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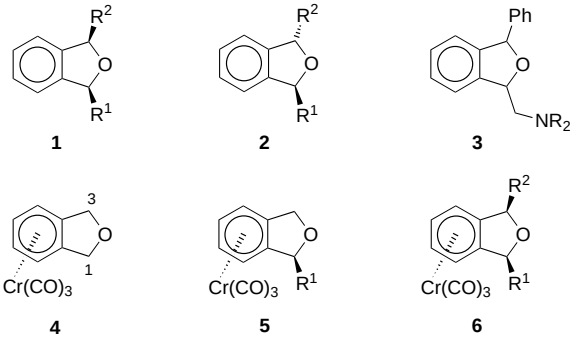
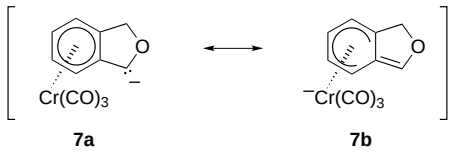
Benzylic *endo*-Alkylation of Phthalan – $Cr(CO)_3$ Complexes via Temporary Silylation: An Entry to *trans*-1,3-Disubstituted Dihydroisobenzofurans**

Saskia Zemolka, Johann Lex, and Hans-Günther Schmalz*

Substituted 1,3-dihydroisobenzofurans (phthalans) represent an interesting class of compounds owing to their promising pharmacological potential,[1] but they have received only little attention from synthetic chemists in the past.[2] In particular, almost no general methods are available for the stereoselective synthesis of *cis*- or *trans*-1,3-disubstituted derivatives of type **1** and **2**, respectively.[3] With regard to the usefulness of such compounds as intermediates for the synthesis of bioactive oxonanes[4] and the established biological activity of compounds of type **3**,[5] the search for efficient stereoselective entries to 1,3-disubstituted phthalans remains a challenging task.



In 1989, Davies and co-workers reported the preparation of a few *cis*-configured compounds of type **1** (R^1, R^2 = Me, D) starting from the [phthalan – $Cr(CO)_3$] complex **4**.[6] In two successive benzylic deprotonation/alkylation steps, **4** can be transformed (via *rac*-**5**) into bis-*exo*-alkylated complexes of type **6**, from which the free ligands **1** are easily obtained by oxidative decomplexation.[6] The method exploits both the ability of the $Cr(CO)_3$ fragment to stabilize a negative charge in the benzylic position[7] and the strong steric effect of the metal fragment (shielding of the *endo* face).[7b, 8] The stabilization of the anionic intermediate **7a** derived from **4** by benzylic deprotonation can be understood in terms of the resonance structure **7b** in which the charge is delocalized to the $Cr(CO)_3$ unit (Scheme 1).[9]



Scheme 1. Resonance structures of the benzylic anion derived from **4**.

In the course of our research on the application of chiral arene – $Cr(CO)_3$ complexes in the stereoselective synthesis of bioactive compounds,[10] we were interested in using the silylated complex **8** as a building block for the synthesis of new 1,3-disubstituted phthalans. Compound **8** was selected since it is easily prepared, even in the optically active form,[11] from the parent complex **4**. Herein we disclose the results of a study which has led to the discovery of some unexpected, remarkably selective transformations and to the development of an efficient and completely stereoselective route to 1-*endo*-alkylated complexes and to *trans*-1,3-disubstituted phthalans.

When complex *rac*-**8** was treated with *t*BuLi at low temperatures (– 100 to – 78 °C) followed by quenching of the resulting anion with different electrophiles, we were surprised to find that the 1,1-disubstituted products (*rac*-**11**) were formed with complete regio- and diastereoselectivity (Table 1). Evidently, the deprotonation of *rac*-**8** does not, as

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[+] X-ray crystallographic analysis.

