Iron-Mediated Allylic Substitution Reactions with Chirality Transfer. Stereochemistry of the Formation of Diastereo- and Enantiomerically Enriched Olefinic and Allylic Tetracarbonyl Iron Complexes

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(*E*)-Configurated allylic ligands (*S*)-**6a**−**f** and (*S*)-**8**, bearing a leaving group at C(3) (allylic position) and an electron acceptor substituent at C(1), were synthesized from enantiopure (*S*)-ethyl lactate [(*S*)-**1**]. Complexation with $Fe_2(CO)_9$ (**13**) afforded diastereomeric mixtures of their (η^2-alkene)tetracarbonyliron(0) complexes **14a′**/**a″**−**f′**/**f″** (acceptor group, *Acc* = SO_2-Ph) and **15′**/**″** (*Acc* = CO_2Me) (48% − quant.; de < 3−70%), each diastereomer in enantiopure form (*Note: descriptors ′ and ″ denote major and minor diastereomer*). Synthetically useful results were obtained for allylic ligands bearing a benzylic protecting group [(*S*)-**6a** and (*S*)-**8**] and using hexane or diethyl ether as solvent (**14a′**/**a″**: quant., de = 70%; **15′**/**″**: 75−88%, de = 10−16%). Complexes **14a′**/**a″** were fractionally crystallized, and their molecular structures were determined by X-ray diffraction, allowing for an assignment of the absolute configurations of complexes **14a′**/**a″**−**f′**/**f″** and **15′**/**″**. "W"-shaped complexes **14a′**, **15″** (Ψ-*exo*-**14**,**15**) were expected to yield *syn*-Me,*syn*-*Acc*-configured and "S"-shaped complexes **14a″**, **15′** (Ψ-*endo*-**14**,**15**) accordingly *anti*-Me,*syn*-*Acc*-configured cationic complexes **18** and **19** upon treatment with HBF_4. Complex **14a′** (de = ee > 99%) reacted quantitatively to the *syn*-Me-substituted (η^3-allyl)tetracarbonyliron(1+) complex **18′** (*syn*-Me,*syn*-SO_2Ph-**18**) (*syn*-Me/*anti*-Me > 99:1, ee > 99%). Diastereomeric mixtures of complexes **14a′**/**a″** gave mixtures of complexes **18′**, **18″** (*anti*-Me,*syn*-SO_2Ph-**18**) and *ent*-**18″** (*ent*-*syn*-Me,*syn*-SO_2Ph-**18**). Conversion of complex **14a″** to **18″** or complex **18″** itself was subjected to an *anti*-Me → *syn*-Me isomerization process, yielding eventually a diastereomeric mixture of complexes **18″** and *ent*-**18″**, thus lowering the overall enantiomeric purity of *syn*-Me,*syn*-SO_2Ph-substituted complexes **18**. Conversion of a mixture of **15′**/**″** (de = 10%) to cationic complexes **19′**/**″** did not exhibit significant *anti*-Me → *syn*-Me isomerization (*syn*-Me:*anti*-Me = 1:1.19, *ee* > 96% for both diastereomers). Nucleophilic *anti*-addition of silyl enol ether **20** to complex **18′** or silyl ketene acetal **21** to a complex mixture **19′**/**″** afforded enantiopure alkenyl sulfone (*R*)-**23** or ester (*S*)-**24** (82% − quant., ee >96 to >99%). Addition to a complex mixture containing **18′**, **18″**, and *ent*-**18′** yielded **23**, albeit with lower enantiomeric purity (ee = 59−66%). The chirality transfer process of the iron-mediated allylic substitution proceeds with overall retention (double inversion) of stereochemistry with respect to the stereogenic center of the starting materials, conservation of (*E*)-double bond geometry, and complete γ-regioselectivity for the nucleophilic addition reactions. Differences of configurative stability of the *anti*-configured Me groups in the cationic π-allyl complexes **18″** and **19′** were found requiring appropriate consideration if used in stereocontrolled organic synthesis.

Introduction

Among the various carbon−carbon and carbon−heteroatom bond forming reactions catalyzed or promoted by transition metals,[1−3] π-allyl transition metal complexes have been recognized as versatile allylating reagents in organic synthesis, with η^3-allyl complexes of palladium being the most frequently and intensively studied species.[4] Other important transition metal η^3-allyl complexes include Ni,[5] Ru,[6] Rh,[7] Ir,[8] Mo,[9] W,[10] Cu,[11] Mn,[12] Pt,[13] Fe,[14] Co,[15] or Re atoms.[16] Generally, η^3-allyl transition metal complexes can function as

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either electrophilic or nucleophilic allylating agents, depending on the properties of the transition metal and the coordinated ligand.

Cationic metal π-complexes of polyenic ligands have received considerable attention as useful carbocation equivalents stabilized by coordination to a transition metal−ligand moiety and which possess an enhanced reactivity toward a multitude of carbon and heteroatom nucleophiles.[17] Nucleophilic addition reactions are generally subject to complete stereocontrol by the metal−ligand fragment, while regiochemical outcomes are most often controlled by substitution pattern, the nature of substituents, or both. Transition metal π-complexes of unsymmetrically substituted ligands in which an achiral metal−ligand fragment distinguishes the two enantiotopic faces of a ligand possess planar chirality.[18] In their enantiomerically pure form they are of significance as valuable building blocks for the regio- and stereocontrolled synthesis of organic target molecules. Organoiron complexes are often employed stoichiometrically and frequently display excellent regio- and stereocontrol. In particular, (chiral) ferrocenyl, (η^4-diene)tricarbonyliron(0), or (η^5-cyclohexadienyl)tricarbonyliron(1+) complexes have become useful reagents with widespread use in organic synthesis.[19]

Nucleophilic attack by soft carbon and heteroatom nucleophiles to alkyl- or aryl-substituted cationic tetracarbonyl(η^3-allyl)iron complexes occurs regioselectively at a less and/or at a *syn*-substituted allyl terminus.[20]

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Our group,[21] and groups of Green,[22] Speckamp,[23] and Jackson,[24] demonstrated that nucleophilic addition to cationic tetracarbonyl(η^3-allyl)iron complexes substituted with electron-withdrawing functionalities on the allyl moiety such as SO_2Ph, CO_2R, and $CONR_2$ groups proceeds with complete γ-regioselectivity with respect to the electron acceptor group.

In addition, Nakanishi and co-workers reported the synthesis of nonracemic, electron acceptor substituted, neutral dicarbonylnitrosyl(η^3-allyl)iron complexes useful in regio- and enantioselective allylic amination reactions.[25] The utility of Ley's (π-allyl)tricarbonyliron lactone and lactame complexes, respectively, for 1,5 or 1,7 remote asymmetric induction has been illustrated extensively in recent years.[26]

Our efforts to develop a synthetically useful iron-mediated allylic substitution methodology for the synthesis of highly enantiomerically enriched organic compounds led to the development of several concepts.[27] As the most versatile concept, the "chirality transfer" or "self-reproduction of chirality" approach involves diastereoselective complexations of enantiopure (*E*)-configured acceptor-substituted olefins to yield diastereomerically enriched (η^2-alkene)$Fe(CO)_4$(0) complexes (Figure 1).[28,29] The corresponding planar chiral (η^3-allyl)-$Fe(CO)_4$(1+) complexes can be obtained in virtually diastereo- and enantiomerically pure form. They represent synthetic equivalents of chiral a^4-synthons **A**, which are useful for "Umpolung" (reversed reactivity) of classical d^4-chemistry.[30] Nucleophilic addition and subsequent demetalation leads to the corresponding allylic substitution products. The overall stereochemical outcome of the "chirality transfer" process was unambiguously verified by the synthesis of various natural products in their absolute configurations[21d−f,i] and by X-ray determination of the molecular structure of some addition products.[31]

In this article we wish to disclose a comprehensive synthetic, mechanistic, and stereochemical study to elucidate the stereochemistry of the formation of diastereo- and enantiomerically enriched olefinic and allylic tetracarbonyl iron complexes involved in our iron-mediated allylic substitution process with chirality transfer. The effect of various reaction parameters such as different leaving groups, solvent polarity, and temperature and their influence on the overall stereochemistry will be discussed. The determination of the molecular structure of various important intermediates will be presented. A proposal of how the chirality information is conserved and transferred in all of the different steps during formation and reaction of olefinic and allylic tetracarbonyl iron complexes based on the results obtained will be given.

Results and Discussion

Synthesis of Enantiopure (*E*)-Configured Acceptor-Substituted Alkenes 6 and 8. For our study, we focused on (*E*)-configured electron acceptor substituted alkene ligands of type (*S*)-**6**, which in turn were derived from (−)-(*S*)-ethyl lactate [(*S*)-**1**] as the enantiopure

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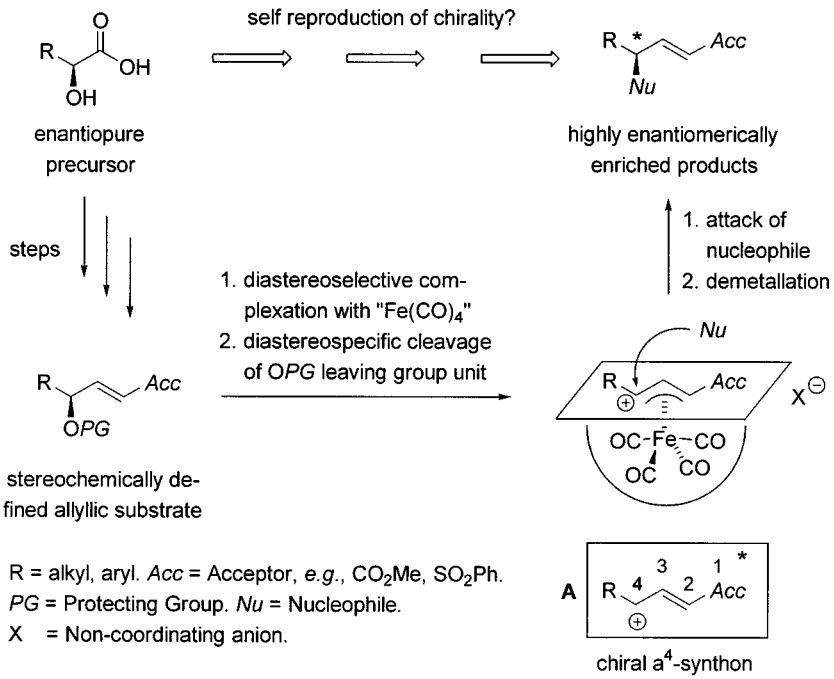

Figure 1. Principle of the "chirality transfer" or "self-reproduction of chirality" approach in our iron-mediated allylic substitution reaction. Diastereoselective complexation of enantiopure (*E*)-configured acceptor-substituted alkenes yields intermediate (η^2-alkene)tetracarbonyliron(0) complexes. The corresponding enantiomerically enriched planar chiral (η^3-allyl) tetracarbonyliron(1+) complexes react in a regio- and face selective fashion with various nucleophiles to highly enantiomerically enriched allylic substitution products of defined stereochemistry. The entire reaction cycle is supposed to proceed with overall conservation of chirality information from central to planar back to central chirality.

chiral precursor (Schemes 1a−c) (*Acc* = SO_2Ph, CO_2-Me). Ester (*S*)-**1** was converted in good yields (66−95%) into the *O*-protected ethyl lactate derivatives (*S*)-**3a**−**c** following appropriate standard OH group protection protocols (Scheme 1a).[32] (For specific reagents, conditions, and yields see captions of Scheme 1.) The bulky 2-(methylene)naphthalene protecting group was introduced in a two-step procedure via the amide (*S*)-**2**,[32b] followed by standard Williamson etherification of (*S*)-**2** to give the *O*-protected amide (*S*)-**3d** (Scheme 1a).

The *O*-protected α-hydroxy esters (*S*)-**3a**−**c** were reduced with DIBAH to yield the corresponding aldehydes (*S*)-**4a**−**c** (89−98%) (Scheme 1a). Amide (*S*)-**3d** gave after reduction with Red-Al aldehyde (*S*)-**4d** (58%) (Scheme 1a).[32b] The enantiomeric excesses of the aldehydes (*S*)-**4a**−**d** were indirectly determined by ^{1}H NMR and ^{13}C NMR spectroscopy after conversion to their corresponding diastereomerically pure SAMP-hydrazones with the chiral enantiopure auxiliary SAMP [(−)-(*S*)-1-amino-2-methoxymethyl)pyrrolidine].[33] Comparison with appropriate epimeric mixtures of SAMP-hydrazones from racemic aldehydes *rac*-**4a**−**d** showed that both the *O*-protection and the reduction steps proceeded virtually without racemization [(*S*)-**4a**−**d**: ee > 98%]. Aldehydes (*S*)-**4a**−**d** were subjected to a modified Horner−Wadsworth−Emmons olefination procedure with the phenylsulfonyl-substituted phosphonate **5** to yield alkenes (*S*)-**6a**−**d** (72−90%) (Scheme 1a).[34,35] The methoxycarbonyl-substituted alkene (*S*)-**8** was obtained from aldehyde (*S*)-**4a** with methyl diethylphosphonoacetate (**7**) (86%).[34,36,37] Acidic cleavage of the TBDMS protecting group of compound (*S*)-**6c** yielded alkenyl sulfone (*S*)-**6e** in quantitative yield.[32a,38] Acylation of compound (*S*)-**6e** to (*S*)-**6f** (49%) was performed under standard conditions (Scheme 1c).[32a,39] The ^{1}H NMR spectra of purified compounds (*S*)-**6a**−**f** and (*S*)-**8** displayed typical coupling constants $^3J_{trans}$ of ca. 15 Hz. The enantiomeric excesses of compounds (*S*)-**6a**−**f** and (*S*)-**8** were determined by HPLC employing chiral stationary phases. Comparison of racemic material *rac*-**6a**−**f** and *rac*-**8** with compounds (*S*)-**6a**−**f** and (*S*)-**8** showed that no significant racemization occurred [(*S*)-**6a**−**f**, (*S*)-**8**: ee > 99%].

