schmalz, H.-G.; Bats, J. W. *Tetrahedron Lett.* **1998**, *39*, 1537; c) Schellhaas, K.; Schmalz, H.-G.; Bats, J. W. *Chem. Eur. J.* **1998**, *4*, 57; e) see ref. 3.
3. Majdalani, A.; Schmalz, H.-G. *Synlett* **1997**, 1303.
4. Geller, T.; Jakupovic, J.; Schmalz, H.-G. *Tetrahedron Lett.* **1998**, *39*, 1541.
5. Schmalz, H.-G.; Siegel, S.; Bats, J.W. *Angew. Chem.* **1995**, *107*, 2597; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2383.
6. a) Taniguchi, N.; Kaneta, N.; Uemura, M. *J. Org. Chem.* **1996**, *61*, 6088; b) Taniguchi, N.; Uemura, M. *Synlett* **1997**, 51; c) Taniguchi, N.; Uemura, M. *Tetrahedron Lett.* **1997**, *38*, 7199; d) Merlic, C. A.; Walsh, J. C. *Tetrahedron Lett.* **1998**, *39*, 2083; for earlier examples of reactions which (possibly) involve $Cr(CO)_3$ complexed benzylic radicals, see: e) Top, S.; Jaouen, G. *J. Organomet. Chem.* **1987**, *336*, 143; f) Kirss, R. U.; Treichel, P. M.; Haller, K. J. *Organometallics* **1987**, *6*, 242; g) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1989**, *54*, 2904.
7. For an efficient enantioselective route to 1-tetralone-$Cr(CO)_3$ derivatives, see: Schmalz, H.-G.; Millies, B.; Bats, J.W.; Dürner, G. *Angew. Chem.* **1992**, *104*, 640; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 631.
8. For the use of cerium organyls as nucleophiles, see: a) Imamoto, T. *Pure & Appl. Chem.* **1990**, *62*, 747 and ref. cited therein; b) see also ref. 5.
9. General procedure: An argon flushed Schlenk flask was charged with 10 ml of a solution of SmI_2 (0.1 M in THF), 1.5 ml of HMPA and 50 μl of water. The deep violet mixture was cooled to 0 °C and a solution of 0.4 mmol of the starting chromium complex in 5 ml of THF was added over 30 min under stirring. After 1.5 h at 0 °C 3 ml of water were added to the still violet reaction mixture under argon and the resulting brownish suspension was transferred into a separating funnel containing 2N HCl and EtOAc (30 ml each). The organic layer was washed with 2N HCl, saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by preparatory radial chromatography (EtOAc/hexane) to give the product as a yellow solid.
10. Data for *rac*-**13**: M.p.: 63 °C; IR (ATR): 3077, 2943, 2863, 1952, 1864, 1458, 1430 (cm^{-1}); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.52-1.73 (m, 3 H), 1.76-1.94 (m, 3 H), 2.10 (m, 1 H), 2.31 (m, 1 H), 2.54 (m, 1 H), 2.63 (m, 2 H), 5.02 (d, 1 H, J = 6.5 Hz), 5.03 (d, 1 H, J = 10 Hz), 5.07 (ψt, 1 H, J = 6.5 Hz), 5.10 (dd, 1 H, J = 17 Hz, 1.5 Hz), 5.45 (ψt, 1 H, J = 6.5 Hz), 5.51 (d, 1 H, J = 6.5 Hz), 5.8 - 5.92 (ddd, 1 H, J = 17 Hz, 10 Hz, 6.5 Hz); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 19.5 (t), 26.3 (t), 29.0 (t), 31.6 (t), 34.8 (d), 35.8 (t), 88.5 (d), 90.3 (d), 95.0 (d), 95.4 (d), 113.1 (s), 114.1 (s), 115.2 (t), 137.9 (d), 234.0 (s).
11. Data for *rac*-**15**: M.p.: 47 °C; IR (ATR): 3075, 2939, 2861, 1953, 1866, 1459, 1430 (cm^{-1}): ^1H NMR (400 MHz, $CDCl_3$): δ = 1.48-1.70 (m, 4 H), 1.74-1.90 (m, 4 H), 2.13 (m, 2 H), 2.50 (m, 1 H), 2.63 (m, 2 H), 5.01 (m, 3 H), 5.07 (dd, 1 H, J = 6.5 Hz, 1 Hz), 5.45 (dd, 1 H, J = 6.5 Hz, 1 Hz), 5.51 (d, 1 H, J = 6.5 Hz), 5.85 (m, 1 H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 19.5 (t), 26.3 (t), 26.9 (t), 29.0 (t), 33.5 (t), 35.5 (d), 36.3 (t), 88.5 (d), 90.2 (d), 94.9 (d), 95.5 (d), 113.1 (s), 114.3 (s), 114.8 (t), 138.4 (d), 234.1 (s).
12. For nucleophilic additions to styrene-$Cr(CO)_3$ derivatives, see: a) Semmelhack, M.F.; Seufert, W.; Keller, L. *J. Am. Chem. Soc.* **1980**, *102*, 6584; b) Uemura, M.; Minami, T.; Hayashi, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 1193; c) see also ref. 1b and references cited therein.
13. For a related reduction of α,β-unsaturated esters and ketones, see: Y. Fujita, S. Fukuzumi, J. Otera, *Tetrahedron Lett.* **1997**, *38*, 2121.
14. For the structural and energetical characterization of such reactive intermediates using density functional calculations, see: Pfletschinger, A.; Dargel, T. K.; Schmalz, H.-G.; Koch, W.; manuscript submitted.
15. We thank Dr. J. Jakupovic for his help with the stereochemical assignment of **20** by NMR spectroscopy.