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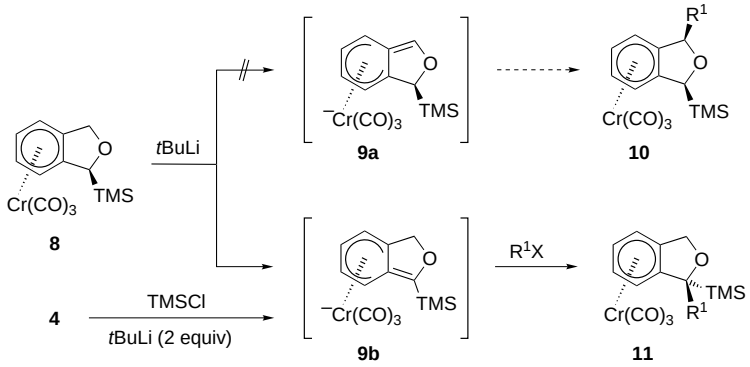
Table 1. Preparation of 1,1-disubstituted complexes of type *rac*-**11** according to Scheme 2.

Starting material	Electrophile (R^1X)	Method[a]	Product	R^1	Yield [%][b]
rac-**8**	MeI	A	*rac*-**11a**	Me	76
rac-**8**	allyl bromide	A	*rac*-**11b**	allyl	80
rac-**8**	*n*BuI	A	*rac*-**11c**	*n*Bu	83
rac-**8**	TMSCl	A	*rac*-**11d**	TMS	72
rac-**8**	$TBSOC_5H_{10}I$	A	*rac*-**11e**	$TBSOC_5H_{10}$	54
rac-**8**	BnOCOCl	A	*rac*-**11f**	CO_2Bn	57
4	MeI	B	*rac*-**11a**	Me	96
4	allyl bromide	B	*rac*-**11b**	allyl	99
4	*n*BuI	B	*rac*-**11c**	*n*Bu	78
4	H_2O	B	*rac*-**11g**	H	96
4	MeOD	B	*rac*-**11h**	D	83

[a] Method A: *rac*-**8**, THF, *t*BuLi (1.1 equiv), $-100 \rightarrow -78\,^\circ C$, 1 h, then R^1X (2.5–5 equiv), $-78 \rightarrow -45\,^\circ C$, 1–5 h (TLC control), then H_2O quench and extractive workup; method B: **4**, THF, TMSCl (1.01 equiv), $-100\,^\circ C$, then *t*BuLi (2.2 equiv), 2 h, $-100 \rightarrow -78\,^\circ C$, then R^1X (3 equiv), $-78 \rightarrow -50\,^\circ C$, 1–3.5 h (TLC control). [b] Yield of isolated product after

originally anticipated (see below), lead to the intermediate *rac*-**9a** (Scheme 2). Instead, the isomeric benzylic anion *rac*-**9b** is generated, which is subsequently alkylated by the



Scheme 2. Unexpected formation of 1,1-disubstituted complexes of type **11** by deprotonation/alkylation of **8**. For details see Table 1.

electrophile (R^1X) from the unhindered *exo* face. Thus, the bulky TMS group ends up in the *endo* position with respect to the $Cr(CO)_3$ fragment, as found in the X-ray crystal structures of **11a** and *rac*-**11d** (Figure 1).[12]

Starting from **4**, the preparation of 1,1-disubstituted complexes of type *rac*-**11** could also be carried out in an efficient one-pot procedure (Scheme 2): treatment of a solution of **4**

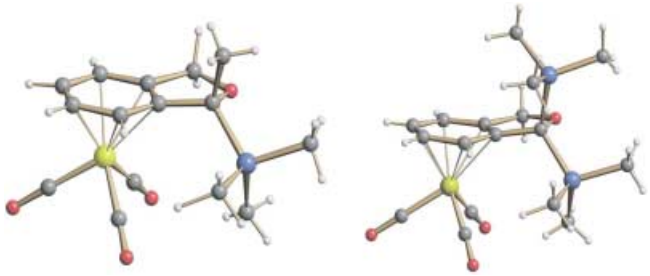
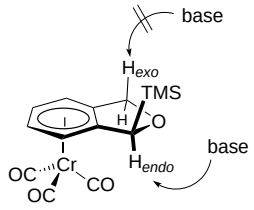


Figure 1. Structure of **11a** (left) and *rac*-**11d** (right) in the crystalline state.[12]

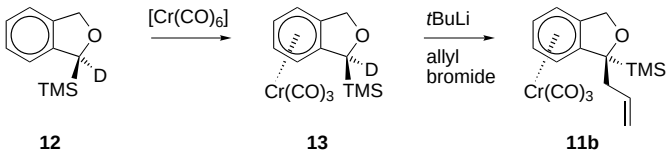
and TMSCl (1 equiv) in THF with *t*BuLi (2 equiv) at low temperatures (-100 to $-78\,^\circ C$) under in situ quench (ISQ) conditions[11, 13] directly afforded a deep red solution of the benzylic anion (*rac*-**9b**), which could be quenched (as before) with different electrophiles to give the products usually even in better yields than in the former two-step procedure (Table 1).