Tetracarbonyl(η^2-alkene)iron(0) Complexes: Stereochemical Considerations. Previous results from Speckamp et al. showed that a uniform configuration of the carbon atom bearing the leaving group (and the nature of the *N*-protecting group) was essential for controlling the absolute stereochemistry and the result-

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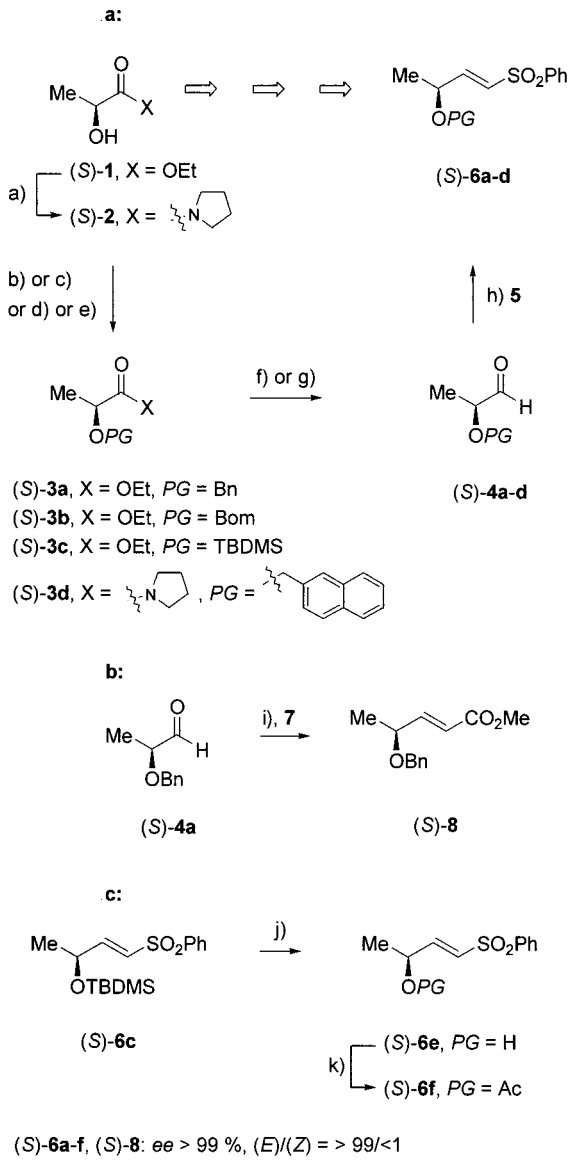
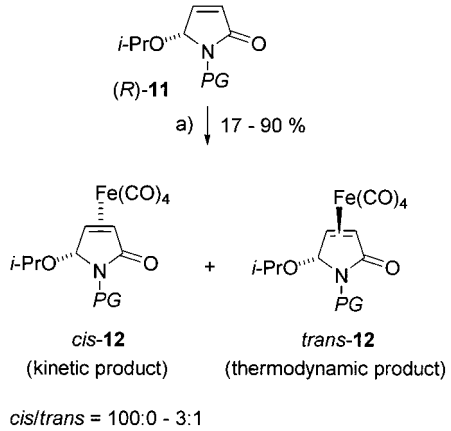
Scheme 1. Synthesis of the Alkenes (*S*)-6a−f and (*S*)-8[a]



[a] Reagents and conditions: (a) 1.0 equiv of (*S*)-**1**, 1.3 equiv of pyrrolidine, neat, room temp, 3 days (84%); (b) 1.0 equiv of (*S*)-**1**, 2.0 equiv of $Cl_3C(C{=}NH)OBn$, cat. TfOH, cyclohexane/CH_2Cl_2 (7:1), room temp, 5 days (95%); (c) 1.0 equiv of (*S*)-**1**, 1.25 equiv of BomCl, 1.5 equiv of *i*-Pr_2EtN, CH_2Cl_2, 0 °C to room temp, 16 h (78%); (d) 1.0 equiv of (*S*)-**1**, 1.2 equiv of TBDMSCl, 1.5 equiv of imidazole, DMF, 0 °C to room temp, 6 h (87%); (e) 1.0 equiv of (*S*)-**2**, 1.1 equiv of NaH (3 × washed with *n*-hexane), 1.1 equiv of 2-(bromomethyl)naphthalene, THF/DMF (3:1), 0 °C to room temp, 12 h (79%); (f) 1.0 equiv of (S)-**3a-c**, 1.4 equiv of DIBAH in hexane, Et_2O, −78 °C, 2 h, then H^+ (89−98%); (g) 1.0 equiv of (*S*)-**3d**, 0.6 equiv of Red-Al, toluene, −10 °C, 2 h, then H^+ (58%); (h) 1.0 equiv of (*S*)-**3a**−**d**, 1.0 equiv of $(EtO)_2(P{=}O)CH_2SO_2Ph$ (**5**), 1.2 equiv of LiBr, 1.1 equiv of Et_3N, acetonitrile, 0 °C to room temp, 12 h (72−90%); (i) 1.0 equiv of (*S*)-**3a**, 1.0 equiv of $(EtO)_2(P{=}O)CH_2CO_2Me$ (**7**), 1.2 equiv of LiBr, 1.1 equiv of Et_3N, acetonitrile, 0 °C to room temp, 12 h (86%); (j) 1.0 equiv of (*S*)-**6c**, 3% HCl in MeOH, 50 °C, 4 h (quant.); (k) 1.0 equiv of (*S*)-**6e**, 2.0 equiv of AcCl, 2.0 equiv of Et_3N, cat. DMAP, CH_2Cl_2, room temp 12 h (49%). Abbreviations: *PG*: protecting group, TfOH: trifluoromethane sulfonic acid (F_3CSO_3H), BomCl: benzyl chloromethyl ether ($BnOCH_2Cl$), TBDMSCl: *tert*-butyldimethylsilyl chloride (*t*-$BuMe_2SiCl$), DIBAH: diisobutylaluminum hydride (*i*-Bu_2AlH), Red-Al: sodium bis(2-methoxyethoxy)aluminum hydride {$Na[Al(OCH_2CH_2OMe)_2H_2]$}, DMAP: 4-*N*,*N*-(dimethylamino)pyridine.

Scheme 2. Synthesis of Tetracarbonyliron(0) *N*-Protected-5-(*R*)-isopropoxy-3-pyrrolin-2-ones *cis*-12 and *trans*-12[23] [a]



[a] Reagents and conditions: (a) 2.0 equiv of $[Fe_2(CO)_9]$ (**13**), benzene, or Et_2O, room temp, 18 h.

ing diastereomeric ratio during the complexation of *N*-protected 5-(*R*)-isopropoxy-3-pyrrolin-2-ones (*R*)-**11** to give tetracarbonyl(η^2-alkene)iron(0) complexes *cis*- and *trans*-**12** (Scheme 2).[23]

We hypothesized first that the leaving group unit (O*PG*) in ligands (*S*)-**6a**−**f** and (*S*)-**8** may effectively differentiate the diastereotopic half rooms defined by the plane through the double bond, and, second, that it controls as well the approach of the coordinatively unsaturated $Fe(CO)_4$ moiety through a precoordination mode (Figure 2).[21] Complexation of unsymmetrically substituted olefins of type (*S*)-**6a**−**f** and (*S*)-**8** bearing a stereogenic center at the allylic position results in the formation of a mixture of diastereomers **A** and **B** in which the metal−ligand fragment distinguishes between the two diastereotopic faces defined through the plane of the olefinic bond. It can be proposed that steric hindrance of both the leaving group unit and the iron tetracarbonyl fragment in **B** results in a favored conformation of the single bond and leads to the less strained conformer **C** (Figure 2). The structure of the backbone of structure **A**, counting from the acceptor functionality to the terminal methyl group, can be regarded as "W"-shaped, whereas the same fragment in **C** can be regarded as "S"-shaped (S ≡ sickle). According to a nomenclature introduced by Lillya et al. for related tricarbonyl(η^4-diene)iron(0) complexes, diastereomer **A** can be assigned the Ψ-*exo* isomer (leaving group unit directed *exo* or *anti* relative to the tetracarbonyliron moiety, structure **D**) and diastereomer **C** is assigned the Ψ-*endo* isomer (leaving group unit directed *endo* or *syn* relative to the tetracarbonyliron moiety, structure **E**).[40] Regarding the metal fragment−carbon double bond binding mode as a "ferracyclopropane" substructure (structures **F** and **G**), the newly generated stereogenic centers (indicated with *) are in an inverted stereochemical relationship to each other, although **F** and **G** possess still identical stereochemistry at the allylic position. C(1) denotes the α-carbon atom of the complexed double bond next to the acceptor functionality, C(2) the β-position, and C(3) the carbinol atom in the γ-position.

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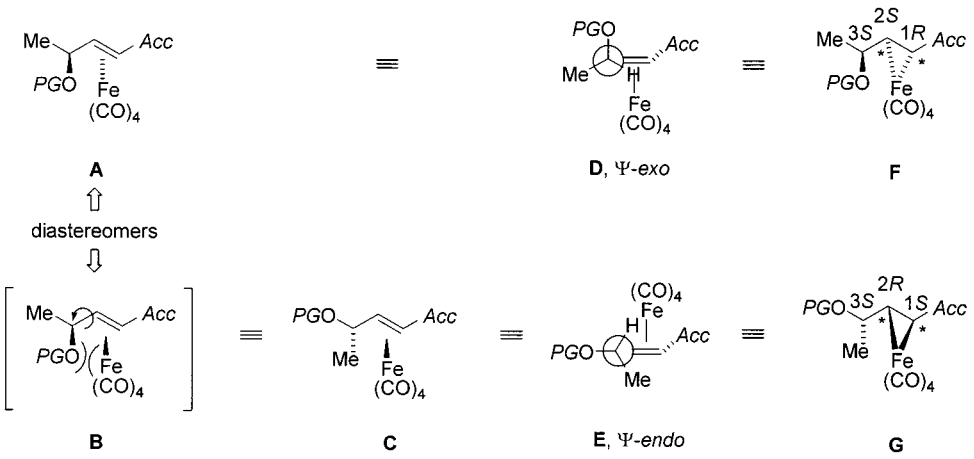
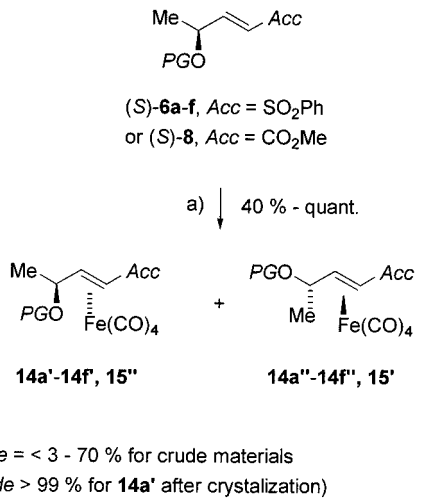


Figure 2. Working hypothesis: Complexation of the double bond of (*E*)-configured alkenes of type (*S*)-**6a**−**f**/(*S*)-**8** by an $Fe(CO)_4$ unit leads to the formation of two possible diastereomers (structures **A** and **B**). Structure **C** presents a less strained conformer of structure **B**. A Newman projection of the diastereomeric complexes (structures **D** and **E**) allows a relative stereochemical assignment according to Lillya's Ψ-*exo*/Ψ-*endo* nomenclature.[40] A partial "ferracyclopropane structure" (structures **F** and **G**) allows designation of absolute stereochemical descriptors. C(1) designates the α-carbon atom next to the acceptor functionality, and C(2) the *β*-position (see text for details). Cahn−Ingold−Prelog (CIP) priority: *Acc* > C(1) > C(2). Abbreviations: *Acc*: acceptor group.

Scheme 3. Synthesis of (η^2-Alkene)tetracarbonyliron(0) Complexes 14a−f and 15[a]



[a] Reagents and conditions: (a) 1.3 equiv of $[Fe_2(CO)_9]$ (**13**), solvent, room temp, 3 h to 3 days, CO atmosphere, exclusion of light.

Synthesis of Tetracarbonyl(η^2-alkene)iron(0) Complexes 14 and 15. Anticipating that various factors such as the nature of the leaving group moiety (O*PG* = leaving group) and the reaction conditions strongly govern the diastereoselectivity of the complexation reaction, we hoped to find a synthetically useful set of reaction conditions to achieve highly diastereoselective complexation. Adapting a protocol developed by Nicholas et al.,[20r] reaction of alkenes (*S*)-**6a**−**f** and (*S*)-**8** with a slight excess of nonacarbonyldiiron (**13**) $[Fe_2(CO)_9]$ in diethyl ether under an atmosphere of carbon monoxide led to a gradual disappearance of the insoluble $Fe_2(CO)_9$ (**13**) and yielded the corresponding diastereomeric tetracarbonyl(η^2-alkene)iron(0) complexes **14a′/a″**−**14f′/f″** and **15′/15″** (Scheme 3, Table 1, entries 1−7).[41,42] The reaction was stopped when the suspended reactants were almost dissolved to form a clear solution and only small amounts of decomposition products of $Fe_2(CO)_9$. Successive filtration through a pad of sand, Celite, and a micropore sized PTFE-filter (PTFE = poly(tetrafluoroethylene)) yielded the crude complexes **14a′/a″**−**14f′/f″** and **15′/15″** as bright yellow to orange oils or solids in almost quantitative yield as mixtures of diastereomers (for complexes **14a′/a″**−**14f′/f″**: de = 15−70%; for complexes **15′/″**: de = 12−16%). While diastereomeric complexes **14a**,**e**−**f** (Table 1, entries 1, 5, and 6) were obtained in NMR spectroscopically pure form, complexes **14b**−**d** were subjected to chromatographic purification on silica gel (collection of the yellow bands) (Table 1, entries 2−4). This was accompanied by partial decomposition of the products (Table 1, entries 2−4) and a slight enrichment of the major diastereomer (Table 1, entry 3). Conversion of alkene (*S*)-**8** to its diastereomeric mixture of complexes **15′** and **15″** was incomplete in numerous cases. A range of 12−23% of unreacted (*S*)-**8** was always detected in the isolated crude product (Table 1, entries 7 and 13).

The influence of polarity and coordination ability of the solvent and the temperature on the diastereoselectivity of the complexation of ligand (*S*)-**6a** to complexes **14a′/a″** and (*S*)-**8** to **15′/″** was examined next (Table 1, entries 8−13). Reaction in unpolar solvents such as *n*-hexane or pentane proceeded slowly in favor of the major diastereomer **14a′** (quant. conversion, de = 40−70%). The diastereomeric excess of **14a′** was significantly improved by fractional crystallization from *n*-hexane/diethyl ether mixtures at −22 °C (de = ee >95 to >99%) (Table 1, entries 8 and 9). The conversion of (*S*)-**8** to complexes **15** could not be improved (Table 1, entry 7 vs 13). More polar (CH_2Cl_2, THF) or aromatic (toluene) solvents seemed to accelerate the reaction (clear solution after ca. 3 h), but conversions of (*S*)-**6a** to complexes **14a′/a″** were incomplete (34−69% unreacted starting material), and only moderate diastereomeric excesses were obtained (de = <3−39%) (Table 1,

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Table 1. Complexation of the Alkenes (*S*)-6a−f and (*S*)-8 to Their Corresponding Diastereomeric (η^2-Alkene)tetracarbonyliron(0) Complexes 14a′/a″−14f′/f″ and 15′/″

entry	leaving group	complexation of ligands (*S*)-**6**/(*S*)-**8**	solvent	conditions	yield [%]	de [%]
1	OBn	**6a** → **14a′/a″**	Et_2O	rt, 16 h	>90[a] (40−58)[b]	25−57[c] (>95)[d]
2	OBom	**6b** → **14b′/b″**	Et_2O	rt, 16 h	(72)[e]	(18)[f]
3	OTBDMS	**6c** → **14c′/c″**	Et_2O	rt, 16 h	(90)[e]	(15−16)[f]
4	$OCH_2C_{10}H_7$	**6d** → **14d′/d″**	Et_2O	rt, 16 h	(48)[e]	(45)[f]
5	OH	**6e** → **14e′/e″**	Et_2O	rt, 16 h	quant.[a]	35[c]
6	OAc	**6f** → **14f′/f″**	Et_2O	rt, 16 h	93−98[a] (62)[c]	22−26[c]
7	OBn	**8** → **15′/15″**	Et_2O	rt, 16 h	77−88[g]	12−16[c]
8	OBn	**6a** → **14a′/a″**	hexane	rt, 3 days	> 90[a] (40−64)[b]	40−70[c] (>99)[d]
9	OBn	**6a** → **14a′/a″**	pentane	rt, 3 days	(67),[b] (46)[h]	(>99)[d]
10	OBn	**6a** → **14a′/a″**	THF	rt, 3 h	*i,j*	23[c]
11	OBn	**6a** → **14a′/a″**	CH_2Cl_2	rt, 3 h	*i,k*	3
12	OBn	**6a** → **14a′/a″**	toluene	rt, 16 h	*i,l*	39
13	OBn	**8** → **15′/15″**	hexane	rt, 3 days	75[m]	12
14	OBn	**6a** → **14a′/a″**	Et_2O	0 °C, 2 days	*n*	
15	OBn	**6a** → **14a′/a″**	Et_2O	reflux, 3 h	*i,o*	
16	OBn	**6a** → **14a′/a″**	THF	reflux, 3 h	*i,o*	

[a] Yield of the isolated crude, ^{1}H NMR spectroscopically pure product. [b] In parentheses, yield after fractional crystallization from *n*-hexane/Et_2O mixtures. [c] Diasteroisomeric excess of the crude product determined by ^{1}H NMR spectroscopy (300 MHz, C_6D_6). [d] In parentheses, diastereomeric excess determined after fractional crystallization from *n*-hexane/Et_2O mixtures by ^{1}H NMR spectroscopy (500 MHz, C_6D_6). [e] In parentheses, yield after purification by column chromatography on silica gel determined by ^{1}H NMR spectroscopy (300 MHz, C_6D_6). [f] In parentheses, diastereomeric excess after purification by column chromatography on silica gel. [g] 12−23% of unconverted starting material (*S*)-**8** as determined by ^{1}H NMR spectroscopy (300 MHz, C_6D_6). [h] Isolated yield after second fractional crystallization. [i] Yield not determined. [j] 34% of unconverted starting material (*S*)-**6a** as determined by ^{1}H NMR spectroscopy (300 MHz, C_6D_6). [k] 58−69% of unconverted starting material (*S*)-**6a** as determined by ^{1}H NMR spectroscopy (300 MHz, C_6D_6). [l] 42% of unconverted starting material (*S*)-**6a** as determined by ^{1}H NMR spectroscopy (300 MHz, C_6D_6). [m] 25% of unconverted starting material (*S*)-**8** as determined by ^{1}H NMR spectroscopy (300 MHz, C_6D_6). [n] No reaction. [o] Decomposition of $Fe_2(CO)_9$.

entries 10−12). At 0 °C in diethyl ether, (*S*)-**6a** did not react to give $Fe_2(CO)_9$ to give complexes **14a′/a″** (Table 1, entry 14). At higher reaction temperatures, either in refluxing diethyl ether or THF, the generation of side products such as dodecacarbonyltriiron [$Fe_3(CO)_{12}$] was generally observed, besides low diastereoselectivities (de < 20%) (Table 1, entries 15 and 16). Hence, although complexation of (*S*)-**6a** in *n*-hexane or pentane to give complexes **14a′** and **14a″** was subject to long reaction times and some fluctuation with respect to diastereomeric excess of the crude materials (de = 40−70%) obtained, highly diastereo- and enantiomerically enriched material **14a′** (de = ee >95−99%) was obtained routinely in 40−64% isolated yield after crystallization, thus demonstrating this method to be synthetically useful.

Determination of Diastereomeric Excesses and Spectroscopic Properties of Tetracarbonyl(η^2-alkene)iron(0) Complexes 14a−f and 15. Complexation of ligands (*S*)-**6a**−**f** and (*S*)-**8** resulted in every case in diastereomeric mixtures of tetracarbonyl(η^2-alkene)-iron(0) complexes **14a′**−**f′** and **14a″**−**f″** and **15′** and **15″** (Table 1, Figures 3a−c). (*Note: The descriptor ′ denotes in all cases the major diastereomer, the descriptor ″ the minor diastereomer*). Diastereomeric excesses were determined by ^{1}H and ^{13}C NMR spectroscopy. Among several other suitable proton NMR resonances, either of the allylic scaffold or of the acceptor groups, the doublet signal of the methyl group in complex mixtures **14a**−**f** and **15** proved to be a particularly valuable "NMR spectroscopical indicator". All major diastereomers **14a′**−**f′** exhibited a significantly downfield shifted doublet resonance signal in comparison to the minor diastereomers **14a″**−**f″** (Figure 3a and Figure 3b). In contrast, the major diastereomer **15′** showed an upfield shifted methyl resonance (Figure 3c).

Best diastereomeric excesses were obtained for complexation of ligand (*S*)-**6a**, bearing the OBn leaving group unit, in *n*-hexane, pentane, or diethyl ether to give complexes **14a′/a″** (de = 40−70% for repeated trials) (Table 1, entries 1, 8, and 9). All other leaving group combinations (O*PG*) for complexes **14b′/b″**−**f′/f″** were inferior with respect to both control of diastereoselectivity (de = 15−45%) and practical ease (e.g., synthesis of starting materials) (Table 1, entries 2−6, 10−12). The modest diastereoselectivity and the complexation of (*S*)-**8** to complexes **15′/″** could not be improved and furnished mixtures of diastereomeric complexes **15′** and **15″** in every case (average de ∼12%, conversion of (*S*)-**8** ca. 77−88%) (Table 1, entries 7 and 13).

IR spectroscopic analysis of complexes **14a**−**f** and **15** displayed up to four Fe−CO valence vibrations in the range of ν = 1990−2100 cm^{-1} with the most energetic absorption at ν = ca. 2100 cm^{-1}, which can be assigned to an axially bound CO group. These results indicate clearly that compounds **14a**−**f** and **15** are monomeric and, generally, the $Fe(CO)_4L$ fragments of **14a**−**f** and **15** have a trigonal bipyramidal structure where the olefinic ligands lie in an equatorial position. Mass spectroscopic analysis of complexes **14a**−**f** and **15** displayed a distinct fragmentation pattern due to successive loss of CO ligands [$M^{\bullet+} - (CO)_n$ (n = 1−4)] with a high relative intensity for the fragment $M^{\bullet+} - (CO)_4$, which degenerates further either by loss of the protecting group unit (*PG*) or by β-elimination of a HO*PG* moiety.

NMR spectroscopic studies (^{1}H−^{13}C HETCOR) of complexes **14a**−**f** and **15** revealed the expected high-field shift of the "olefinic" hydrogen and carbon atoms upon complexation. This reflects a partial change in the hybridization state of the "olefinic" carbon atoms (sp^2 → sp^3) causing an elongation of the C=C bond distance and a change from double bond to single bond character. The $^3J_{trans}$ coupling constants for the AB system (Hα)−(Hβ) of the complexed olefinic bond are decreased from ca. 15 Hz in alkenes (*S*)-**6a**−**f** and (*S*)-**8** to 10−11 Hz in

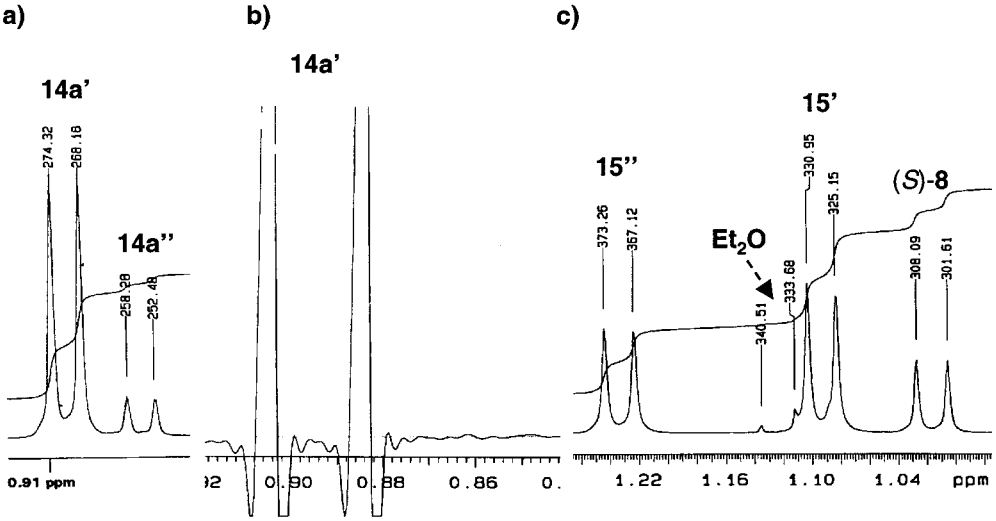

Figure 3. (a) ^{1}H NMR doublet signals of the CH_3 group connected to the carbon C(3) of a mixture of diastereomeric complexes **14a′** and **14a″** (300 MHz, C_6D_6, de = 74%). (b) ^{1}H NMR doublet signal of the CH_3 group of a diastereo- and enantiopure sample of complex **14a′** (500 MHz, C_6D_6, de = ee > 99%). (c) ^{1}H NMR doublet signals of the CH_3 group connected to the C(3) carbon of a mixture of starting material (*S*)-**8** and diastereomeric complexes **15′** and **15″** (300 MHz, C_6D_6, de = 16%). (*Note: The descriptor ′ denotes the major diastereomer, and the descriptor ″ the minor diastereomer.*)