The clean access to compounds of type **11** opened interesting perspectives for further transformations (see below). However, we were puzzled by the fact that deprotonation of **8** with *t*BuLi selectively affords the intermediate **9b**, even at $-100\,^\circ C$ (i.e. kinetic control). We had expected the isomeric species **9a** to be formed, anticipating the benzylic deprotonation of **8** to occur from the *exo* face.[14] Clearly, **9b** is thermodynamically more stable than **9a** as a result of the α-silyl effect.[15] The question was whether an *endo* deprotonation had occurred at the highly hindered silylated position of **8** (H_{endo} at C1) or if **9b** was possibly formed by rearrangement of **9a** generated by a "standard" *exo* deprotonation at the unhindered opposite benzylic position (H_{exo} at C3) (Schemes 2 and 3).



Scheme 3. Deprotonation (3-*exo* versus 1-*endo*) of complex **8**.

To distinguish between these two possibilities, we decided to employ the deuterated derivative *rac*-**13** (*rac*-[D_1]**8**) in a deprotonation/alkylation sequence. Compound *rac*-**13** was prepared by diastereoselective complexation ([$Cr(CO)_6$], nBu_2O/THF, reflux) of *rac*-**12**,[16] which in turn was obtained from *rac*-**11h** by oxidative decomplexation. When *rac*-**13** was deprotonated with *t*BuLi at $-78\,^\circ C$ and the resulting anion was quenched with allyl bromide, the completely dedeuterated product *rac*-**11b** was isolated in 69% yield (Scheme 4).[17] This result clearly demonstrates that, in contrast to established arene–$Cr(CO)_3$ chemistry,



Scheme 4. Proof of the 1-*endo*-deprotonation of **8** by using the deuterated derivative **13**. The experiment was carried out with the racemic compounds. Reagents and conditions: step 1: [$Cr(CO)_6$] (1.08 equiv), nBu_2O/THF (10:1), $155\,^\circ C$, 27 h; step 2: *t*BuLi (1.1 equiv), THF, $-78\,^\circ C$, 2 h, then allyl bromide (2 equiv), 2 h.

the deprotonation of *rac*-**8** indeed proceeds from the *endo* face (at the silylated position). Most likely, the enhanced acidity at C1 as a result of the TMS substituent overcompensates the shielding of the *endo* face by the $Cr(CO)_3$ fragment in this specific case (Scheme 3).[18]

Desilylation of compounds of type *rac*-**11** with tetrabutylammonium fluoride (TBAF) in the presence of water furnished the monosubstituted complexes *rac*-**15** as pure *endo*

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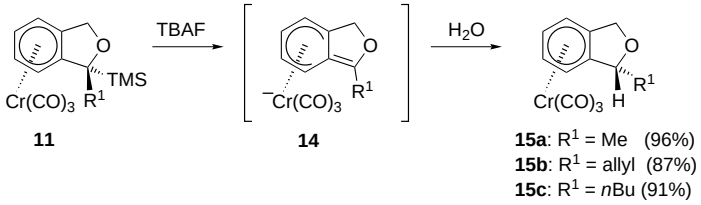
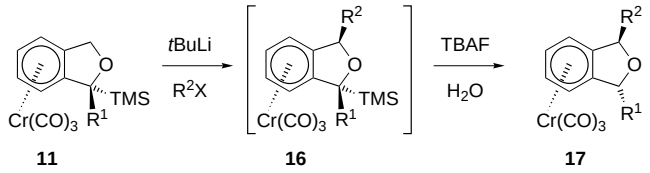
diastereomers in excellent yields through diastereoselective protonation of the intermediate anion *rac*-**14** from the *exo* face (Scheme 5).[19]



Scheme 5. Desilylation of complexes of type **11** leads to *endo*-alkylated products of type **15** through *exo* protonation of the intermediate **14**. Reagents and conditions: THF, H_2O, 0 °C, TBAF (3 equiv), 10 min, room temperature, 12 h.