Table 2. NMR Spectroscopic Details of Uncomplexed Ligands (*S*)-6a/(*S*)-8 and Their Corresponding (η^2-Alkene)tetracarbonyliron(0) Complexes 14a′/14a″ and 15′/15″

entry	compound	δ(Hα) [ppm]	δ(Hβ) [ppm]	$^3J_{trans}$ [Hz]	δ(Cα) [ppm]	δ(Cβ) [ppm]
1	(*S*)-**6a**[a]	6.52	6.94	14.8	131.21	147.09
2	**14a′**[b]	3.86	3.29	10.3	66.71	57.96
3	**14a″**[b]	3.76	3.30	10.4	65.52	59.23
4	(*S*)-**8**[c]	6.03	6.89	15.8	120.85	149.51
5	**15′**[a]	4.20	3.85	11.0	66.29	42.95
6	**15″**[a]	4.12	3.80	10.9	63.92	44.78

[a] ^{1}H NMR spectra recorded in C_6D_6 at 300 MHz; ^{13}C NMR spectra recorded in C_6D_6 at 75 MHz. [b] ^{1}H NMR spectra recorded in C_6D_6 at 500 MHz; ^{13}C NMR spectra recorded in C_6D_6 at 125 MHz. [c] ^{1}H NMR spectra recorded in $CDCl_3$ at 500 MHz; ^{13}C NMR spectra recorded in $CDCl_3$ at 125 MHz.

complexes **14a**−**f** and **15**. A particularly characteristic feature is the upfield shift of the signals of the atoms at the β-position [≡C(2)] of the alkenyl systems relative to those at the α-position [≡C(1)] with respect to the acceptor group (SO_2Ph or CO_2Me) in comparison to the corresponding free alkenes (*S*)-**6a**−**f** and (*S*)-**8** (Table 2). For comparable cyclic tetracarbonyl(η^2-alkene)iron(0) complexes possessing naturally a (*Z*)-configured double bond this change is not observable.[23,43] The proton NMR spectroscopic observations are all in accordance with a partial "ferracyclopropane" substructure of the (η^2-alkene)$Fe(CO)_4$ unit, allowing assignment of absolute configurations of the stereogenic centers at the complexed "olefinic" carbon atoms according to the Cahn−Ingold−Prelog notation (vide supra).[44]

The CO ligands gave a single broad ^{13}C NMR resonance signal at δ ca. 207 ppm indicative of their rapid exchange by Berry pseudorotation. All NMR experiments established that the complexes show no tendency to epimerize in solution at room temperature. In contrast, we and Speckamp et al. described a slow isomerization of cyclic tetracarbonyl(η^2-alkene)iron(0) complexes in dichloromethane.[23,43]

Determination of the Molecular Structure of Complexes 14a′ and 14a″ and Assignment of the Absolute Configurations of Complexes 14a−f and 15. Only few sulfonyl-substituted tetracarbonyl(η^2-alkene)iron(0) complexes have been described in the literature so far.[45] Complex **14a′** was obtained by fractional crystallization from partly concentrated solutions (*n*-hexane/diethyl ether) at −22 °C in virtually diastereo- and enantiomerically pure form (de = ee > 99%) as pale yellow needles or plates (vide infra).[21g,42] The minor diastereomer **14a″** was obtained as well by repeated crystallization from concentrated mother liquors (light petroleum/diethyl ether) in virtually diastereo- and enantiomerically pure form (de > 99% by NMR) as pale yellow needles. The molecular structures of both complexes, **14a′** (major diastereomer) (Figure 4), and **14a″** (minor diastereomer) (Figure 5), were determined by X-ray crystallography.[21g,46] The molecular

(43) Enders, D.; Schmitz, T.; Raabe, G.; Krüger, C. *Acta Crystallogr.* **1991**, *C47*, 37.

(44) Helmchen, G. In *Methods of Organic Chemistry*; Houben-Weyl, 1995; Vol. E, p 21a. (b) Prelog, V.; Helmchen, G. *Angew. Chem.* **1982**, *94*, 614; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 567. (c) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem.* **1966**, *78*, 413.

(45) (a) Guilard, R.; Dusalisoy, Y. *J. Organomet. Chem.* **1979**, *77*, 393. (b) McCaskie, J. E.; Chang, P. L.; Nelson, T. R.; Dittmer, D. C. *J. Org. Chem.* **1973**, *38*, 3963. (c) Nesmeyanov, A. N.; Rybin, L. V.; Rybinskaya, M. I.; Gubenko, N. T.; Leshcheva, I. F.; Ustynyuk, Y. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1968**, *38*, 1428. (d) Ibbotson, A.; Reduto dos Reis, A. C.; Saberi, S. P.; Slawin, A. M. Z.; Thomas, S. E.; Tustin, G. J.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1251.

(46) Suitable crystals for the X-ray structure determination were obtained from diethyl ether/petroleum ether at 4 °C. $C_{21}H_{18}O_7SFe$, crystal dimensions ca. 0.4 × 0.4 × 0.2 mm, monoclinic, space group $P2_1(4)$, a = 6.503(2) Å, b = 7.209(3) Å, c = 23.091(6) Å, β = 93.40(1)°, V = 1080.6 Å^3, Z = 2, M_{calcd} = 470.28, ρ_{calcd} = 1.445 g cm^{-3}. Total

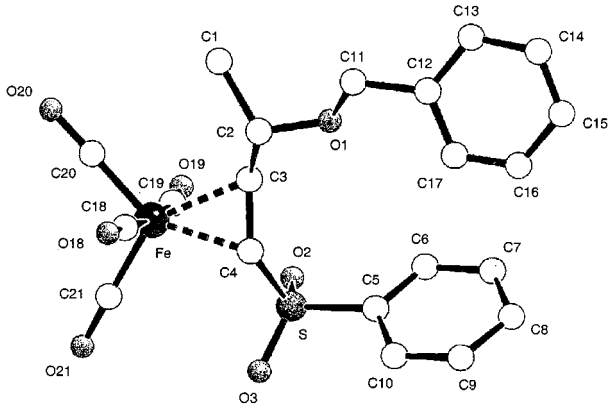

Figure 4. Molecular structure of the major diastereomer **14a′** (SCHAKAL representation).[48]

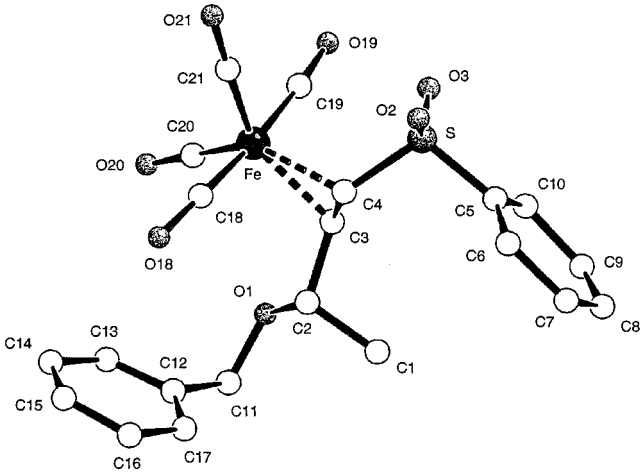

Figure 5. Molecular structure of the minor diastereomer **14a″** (SCHAKAL representation).[48]

structure of complex **14a′** was solved according to the Patterson method (SHELXS-86) and employing the Xtal3.2 program package for additional crystallographic calculations.[47] Some structural aspects concerning the stereochemistry of the ligands complexed in **14a′** and **14a″** and the conformation of their (carbon) backbones merit closer inspection (Figures 4 and 5).

(*Note: The atomic numbering scheme of Figure 4 and Figure 5 is different from the numbering scheme in Figure 2 (structures **F** and **G**). Carbon atom C(4) in Figure 4 or 5 corresponds to carbon atom C(1) in Figure 2, C(3) in Figure 4 or 5 corresponds to carbon atom C(2) in Figure 2, and C(2) in Figure 4 or 5 corresponds C(3) in Figure 2*).

The SO_2Ph unit of complex **14a′** is twisted away from the $Fe(CO)_4$ moiety (C(2)−C(3)−C(4)−S −137(1)°), and the terminal methyl group is slightly inclined toward the Fe atom (C(1)−C(2)−C(3)−C(4) −151(1)°) (Figure 4). The complexed ligand adopts a "W"-shaped geometry, counting from the terminal methyl group to the sulfur atom (Figure 2, structure **D** and Figure 4), demonstrating conservation of (*E*)-double bond geometry of the complexed ligand (*S*)-**6a**. As a result of the absolute configuration at the 3-position, the side of the double bond unit is selectively blocked by the $Fe(CO)_4$ moiety, which lies *trans* or *anti* with respect to the OBn leaving group.

Many attempts to isolate crystals of sufficient quality for a clean refinement of the structure of complex **14a″** met with failure. Only poorly diffracting samples could be obtained in this case, and consequently, the number of observed reflections was too low to allow anisotropic refinement of the solved structure. Although no detailed discussion of structural parameters is possible under these conditions, the isotropically refined structure not only proves the molecule's constitution but also gives a good impression of its absolute configuration (Figure 5).

The benzyloxy group, the phenylsulfonyl group, and the bulky tetracarbonyliron moiety are the most sterically demanding groups. Hence, these groups are arranged in a particular fashion whereby they are as far apart as possible from each other. In the minor diastereomer **14a″** the phenylsulfonyl unit and the terminal methyl group are twisted away from the $Fe(CO)_4$ moiety, resulting in an "S"-shaped geometry (S ≡ sickle) of the (carbon) skeleton (Figure 2, structure **C** and Figure 5). Here, the leaving group unit is now positioned in the plane defined by C(2)−C(3)−C(4). In general, all topological features and structural parameters correlate with experimental and analytical data found for related acceptor-substituted tetracarbonyl(η^2-alkene)iron complexes including a distorted trigonal bipyramidal geometry, an unsymmetrically coordinated double bond, and a perpendicular relation of the planes through C(3), C(4), Fe, C(20), and C(21) and the plane defined by atoms C(18), Fe, and C(19) (Figures 4 and 5).[21g,23,43,45,49]

The most significant differences between the diastereomers **14a′** and **14a″** are the different diastereotopicities of the double bond complexed and, therefore, the adoption of different conformations around the single bond between the double bond and the carbinol atom bearing the leaving group unit (O*PG*) (Figures 2, 4, and 5). In related cyclic systems the complexation seems kinetically to favor the sterically more hindered *cis* products (Ψ-*endo*, Figure 2).[23,43] Apparently, the observed *trans* selectivity (Ψ-*exo*, Figure 2) in the examples examined might be the result of thermodynamic equilibration.

*(Note: For the assignment of the absolute configuration of the coordinated carbon atoms of the complexes **14a′** and **14″** the atomic numbering scheme of Figure 2 is used).*

The crystallographic structure determination of complexes **14a′** and **14a″** and the NMR spectroscopic results clearly indicate the relative arrangement of the leaving group unit (O*PG*) bond on the carbinol atom C(3) and the $Fe(CO)_4$ moiety in complexes **14a**−**f** and **15**. This information allows as well for the designation of the absolute configuration of the newly generated stereogenic centers of the coordinated double bond of com-

number of electrons per unit cell $F(000) = 484$, Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator), $\mu = 8.26$ cm^{-1}, no absorption correction, Enraf-Nonius four-circle diffractometer, $\Omega/2\theta$ scans, 20 °C; 2670 independent reflections ($\pm h + k + l$), of which 1279 observed ($I > 2\sigma(I)$), $R_{av} = 0.07$, sin $\theta/\lambda_{max} = 0.649$. Structure solution according to Patterson methods (SHELXS-86), all other crystallographic calculations were carried out with the Xtal3.2 program package.[49] Positions of hydrogen atoms calculated; 270 refined parameters, $R = 0.068$, ($R_w = 0.073$), residual electron density −1.3/ +1.3 e Å^{-3}. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-58339.

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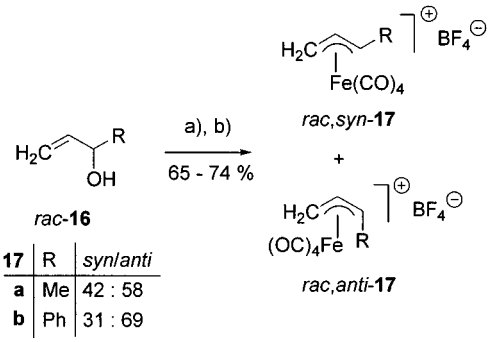
Scheme 4. Synthesis of Diastereomeric *Syn*- and *Anti*-Configured (η^3-Allyl)tetracarbonyliron(1+) Complexes 17 from Racemic Secondary Allylic Alcohols 16[20r] [a]



17	R	syn/anti
a	Me	42 : 58
b	Ph	31 : 69

[a] Reagents and conditions: (a) 1.0 equiv of $[Fe_2(CO)_9]$ (**13**), Et_2O, room temp, 10 h, CO atmosphere. [b] HBF_4 in HOAc/Ac_2O, room temp, 15 min.

plexes **14a**−**f** and **15** [at C(4) and C(3) in Figure 4 or Figure 5; C(1) and C(2) according to structures **F** and **G** in Figure 2]. In the major diastereomer **14a′** the absolute configuration of carbon atom C(1) can be assigned to be (*R*) according to the Cahn−Ingold−Prelog notation.[44] Since carbon atom C(2) is not independent from C(1) [(*R*)], its configuration must be consequently assigned to be (*S*). It is sufficient to assign only one stereochemical descriptor for the complexed double bond, e.g., **14a′** ≡ (1*R*,2*S*,3*S*)-**14a** ≡ (1*R*,3*S*)-**14a**. For the minor diastereomer, similar conclusions lead to the assignment (1*S*,2*R*,3*S*) [**14a″** ≡ (1*S*,2*R*,3*S*)-**14a** ≡ (1*S*,3*S*)-**14a**]. In analogy with these results, all major diastereomers **14a′**−**f′** possess the absolute configuration (1*R*,2*S*,3*S*), and consequently, all minor diastereomers **14a″**−**f″** possess the absolute configuration (1*S*,2*R*,3*S*). As a consequence of a lower ranking Cahn−Ingold−Prelog priority of the methoxycarbonyl functionality in complexes **15**, the major diastereomer **15′** possesses the absolute configuration (1*R*,2*S*,3*S*), showing that in this case the structure with the "S"-shaped backbone is slightly favored. The minor diastereomer **15″** possesses consequently the (1*S*,2*R*,3*S*)-configuration. According to Figure 2, complexes (1*R*,2*S*,3*S*)-**14a-f** (**14a′**−**f′**) and (1*S*,2*R*,3*S*)-**15** (**15″**) should conform with a Ψ-*exo*-**14a**−**f**, **15** assignment, while complexes (1*S*,2*R*,3*S*)-**14a**−**f** (**14a″**−**f″**) and (1*R*,2*S*,3*S*)-**15** (**15′**) should conform with an Ψ-*endo*-**14a**−**f**, **15** assignment.

Tetracarbonyl(η^3-allyl)iron(1+) Complexes: Stereochemical Considerations. It has been demonstrated that conversion of secondary allylic alcohols of type *rac*-**16** into their corresponding methyl- or phenyl-substituted tetracarbonyl(π-allyl)iron(1+) complexes **17** gave rise to diastereomeric mixtures of *syn*-R and *anti*-R isomers (Scheme 4).[20r] (*E*)-Configured alkenes gave stereospecifically *syn*-configured and (*Z*)-configured alkenes gave stereospecifically *anti*-configured (π-allyl)-tetracarbonyliron cation complexes. The formation of the intermediate tetracarbonyl(η^2-alkene)iron(0) complexes supposedly followed stereochemical pathways similar to those described in the previous sections.

We proposed an overall stereochemical scheme for the transformation of (η^2-alkene)tetracarbonyliron(0) complexes of type **14a**−**f** and **15** to their corresponding cationic (η^3-allyl)tetracarbonyliron(1+) complexes (Figure 6). Cleavage of the C−O bond of the O*PG* leaving group of structures **A** and **C** supposedly proceeds with formation of a new C−Fe bond and inversion of the absolute stereochemistry at C(3). Cleavage of the O*PG* group of the "W"-shaped complex **A** should result in the stereospecific generation of the *syn-Me,syn-Acc*-configured cationic complex **B**. Analogous treatment of complex **C** should yield a (η^3-allyl)tetracarbonyl species **D** with a *syn*-configured acceptor group and an *anti*-configured methyl group (*anti-Me,syn-Acc*). Therefore, diastereomeric structures **B** and **D** both possess the identical absolute configuration at carbon atom C(3). *Syn*-configured allyl complexes are thermodynamically more stable than the corresponding *anti*-configured complexes, and numerous (π-allyl)metal complexes especially those derived from palladium undergo rapid *anti* → *syn* isomerization processes *prior* to the nucleophilic attack.[50] Isomerization of the *anti*-Me-configured structure **D** to the *syn*-Me-configured complex may proceed via a $\pi-\sigma-\pi$ mechanism and would lead to structure **B** with conservation of the absolute configuration at C(3) (double inversion) possibly involving an intermediate enyl structure **E**, where the $Fe(CO)_4$ moiety is both σ- and π-bound to the organic ligand.[51] On the other hand, an *anti*-Me → *syn*-Me isomerization mechanism without migration of the $Fe(CO)_4$ moiety to the other enantiotopic face of the double bond would lead to structure *ent*-**B** with inverted absolute configuration at C(3) (epimerization process).

Synthesis of (η^3-Allyl)tetracarbonyliron(1+) Complexes 18 and 19. Ether solutions of diastereomerically enriched or pure (η^2-alkene)tetracarbonyliron(0) complexes, **14a′**/**a″**, **14f′**/**f″**, and **15′**/**″** were treated with a slight excess of a solution of anhydrous tetrafluoroboric acid in diethyl ether to cleave the O*PG* leaving group unit (Scheme 5, Table 3).[20r,21g,42] The corresponding (η^3-allyl)tetracarbonyliron(1+) complexes **18′**/**″** and **19′**/**″** immediately precipitated as yellow-white solids and were obtained as mixtures of diastereomers in NMR spectroscopically pure form. Further purification procedures such as precipitation from nitromethane solution with cold diethyl ether resulted in substantial loss of material and led to selective enrichment of *syn*-Me-configured isomers.

The diastereomerically pure complex **14a′** (de, ee > 99%) gave the tetracarbonyl iron complex **18′** in virtu-

(48) Keller, E. *SCHAKAL 86*; University of Freiburg, 1986.
(49) (a) Cano, A. C.; Zúñiga-Villarreal, N.; Alvarez, C.; Toscano, T. R. A.; Cervantes, M.; Diaz, A.; Rudler, H. *J. Organomet. Chem.* **1994**, *464*, C23. (b) Chow, T. J.; Hwang, J.-J.; Wen, Y.-S.; Lin, S.-C. *J. Chem. Soc., Dalton Trans.* **1994**, 937. (c) Rybin, L. V.; Rybinskaya, M. I. *Russ. Chem. Rev.* **1993**, *62*, 637. (d) Liu, L.-K.; Sun, C.-H.; Yang, C.-Z.; Wen, Y.-S.; Wu, C.-F.; Shih, S.-Y.; Lin, K.-S. *Organometallics* **1992**, *11*, 972. (e) Hsiou, Y.; Wang, Y.; Liu, L.-K. *Acta Crystallogr.* **1989**, *45*, 721. (f) Lei, P.-S.; Vogel, P. *Acta Crystallogr.* **1986**, *5*, 2500. (f) Whitesides, T. H.; Slawen, R. W.; Calabrese, J. C. *Inorg. Chem.* **1974**, *13*, 1895. (g) Luxmoore, A. R.;. Truter, M. R. *Acta Crystallogr.* **1962**, *15*, 1117.
(50) For an example see: Lin, S.-H.; Chen, C.-C.; Vong, W.-J.; Liu, R.-S. *Organometallics* **1995**, *14*, 1619. For a thermodynamically preferred *anti*-configurated (η^3-allyl)dicarbonyl[hydrotris(1-pyrazolyl)-borato]molybdenum complex see: Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132.
(51) Enyl complexes are by definition those that contain discrete σ- and π-metal carbon interactions within a single ligand. Sharp, P. R. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Chapter 2, p 272. Enyl complexes are discussed as intermediates for example in Rh-, Ir-, and Fe-catalyzed allylic substitutions with chirality transfer. See refs 7, 8, 14.

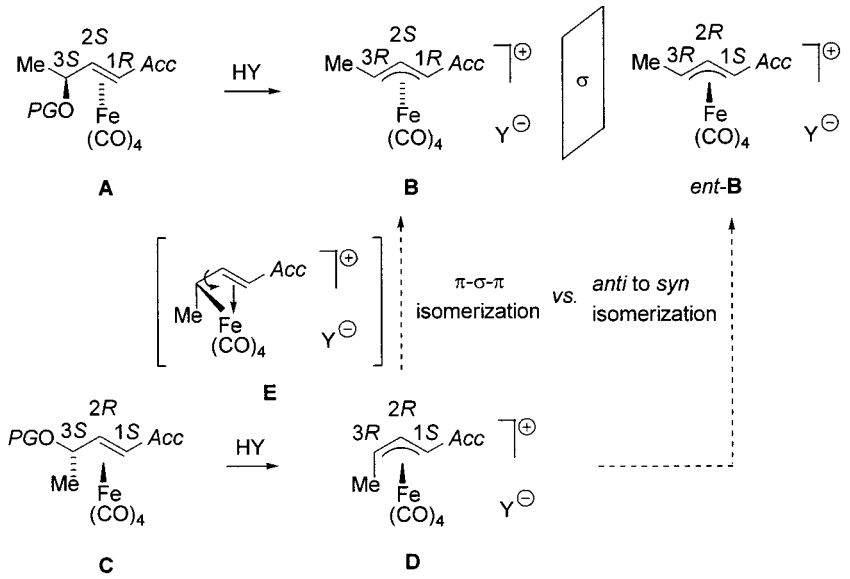
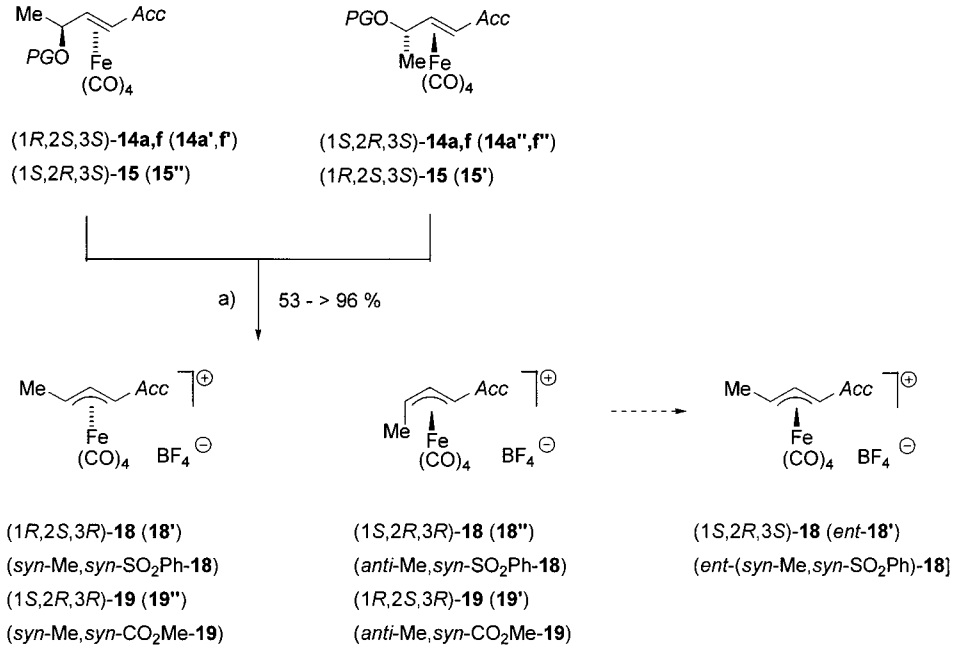


Figure 6. Working hypothesis: Acidic cleavage of the O*PG* leaving group unit from either structure **A** ("W"-shaped) or **B** ("S"-shaped) supposedly yields stereospecifically structures **C** and **D** and proceeds with formal formation of a C−Fe bond and inversion of the absolute stereochemistry at carbon atom C(3). Structure **D** may isomerize to the thermodynamically favored structure **B** or *ent*-**B** with the *syn*-configured methyl group. A $\pi-\sigma-\pi$ mechanism, involving possibly an enyl-structure **E**, would proceed with an overall retention (double inversion) of stereochemistry at carbon atom C(3). *Anti*-Me to *syn*-Me isomerization of structure **D** with an inversion of absolute stereochemistry only at carbon atom C(3) should result in the formation of structure *ent*-**B** (epimerization). Cahn−Ingold−Prelog (CIP) priority: C(1) > C(2). Abbreviations: HY: strong acid with noncoordinating anion. σ: mirror plane.