The newly developed, unique entry to *endo*-alkylated products prompted us to investigate the possibility of utilizing the silylated complexes *rac*-**11** in the synthesis of *trans*-1,3-disubstituted phthalans. Indeed, after subjecting complexes of type *rac*-**11** to the typical deprotonation/alkylation conditions and direct desilylation of the intermediates *rac*-**16**, the *trans*-1,3-disubstituted complexes *rac*-**17** were obtained as pure diastereomers (Scheme 6, Table 2). The expected *trans* con-



Scheme 6. One-pot synthesis of *trans*-1,3-disubstituted phthalan complexes of type **17**. For details, see Table 2.

Table 2. Preparation of *trans*-1,3-disubstituted complexes of type *rac*-**17** according to Scheme 6.[a]

Starting material	Electrophile (R^2-X)	Product	R^1	R^2	Yield [%][b]
rac-**11a**	allyl bromide	*rac*-**17a**	Me	allyl	91
rac-**11a**	*n*BuI	*rac*-**17b**	Me	*n*Bu	76
rac-**11a**	BnBr	*rac*-**17c**	Me	Bn	72
rac-**11a**	MeSSMe	*rac*-**17d**	Me	S-Me	67
rac-**11a**	Et_2NCOCl	*rac*-**17e**	Me	$CONEt_2$	56
rac-**11a**	EtOCOCl	*rac*-**17f**	Me	CO_2Et	56[c]
rac-**11b**	*n*BuI	*rac*-**17g**	allyl	*n*Bu	50
rac-**11b**	MeI	*rac*-**17h**	allyl	Me	77
rac-**11c**	BnBr	*rac*-**17i**	*n*Bu	Bn	77

[a] THF, *t*BuLi (1.1 equiv), −78 °C, 2 h, then R^2X (2–4 equiv), −78 → −10 °C, 1 to 5 h (TLC control), then H_2O, room temperature, 0 °C, then TBAF (1.5–7.5 equiv), room temperature, 12 h; extractive workup. [b] Yield of isolated product after chromatographic purification. [c] Inverse addition: the anion was added at −78 °C to R^2X in THF, then 2 h, −78 °C.

figuration of the products was unequivocally proven by means of X-ray crystallographic analysis in the cases of *rac*-**17b** and *rac*-**17f** (Figure 2)[12] and NMR spectroscopic correlations.

To demonstrate the applicability of the developed methodology in the preparation of nonracemic compounds, the chirogenic step (i.e. the deprotonation of the prochiral complex **4**) was performed enantioselectively[11] by using the

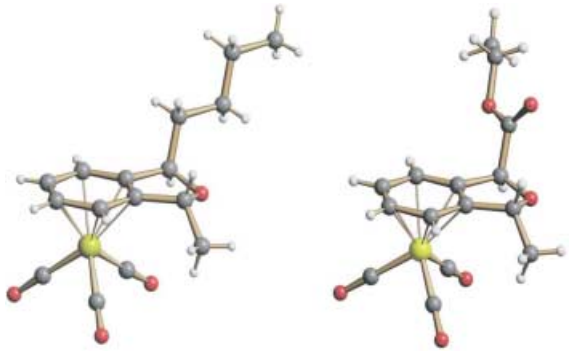
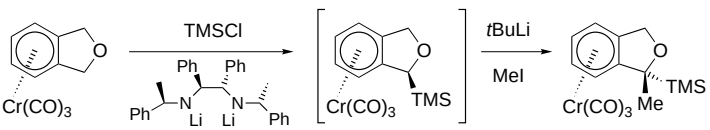


Figure 2. Structure of *rac*-**17b** (left) and *rac*-**17f** (right) in the crystalline state.[12]

chiral amide base **18**.[20] Therefore, **4** was treated with **18** (1 equiv) in the presence of TMSCl (ISQ conditions) at −100 °C, and the intermediate **8** (formed in situ) was directly converted by deprotonation with *t*BuLi and an electrophilic quench (MeI) into complex **11a**[12] with >99 % *ee* (HPLC) in 75 % yield (Scheme 7, Figure 1).[21] By combining the transformations shown in Scheme 7 (**4** → **11**) and Scheme 6 (**11** → **17**) the diastereo- and enantioselective synthesis of *trans*-1,3-disubstituted phthalan complexes can be carried out through a short and efficient sequence of two one-pot procedures.