Scheme 5. Synthesis of Diastereomeric (η^3-Allyl)tetracarbonyliron(1+) Complexes 18′/″ and 19′/″[a]



[a] Reagents and conditions: (a) 1.0 equiv of of complex **14a′/a″**, **14f′/f″** or **15′/″**, 1.3 equiv of 54% HBF_4 in Et_2O, 30 °C, 1 h. Abbreviations: *ent*: enantiomeric form.

ally quantitative yield (>95%) as a single *syn*-Me,*syn*-SO_2Ph-substituted diastereomer (*syn*-Me/*anti*-Me > 99:1, de > 99%) according to ^{1}H NMR spectroscopic analysis (Table 3, entry 1). The transformation of (1*R*,2*S*,3*S*)-**14a** (**14a′**) to **18′** proceeded with conservation of the (*E*)-double bond geometry, leading to a *syn*-configured SO_2Ph group and retaining the overall "W"-shaped appearance of the allylic ligand (*syn*-Me) (Figure 6). Transformation of mixtures of complexes **14a′/a″** with various diastereomeric excesses (de = 42 or 30%) in favor of the diastereomer **14a′** yielded diastereomeric mixtures of the cationic complexes **18′** and **18″**, albeit in lower isolated yield of 74 and 68% (Table 3, entries 2 and 3). ^{1}H NMR spectroscopic analysis of these samples showed that each material was obtained as a pure *syn*-Me,*syn*-SO_2Ph-configured allyl complex **18′** containing basically no traces of the corresponding *anti*-Me,*syn*-SO_2Ph diastereomers **18″**. Complete mass transfer and the absence of isomerization processes for these transformations suggest theoretically a *syn*-Me/*anti*-Me ratio

Table 3. Conversion of Diastereomeric Mixtures of (η^2-Alkene)tetracarbonyliron(0) Complexes 14a′/a″, 14f′/f″, and 15′/″ to the Corresponding Mixtures of Diastereomeric (η^3-Allyl)tetracarbonyliron(1+) Complexes 18′/″ and 19′/″

entry	OPG[a]	conversion **14**, **15** → **18**, **19**[b]	de[c] **14**, **15** [%]	yield[d] **18**, **19** [%]	*syn*-Me/*anti*-Me[e]	de[f] **18**, **19** [%]	*syn*-Me/*anti*-Me[g] de [%][g]
1	OBn	**14a′/a″** → **18′/″**, *ent*-**18′**	>99[h]	>95	>99:1[i]	99[i]	99:1 (99)
2	OBn	**14a′/a″** → **18′/″**, *ent*-**18′**	42[h]	74	>99:1[i]	99[i]	2.45:1 (42)
3	OBn	**14a′/a″** → **18′/″**, *ent*-**18′**	30[h]	68	>99:1[i]	99[i]	1.86:1 (30)
4	OBn	**14a′/a″** → **18′/″**, *ent*-**18′**	75[j]	58	1:1.36	15	1:7.0 (75)
5	OAc	**14f′/f″** → **18′/″**, *ent*-**18′**	24−26[h]	64	3.11:1	51	1.63:1 (24−26)
6	OAc	[*rac*−**6f** →] **14f′/f″**[k] → *rac*-**18′/″**	*l*	80−94[m]	2.94:1	49	*l*
7	OBn	**15′/15″** → **19′/″**	12−16	95[n]	1:1.27−1:1:38	12−16	ca. 1:1.3 (ca. 13)
8	OBn	[(*S*)-**8** →] **15′/″**[o] → **19′/″**	10[h]	87	1:1.19	9	*l*

[a] *PG*: protecting group. [b] Reagents and conditions: 1.0 equiv of complex **14a′/a″**, **14f′/f″**, or **15′/″**, 1.3 equiv of 54% HBF_4 in Et_2O, 30 °C, 1 h. [c] Diastereomeric ratios of complexes **14** and **15** determined by ^{1}H NMR spectroscopy (300 MHz, C_6D_6). See Table 1 for details. [d] Yield of isolated material in ^{1}H NMR spectroscopically pure form. [e] Unless otherwise stated, *syn*-Me/*anti*-Me ratios of complexes **18′/″** and **19′/″** determined by ^{1}H NMR spectroscopy (300 MHz, d_3-nitromethane). [f] Unless otherwise stated, diastereomeric excesses of complexes **18′/″** and **19′/″** determined by ^{1}H NMR spectroscopy (300 MHz, d_3-nitromethane). [g] Theoretically expected *syn*-Me/*anti*-Me ratio or, in parentheses, diastereomeric excesses. [h] Diastereomeric excesses of complexes **14a′/f′** over complexes **14a″/f″**. [i] No traces of the minor diastereomer detectable by high-resolution ^{1}H NMR spectroscopy (500 MHz, d_3-nitromethane). [j] Diastereomeric excess of complex **14a″**. [k] Obtained from *rac*-**6f** and used as a crude complex mixture **14f′/f″** as starting material. [l] Not determined. [m] Averaged yields over 2 steps starting from *rac*-**6f**. [n] Averaged yield of isolated material from several trials. [o] Obtained from (*S*)-**8** and used as a crude complex mixture **15′/″** as starting material.

of 2.45:1 or 1.86:1 (Table 3, entries 2 and 3). A sample of complex **14a** with a diastereomeric excess of 75% favoring the diastereomer (1*S*,2*R*,3*S*)-**14a** (**14a″**) gave allyl complex **18** in only 58% yield as a mixture of *syn*-Me/*anti*-Me-configured diastereomers in a ratio of 1:1.36 (theoretically expected value 1:7.0) (Table 3, entry 4).

A sample of a diastereomeric mixture of the acetoxy-substituted (η^2-alkene)tetracarbonyliron complex **14f′/f″** (de ca. 25%) was converted in 64% yield to a diastereomeric mixture of complexes **18′/″** (Table 3, entry 5). ^{1}H NMR experiments showed a *syn*-Me/*anti*-Me ratio of 3.11:1 (de = 51%), which differs significantly from the theoretically calculated values of a *syn*-Me/*anti*-Me ratio of 1.63:1 (de = 24−26%). The result was confirmed by reacting a racemic sample of alkene **6f** (*rac*-**6f**) in 80% overall yield via a diastereomeric mixture of complexes *rac*-**14f′/f″**directly to a diastereomeric mixture of complexes *rac*-**18′/″** [*syn*-Me/*anti*-Me 2.94:1 (de = 49%)] (Table 3, entry 6).[52]

Several purified samples of the methoxycarbonyl-substituted (η^2-alkene) complexes **15′/″** (de = 12−16%) gave quantitatively mixtures of allyl complexes **19′/″** [**19′** ≡ *anti*-Me,*syn*-CO_2Me-**19**, **19″** ≡ *syn*-Me,*syn*-CO_2Me-**19**] in ratios of ca. 1:1.3 (de = 12−16%) but in favor of the *anti*-Me,*syn*-CO_2Me isomer **19′** (Table 3, entry 7). Protonation of a diastereomeric mixture of complexes **15′/″** (de = 10%), which was obtained directly from (*S*)-**8** and used without prior purification, yielded a mixture of the *syn*-Me,*syn*-CO_2Me- and the *anti*-Me,*syn*-CO_2Me-configured allyl complexes **19′/″** in a ratio of 1:1.19 (de = 9%), again in favor of the *anti*-Me,*syn*-CO_2Me isomer **19′** (Table 3, entry 8). For entries 7 and 8 (Table 3), the diastereomeric excesses or (*syn*-Me/*anti*-Me ratios) of the complex mixtures **19′/″** (de = 12−16%, de = 9%) coincide with sufficient accuracy with the diastereomeric excesses of the starting materials **15′/″** (de = 12−16%, de = 10%). It was therefore concluded that in contrast to the conversion of complexes **14a′/a″** or **14f′/f″** to allyl complexes **18′/″**, formation of complexes **19′/″** from

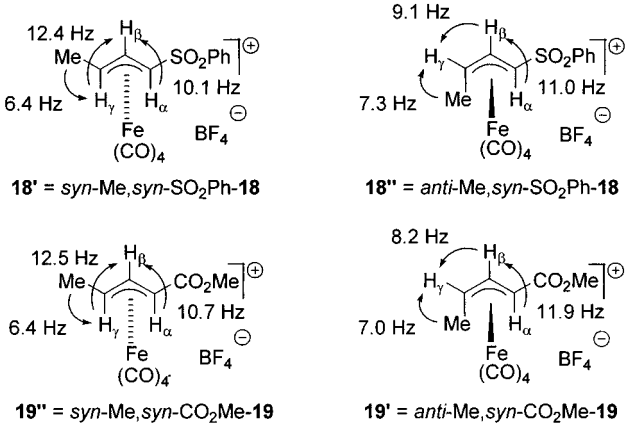


Figure 7. Details of the ^{1}H−^{1}H proton NMR coupling pattern of diastereomeric (η^3-allyl)Fe(CO)$_4$(1+) complexes **18′/″** and **19′/″** (300 MHz, d_3-nitromethane).

complexes **15′/″** proceeded stereospecifically and without suffering any significant *anti*-Me → *syn*-Me isomerization. ^{1}H NMR experiments showed that the *syn*-Me/*anti*-Me ratio of mixtures of complexes **18′/″** changed slowly to favor the *syn*-Me-substituted complex **18′** at 4 °C, but partial decomposition prevented a detailed kinetic investigation.

NMR Spectroscopic Properties and Assignment of the Relative and Absolute Configuration of the (η^3-Allyl)Fe(CO)$_4$(1+) Complexes 18′/″ and 19′/″. The *syn*-Me,*syn*-SO_2Ph- or *syn*-Me,*syn*-CO_2Me-configured complexes (**18′**, *ent*-**18′**, and **19″**) and the *anti*-Me,*syn*-SO_2Ph- or *anti*-Me,*syn*-CO_2Me-configured complexes (**18″** and **19′**) show clearly distinguishable ^{1}H and ^{13}C NMR resonances. In anionic, neutral, or cationic(η^3-allyl)ML_n complexes *anti*-configured methyl groups appear invariably shifted upfield with respect to *syn*-configured methyl groups.[10b,20h,21,51,53] All ^3J ^{1}H−^{1}H coupling constants for the [C(1)−Hα]−[C(2)−Hβ], [C(2)−Hβ]−[C(3)−Hγ], and [C(3)−Hγ]−Me couplings are characteristic for the diastereomeric *syn*-Me- and *anti*-Me-configured complexes **18** and **19** and allow unambiguously to distinguish between them (Figure 7).[20,21] NOE (nuclear Overhauser enhancement) NMR analysis

(52) Alkene *rac*-**6f** was synthesized according to refs 34, 35 and obtained in 83% isolated yield from racemic 2-acetoxypropanal (gift from BASF AG) and the phenylsulfonyl-substituted phosphonate **5**.

Table 4. Details of the ^{1}H and ^{13}C NMR Spectra of Complexes 18′/″ and 19′/″

entry	complex[a]	δ[C(1)−Hα] [ppm]	δ[C(2)−Hβ] [ppm]	δ[C(3)−Hγ] [ppm]	δ[C(1)] [ppm]	δ[C(2)] [ppm]	δ[C(3)] [ppm]
1	**18′**	4.64	6.23	4.93	73.73	97.65	90.58
2	**18″**	5.30	6.12	5.85	77.73	94.46	92.56
3	**19′**	4.27	6.24	5.88	57.85	97.53	90.60
4	**19″**	3.64	6.35	4.97	53.38	100.83	89.26

[a] HETCOR NMR spectroscopic measurements performed on mixtures of complexes **18′/″** and **19′/″**; ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) (d_3-nitromethane).

of complex **18′** confirmed the close proximity of the [C(2)−Hβ] atom and the *syn*-configured methyl group. Due to the electron-withdrawing character of the Fe(CO)$_4$ moiety and the overall positive charge, the cationic complexes **18** and **19** display a remarkable downfield shift for the allylic protons (Table 4).

In most of the (η^3-allyl)ML$_n$ complexes described in the literature, the ^{13}C resonance of the central C(2) atom exhibits a significant downfield shift.[6,10b,21,51,54] ^{1}H−^{13}C correlation NMR spectroscopy (HETCOR) on complexes **18′** and **18″** showed that the C(2) atom is indeed the most downfield shifted. This trend was observed for both diastereomers (Table 4). The closely related substitution pattern of complexes **19′** and **19″** allowed for a similar chemical shift assignment.

The ^{13}C NMR spectroscopic chemical shift of the methyl-substituted allylic termini [C(3)] found at 89−92 ppm (Table 4) can be explained by a deshielding α-effect of the methyl substituent (α-effect +20−30 ppm). Four distinguishable ^{13}C NMR resonance signals in the range from 195 to 199 ppm were observed, indicating both the monomeric character and the high rotational energy barrier at ambient temperature of **18** and **19**.

The transformation of ligands (*S*)-**6** and (*S*)-**8** via the neutral diastereomeric (η^2-alkene)tetracarbonyliron complexes **14** and **15** to the corresponding cationic (η^3-alkene)tetracarbonyliron complexes **18** and **19** proceeded with retention of the double bond geometry, positioning the acceptor group in a *syn*-configuration.[20,21] Therefore, only the two diastereomers with a *syn*-Me,*syn*-*Acc* or *anti*-Me,*syn*-*Acc* substitution pattern become plausible (Figure 6). Each diastereomer obtained should be for itself enantiomerically pure. Stereochemical descriptors are necessary to assign their absolute and relative stereochemistry correctly.