Scheme 7. One-pot, enantioselective synthesis of **11a**. Reagents and conditions: TMSCl (1.01 equiv), **18** (1.08 equiv), THF, −100 °C, then slow addition of **4** in THF, −95 → −85 °C, 45 min., then *t*BuLi (2.3 equiv), −78 °C, 1 h, MeI (5 equiv), 1 h.

In conclusion, we have succeeded in elaborating a general, practical, and fully stereoselective entry to *trans*-1,3-dialkylated dihydroisobenzofurans. The method exploits the remarkable and unexpected finding that the deprotonation of **8** occurs at the substituted benzylic position (from the *endo* face!). Our current investigations are aimed at the application of this method to the synthesis of more sophisticated systems related to bioactive natural products.

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[12] For details of the crystal structure analyses of compounds *rac*-**11d**, **11a**, *rac*-**17b**, and *rac*-**17f**, see Supporting Information. CCDC-179013 (*rac*-**11d**), CCDC-179014 (**11a**), CCDC-179015 (*rac*-**17b**), and CCDC-179016 (*rac*-**17f**) contain 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).
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[16] A diastereomeric mixture of *rac*-**13** and *rac*-**11h** (7.5:1) was formed, which was easily separated by chromatography.
[17] In this case, a by-product (19%) of type **10** was obtained which indicates a strong kinetic isotope effect (abstraction of D_{endo} at C1 *versus* H_{exo} at C3).
[18] A participation of the ring oxygen atom (as a coordinating site) in the *endo* deprotonation step is likely, as other benzylic silylated [arene–$Cr(CO)_3$] complexes do not exhibit such behavior; see, for example: J. Blagg, S. J. Coote, S. G. Davies, D. Middlemiss, A. Naylor, *J. Chem. Soc. Perkin Trans. 1* **1987**, 689.
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[21] The absolute configuration of **11a** was determined by X-ray crystal-structure analysis[12] and confirmed the expected results.[11b]

Chemically Tuning between Ferromagnetism and Antiferromagnetism by Combining Theory and Synthesis in Iron/Manganese Rhodium Borides**

Richard Dronskowski,* Karol Korczak, Heiko Lueken, and Walter Jung

Dedicated to Professor Welf Bronger on the occasion of his 70th birthday

Cooperative magnetic phenomena such as ferromagnetism and antiferromagnetism have not only made up an enormously rich synthetic and theoretical playground for generations of solid-state physicists and chemists,[1, 2] they also form the material basis of the most critical key technology of today's information society, namely data storage and data retrieval.[3, 4] Fortunately enough, within the last two decades modern high-level electronic-structure calculations of the density-functional type have proven to be able to reproduce a number of essential observables (e.g., magnetic moments) in many (inter)metallic magnets with satisfying accuracy, thereby offering a first step in an atomistic understanding of these magnetic properties. Only recently, however, has it been shown that a more chemically oriented theoretical framework, intended to offer semiquantitative signposts for the synthesis of new cooperative magnets, can be constructed simply by identifying bonding "fingerprints" which are characteristic for either metallic ferromagnets or antiferromagnets.[5, 6]

When a nonmagnetic ("spin-restricted") band-structure calculation is performed on a typical ferromagnet such as bcc-Fe, a crystal orbital Hamilton population (COHP) bonding analysis yields *antibonding* Fe–Fe interactions at the Fermi level (Figure 1, top left), which indicates an electronic instability. Upon spontaneous spin polarization ("spin-unrestricted" calculation), bcc-Fe undergoes a distortion, but instead of the atoms the electrons rearrange themselves.[7] Thus, spontaneous magnetization makes the spin-up (α) and spin-down (β) electrons inequivalent, thereby reducing the electronic symmetry, which annihilates the antibonding states and, consequently, lowering the overall energy and the bonding energy by a few percent (Figure 1, top right).[5, 6] For antiferromagnetism, things are a little bit more subtle. A corresponding nonmagnetic band-structure calculation on a typical antiferromagnet such as bcc-Cr results in the Fermi level being positioned exactly between the bonding and

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