According to the Cahn−Ingold−Prelog notation and assuming conservation of topicity of the Fe(CO)$_4$ moiety during the transformation (1*R*,2*S*,3*S*)-**14a** (**14a′**) → **18′**, the absolute configuration of carbon atom C(1) of the major diastereomer complex **18′** was assigned to be (*R*) and carbon atom C(2) to be (*S*) (Figure 4). Cleavage of the O*PG* leaving group (OBn) unit at carbon atom C-3 in the transformation **14a′** → **18′** supposedly proceeds formally with formation of an Fe−C bond via a S_N2-like mechanism. Therefore, inversion of the absolute configuration from (*S*) in the enantiopure starting material to (*R*) occurs since the O and the Fe atom possess the same relative ranking of Cahn−Ingold−Prelog priority. For this reason, allyl complex **18′** with a *syn*-Me,*syn*-SO$_2$Ph substitution pattern can be assigned the (1*R*,2*S*,3*R*) configuration. As explained above, it is sufficient to give only two stereochemical descriptors for the complexed allylic carbon atoms, e.g., **18′** ≡ *syn*-Me,*syn*-SO$_2$Ph-**18** ≡ (1*R*,2*S*,3*R*)-**18** ≡ (1*R*,3*R*)-**18**, and **18″** ≡ *anti*-Me,*syn*-SO$_2$Ph-**18** ≡ (1*S*,2*R*,3*R*)-**18** ≡ (1*S*,3*R*)-**18**. The species *ent*-**18′** represents *ent*-(*syn*-Me,*syn*-SO$_2$Ph)-**18**, therefore possessing the absolute configuration (1*S*,2*R*,3*S*)-**18** ≡ (1*S*,3*S*)-**18** (Scheme 5, Figure 6). As a consequence of a minor Cahn−Ingold−Prelog priority of the methoxycarbonyl functionality in complexes **19′/″**, the major diastereomer **19′** ≡ *anti*-Me,*syn*-CO$_2$Me-**19** possesses the absolute configuration (1*R*,2*S*,3*R*), which is derived from the neutral (η^2-alkene)tetracarbonyliron complex **15′** with the "S"-shaped backbone. The minor diastereomer **19″** ≡ *syn*-Me,*syn*-CO$_2$Me-**19** possesses consequently the (1*S*,2*R*,3*R*) absolute configuration (Scheme 5, Figure 6). *Each allyl complex* (1*R*,2*S*,3*R*)-**18** *and* (1*S*,2*R*,3*R*)-**18**, *or* (1*R*,2*S*,3*R*)-**19** *and* (1*S*,2*R*,3*R*)-**19** *possesses an absolute* (*R*) *configuration at C(3), which means that they possess identical stereochemistry at C(3). The exception is the optical antipode of complex* **18′**, *epimerization product ent*-**18′**, *which has an inverted absolute configuration* (1*S*,2*R*,3*S*).

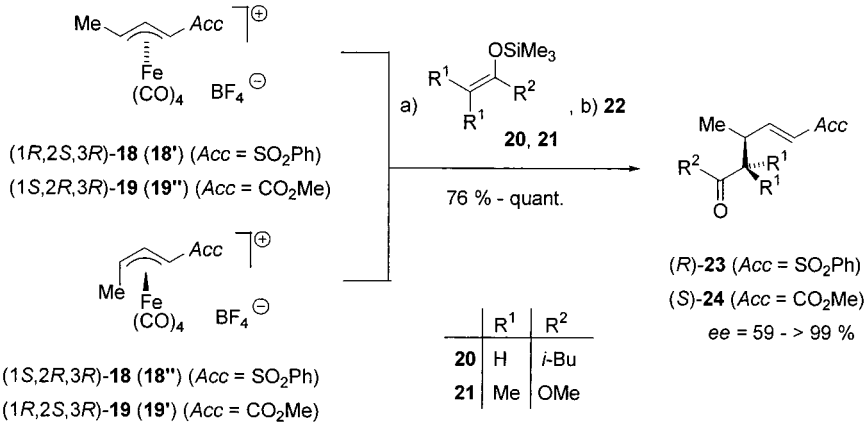
Nucleophilic Addition Reactions of Silyl Enol Ether 20 and Silyl Ketene Acetal 21 to Tetracarbonyl(π-allyl)iron Complexes 18 and 19. The enantiomeric excesses of the cationic iron complexes **18** and **19** could not be determined directly by use of, for example, chiral NMR shift reagents. It was hoped to draw a conclusive correlation between enantiomeric purity and absolute stereochemistry of complexes **18′/″** and **19′/″** on one hand and products obtained after addition of test nucleophiles to them on the other. Among the multitude of nucleophiles known to add to cationic allyl iron complexes of type **18** and **19**,[20−24] soft carbon nucleophiles such as silyl enol ethers or silyl ketene acetals react in a particularly clean manner. Mixtures of (η^3-allyl)tetracarbonyliron(1+) complexes **18′/″** and **19′/″** of different diastereomeric purity were chosen to react with an excess of two different test nucleophiles **20** and **21** (Scheme 6, Table 5).[43,55] The suspended cationic complexes gradually dissolve upon addition of the carbon nucleophiles to furnish initially the soluble intermediate neutral substituted (η^2-alkene)-tetracarbonyliron(0) complexes. Oxidative removal of the tetracarbonyliron moiety with ceric ammonium nitrate (CAN) (**22**) yielded the known 3-substituted alkenyl sulfone (*R*)-**23** and 3-substituted ester (*S*)-**24**, which were isolated after workup and chromatographic purification in excellent to good yield (Table 5).[21b,f]

(53) For an example of an anionic (η^3-allyl)tricarbonyl(1−) complex: Chang, S.; Yoon, J.; Brookhart, M, *J. Am. Chem. Soc.* **1994**, *116*, 1869.

(54) Åkermark, B.; Krakenberger, B.; Hansson, S. *Organometallics* **1987**, *6*, 620.

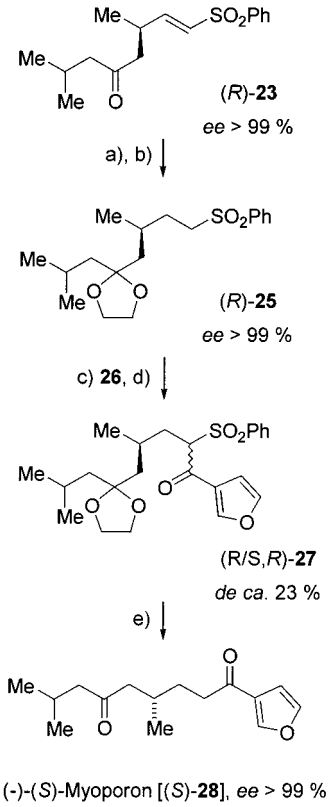
(55) (a) Bonafoux, D.; Bordeau, M.; Biran, C.; Cazeau, P.; Dunogues, J. *J. Org. Chem*. **1996**, *61*, 5532. (b) Emde, H.; Götz, A.; Hofmann, K.; Simchen, G. *Liebigs Ann. Chem*. **1981**, 1643. (c) Ref 21f. (d) Revis, A.; Hilty, T. K. *J. Org. Chem*. **1990**, *55*, 2972. (e) Ainsworth, C.; Chen, F.; Kuo, Y.-N. *J. Organomet. Chem*. **1972**, *46*, 59.

Scheme 6. Synthesis of the 3-Substituted Alkenyl Sulfone (*R*)-23 and the Ester (*S*)-24 by Addition of Silyl Enol Ether 20 and Silyl Ketene Acetal 21 to Complexes 18 and 19[a]



[a] Reagents and conditions: (a) 1.0 equiv of **18′/″** or **19′/″**, CH_2Cl_2, 3.0 equiv of **20** or **21**, −78 °C to room temp, 12 h; (b) 4.0 equiv of aqueous $(NH_4)_2Ce(NO_3)_4$ (CAN, **22**), 0 °C to room temp, 8 h.

Scheme 7. Synthesis of (−)-(*S*)-Myoporon [(*S*)-28] from the Alkenyl Sulfone (*R*)-23[21f a]



[a] Reagents and conditions: (a) cat. 10% Pd/C, EtOAc, 1 atm H_2, room temp, 3 h (quant); (b) 5.0 equiv of $(Me)_3SiOCH_2CH_2OSi(Me)_3$, cat. $(Me)_3SiOTf$, CH_2Cl_2, reflux, 5 days (quant.); (c) (i) 1.2 equiv of *n*-BuLi, THF, −30 °C, 1 h; (ii) 2.0 equiv of furan-3-carboxaldehyde (**26**), −78 °C to room temp, 5 h; (d) Swern-oxidation (2 steps 89%); (e) 50 equiv of Zn-dust, EtOAc/HOAc/THF (3:1:1), few drops of H_2O, reflux, 12 h (93%).

The reactions proceeded with complete γ-regioselectivity with respect to the electron acceptor group [at C(3)] and with conservation of the (*E*)-double bond geometry. Due to the overriding *anti*-directing effect of the $Fe(CO)_4$ fragment, the nucleophilic attack occurs from the opposite side with respect to the $Fe(CO)_4$ moiety (*anti*).[1−3] During the addition step, a new carbon−carbon bond is formed inverting the configuration at C(3) accompanied by simultaneous cleavage of the formal C−Fe bond. Attempts to isolate the intermediately formed neutral C(3)-substituted (η^2-alkene)-tetracarbonyliron(0) complexes and to investigate their stereochemistry failed. It seems plausible that they possess the same relative and therefore absolute stereochemistry with respect to the $Fe(CO)_4$ moiety and C(3) as described for the olefin complexes **14a**−**f**, **15**.

The enantiomeric excesses of compounds **23** obtained (Table 5, entries 1−3) were determined by HPLC employing a chiral stationary phase (Daicel OD) and by comparison with the racemic material *rac*-**23** (Table 5, entry 4) obtained from nucleophilic addition of nucleophile **20** to a complex mixture of *rac*-**18′/″** (Figure 8a). Diastereo- and enantiomerically pure complex **18′** yields (*R*)-**23** in quantitative yield and in virtually enantiopure form (ee > 99) (Figure 8c), while complex mixtures containing **18′/″** and *ent*-**18′** give rise to alkenyl sulfone **23** with lower enantiomeric excesses (ee = 66 and 59%, respectively) (Figure 8b).

The determination of the enantiomeric excess and the absolute configuration [(*S*)] of ester **24** was easily accomplished by comparison of its optical rotation with the optical rotation for compound (*S*)-**24** reported in the literature: $[\alpha]_D^{24}$ −51.3 (*c* 2.98, $CHCl_3$), ee > 96% vs $[\alpha]_D^{24}$ −48.2 (*c* 2.58, $CHCl_3$), ee > 96%.[21b]

The enantiopure building block (*R*)-**23** was previously used in the stereocontrolled synthesis of the naturally occurring hepatotoxic furanosequiterpenoid (−)-(*S*)-myoporon, which allowed for an unambiguous determination of its absolute configuration.[21f] Palladium-catalyzed hydrogenation of the alkenyl sulfone (*R*)-**23** and subsequent protection of the keto functionality as a dioxolane derivative furnished the saturated protected sulfone (*R*)-**25** in quantitative yield and without racemization (ee > 99%). The β-ketosulfone (*R*/*S*,*R*)-**27** was synthesized in 89% overall yield in a two-step procedure by aldol-type addition of furan-3-carboxaldehyde (**26**) to the α-lithio derivative of (*R*)-**25** followed by subsequent Swern oxidation (de = 23%). Simultaneous removal of both the acetal protecting group and the sulfone group of (*R*/*S*,*R*)-**27** was accomplished by reaction with zinc dust under acidic aqueous conditions and gave (−)-(*S*)-myoporon (*S*)-**28** in 93% yield (ee > 99%, HPLC on chiral Daicel OD phase) {$[\alpha]_D^{26}$ −7.0 (*c* 1.39, MeOH) vs

Table 5. Nucleophilic Addition of Nucleophiles 20 and 21 to Complexes 18′/″ and 19′/″ Furnishing Addition Products (*R*)-23 and (*S*)-24

entry	complexes **18**′/″, **19**′/″[a]	*syn*-Me/*anti*-Me[b]	nucleophile[c]	R^1	R^2	product	yield [%][d]	ee [%][e]	$[\alpha]_D^{RT}$ (*c*, $CHCl_3$)
1	**18**′	>99:1	20	H	*i*-Bu	(*R*)-**23**	quant.	>99	−4.7 (1.07)
2	**18**′/″, *ent*-**18**′	>99:1	20	H	*i*-Bu	**23**	76	66	−2.1 (1.26)
3	**18**′/″, *ent*-**18**′	1:1.36	20	H	*i*-Bu	**23**	quant.	59	*f*
4	*rac*-**18**′/″	2.94:1	20	H	*i*-Bu	*rac*-**23**	quant.	0	0
5	**19**′/″	1:1.19	21	Me	OMe	(*S*)-**24**	82	>96[g]	−51.3 (2.98)[g]

[a] Complex mixtures were used except for entry 1. [b] *syn*-Me/*anti*-Me ratio of complexes **18** and **19** determined by ^{1}H NMR spectroscopy (300/500 MHz, d_3-nitromethane). See Table 3 for details. [c] Silyl enol ether **20** and silyl ketene acetal **21** were prepared from their corresponding carbonyl precursors and trimethylchlorosilane. [d] Yield of analytically and spectroscopically pure material after purification by column chromatography on silica gel. [e] Unless otherwise stated, enantiomeric excesses determined by HPLC using a chiral Daicel OD stationary phase in comparison with racemic material. [f] Not determined. [g] Determination of enantiomeric excess and absolute configuration by comparison of the optical rotation with the optical rotation reported in the literature: $[\alpha]_D^{24}$ −48.2 (*c* 2.58, $CHCl_3$), ee > 96%).[21b]

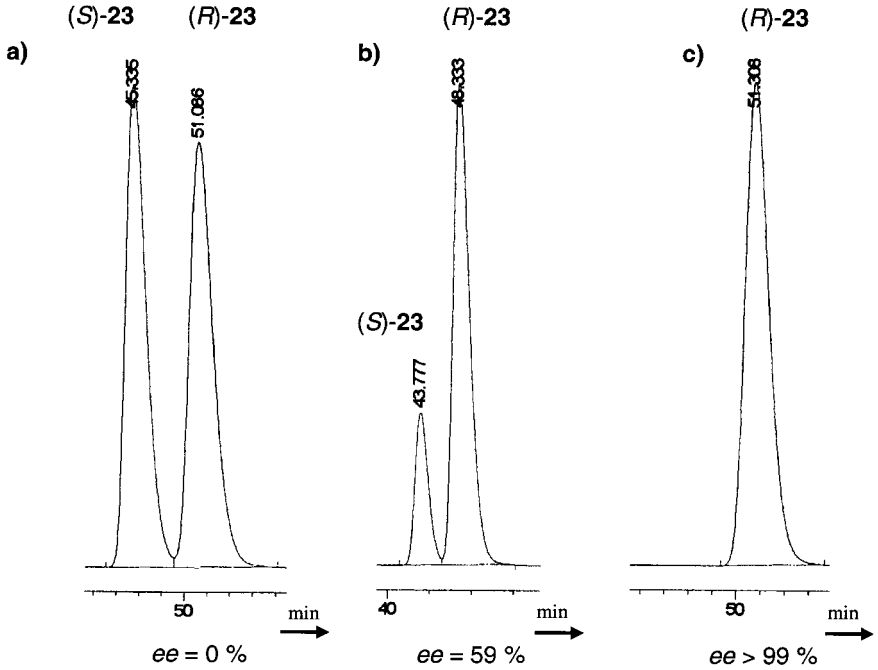


Figure 8. Determination of the enantiomeric excesses of alkenyl sulfone **23** by HPLC using a chiral stationary phase in comparison with racemic material *rac*-**23**; Conditions: Daicel OD, *i*-PrOH/cyclohexane = 2:98, flow 0.5 mL min^{-1}. (a) See Table 5, entry 4; (b) see Table 5, entry 3; (c) see Table 5, entry 1.

$[\alpha]_D^{25}$ −8.5 (*c* 1.54, MeOH)}.[21f,56] Using enantiopure complexes **18**′ or **19**′/″, several other natural products such as pheromones in their absolute natural configurations were synthesized, further supporting the stereochemical conclusions drawn from this study.[21d−f,i]

Mechanistic Discussion and Conclusion

The diastereo- and enantiomerically pure (η^2-alkene)-tetracarbonyliron(0) complex **14a**′ [(1*R*,2*S*,3*S*)-**14a**, Ψ-*exo*-**14a**] (de = ee > 99%) was quantitatively transformed into the corresponding *syn*-Me,*syn*-SO_2Ph-configured (η^3-allyl)tetracarbonyliron(1+) complex **18**′ [(1*R*,2*S*,3*R*)-**18**]. The reaction proceeds without any detectable isomerization or epimerization processes, thus retaining the overall "W"-shaped geometry of the allylic ligand (*syn*-Me/*anti*-Me > 99:1, de = ee > 99%) (Table 3, entry 1). The relative Ψ-*exo*-arrangement of the O*PG* leaving group unit and the $Fe(CO)_4$ moiety (*anti* to each other) in **14a**′ facilitates this transformation, which proceeds with the formal formation of an Fe−C bond and inversion of the absolute stereochemistry at C(3) with respect to the starting material. For the following discussions it will be assumed that the soft test nucleophiles **20** and **21** invariably approach the complexes *anti* with respect to the shielding $Fe(CO)_4$ moiety. Thus, addition of nucleophile **20** to complex **18**′ afforded after oxidative workup alkenyl sulfone (*R*)-**23** in quantitative yield and in enantiopure form (ee > 99%) (Table 5, entry 1). The overall reaction from (*S*)-**6a** via **18**′ to (*R*)-**23** proceeded with virtually complete self-reproduction of chirality (chirality transfer) from C(3)−O [in (*S*)-**6a**] (central chirality) to C(3)−Fe (formally planar chirality) [in (1*R*,2*S*,3*R*)-**18**] to C(3)−C [in (*R*)-**23**] (central chirality) and with retention (double inversion) of the stereogenic center with respect to the starting material.

Mixtures of complexes **14a**′/**a**″ (de = 42, 30, or 75%) result in the formation of complex mixtures **18**′/″ and *ent*-**18**′ albeit in lower isolated yield (Table 3, entries 2−4). These mixtures exhibit by ^{1}H NMR spectroscopic analysis a *syn*-Me/*anti*-Me ratio of > 99:1 (de = 99%) (Table 3, entries 2 and 3) or 1:1.36 (de = 15%) (Table 3, entry 4), which deviate remarkably from theoretically calculated ratios. Each diastereomer, **14a**′ or **14a**″, respectively, supposedly reacts stereospecifically to yield

(56) (a) Burka, L. T.; Iles, J. *Phytochemistry* **1979**, *18*, 873. (b) Burka, L. T.; Kahnert, L.; Wilson, B. J.; Harris, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 2302. (c) Oba, K.; Uritani, I. *Plant Cell Physiol.* **1979**, *20*, 819.

the diastereomeric complexes **18′** (*syn*-Me,*syn*-SO_2Ph-**18**) (from **14a′** or Ψ-*exo*-**14a**) and **18″** (*anti*-Me,*syn*-SO_2-Ph-**18**) (from **14a″** or Ψ-*endo*-**14a**) with formal formation of an Fe−C bond and inversion of the absolute stereochemistry at C(3). Thus, in the absence of isomerization processes, each of them should be obtained in enantiomerically pure form and should react with nucleophile **20** to give alkenyl sulfone (*R*)-**23** in high enantiomeric purity. Complex **14a′** in a mixture consisting of **14a′** and **14a″** reacts supposedly quantitatively and stereospecifically to give complex **18′** (de = ee > 99%). Conversion of complex **14a″** (in a mixture of **14a′**/**a″**) to complex **18″** must be obviously incomplete and must be as well subject to an undetermined degree of an isomerization into a thermodynamically more stable *syn*-Me,*syn*-SO_2-Ph-configured complex. Complex **14a″** [(1*S*,2*R*,3*S*)-**14a**] reacts from the Ψ-*endo*-conformation to form complex **18″** [(1*S*,2*R*,3*R*)-**18**, *anti*-Me,*syn*-SO_2Ph-**18**]. This requires that **14a″** arranges its O*PG* leaving group unit *anti* to the $Fe(CO)_4$ moiety prior to acidic cleavage to yield the "S"-shaped allylic backbone (≡ *anti*-Me,*syn*-SO_2Ph) of **18″**. Low relative yields and *anti*-Me to *syn*-Me isomerization processes for transformations of related Ψ-*endo*-(η^4-diene)tricarbonyliron(0) complexes into their corresponding (η^5-pentadienyl)tricarbonyliron(1+) were also previously reported in the literature.[57]

The *anti*-Me to *syn*-Me isomerization may proceed via one of the possible pathways discussed in Figure 6. A $\pi-\sigma-\pi$ isomerization would result in net retention of absolute stereochemistry at C(3) [(1*S*,2*R*,3*R*)-**18** (**18″**) → (1*R*,2*S*,3*R*)-**18** (**18′**)] including a change of topicity of the $Fe(CO)_4$ group with respect to the allylic plane. An *anti*-Me to *syn*-Me isomerization involving conservation of topicity of the $Fe(CO)_4$ group with respect to the allylic plane would as well result in the formation of a thermodynamically favored *syn*-Me,*syn*-SO_2Ph-configured allyl complex but involving an inversion of absolute configuration only at C(3) [(1*S*,2*R*,3*R*)-**18** (**18″**) → [(1*S*,2*R*,3*S*)-**18** (*ent*-**18′**)]. This analysis means that all complexes **18** with a *syn*-Me,*syn*-SO_2Ph configuration comprising a mixture **18′** (from **14a′**) and *ent*-**18′** (from **14a″**) would have an overall lowered enantiomeric excess, while the remaining complex *anti*-Me,*syn*-SO_2-Ph complex **18″** should be enantiopure.

Consequently, complexes **18′** [(1*R*,2*S*,3*R*)-**18**] and **18″** [(1*S*,2*R*,3*R*)-**18**] react with nucleophile **20** to give alkenyl sulfone (*R*)-**23** with the same absolute configuration. Addition of nucleophile **20** to complex *ent*-**18′** [(1*S*,2*R*,3*S*)-**18**] yields the optical antipode (*S*)-**23**. Therefore, addition of nucleophile **20** to mixtures of **18′**/**″** and *ent*-**18′** (obtained from mixtures of precursor complexes **14a′**/**a″**) must afford alkenyl sulfone **23** with lower enantiomeric excess, as it has been experimentally demonstrated (Table 5, entries 2 and 3, Figure 8) (ee = 66 and 59%). In addition, there is no indication that complexes **18′** (*syn*-Me,*syn*-SO_2Ph-**18**) and **18″** (*anti*-Me,*syn*-SO_2-Ph-**18**) exhibit a different reactivity toward nucleophile **20** since the yields of material **23** obtained are quantitative (Table 5, entries 3 and 4). The stereochemical conclusions gained from the conversion of complexes **14a′**/**a″** to **18′**/**″** should be applicable for the transformation of all complexes of type **14** into complexes of type **18′**/**″**, including **14f′**/**f″** (Table 3, entries 5 and 6). Addition of nucleopile **20** to a mixture of **18′**/**″** and *ent*-**18′** derived from a mixture of precursors **14f′**/**f″** yielded alkenyl sulfone **23** with low enantiomeric excess.[58]

Identical stereochemical considerations allow for a discussion of the stereochemistry of the formation of a complex mixture **19′**/**″** from a mixture of precursor complexes **15′**/**″** (de = 12−16% or 10%, respectively) (Table 3, entries 7 and 8). The observed diastereomeric excesses are basically retained in complexes **19** (de = 12−16% or 9%; *syn*-Me/*anti*-Me ratio = 1:1.30 or 1:1.19). On the basis of the excellent mass balance (>95%), it seems reasonable that in this case complexes Ψ-*exo*-**15** [**15″**, (1*S*,2*R*,3*S*)-**15**] and Ψ-*endo*-**15** [**15′**, (1*R*,2*S*,3*S*)-**15**] react with similar efficiency and stereospecifically to give the corresponding (η^3-allyl)tetracarbonyliron(1+) complexes **19″** [(1*S*,2*R*,3*R*)-**19**, *syn*-Me,*syn*-CO_2Me-**19**] and **19′** ((1*R*,2*S*,3*R*)-**19**, *anti*-Me,*syn*-CO_2Me-**19**]. The lack of any detectable *anti*-Me → *syn*-Me isomerization (according to ^{1}H NMR spectroscopy) suggests that the diastereomers **19′** and **19″** are obviously configurationally stable and each of them is present in highly enantiomerically enriched form. Assuming a uniform *anti*-addition mechanism and that *syn*-Me,*syn*-CO_2Me-**19** [(1*S*,2*R*,3*R*)-**19**,**19″**] and *anti*-Me,*syn*-CO_2Me-**19** [(1*R*,2*S*,3*R*)-**19**, **19′**] exhibit similar reactivity toward the soft nucleophile **21**, one would expect to isolate ester **24** in high yield and in enantiopure form. In fact, the unsaturated ester (*S*)-**24** was obtained in 82% yield and in virtually enantiopure form (ee > 96%) (Table 5, entry 5). The overall reaction from (*S*)-**8** via **19′**/**″** to (*S*)-**24** must again have proceeded with virtually complete self-reproduction of chirality (chirality transfer) and therefore with retention (double inversion) of the stereogenic center with respect to the starting material. Our results are in close accordance for numerous transition metal catalyzed or mediated allylic substitution reactions which were reported to proceed with overall retention of absolute configuration (double inversion), although mechanisms with double retention are discussed as well in the literature.[4,6−9,21,23,25,29] As of now, we cannot offer a conclusive explanation why and how exactly the nature of the substituents influences the configurational stability of *anti*-configured methyl substituents.

In conclusion, we have delineated the mechanistic and stereochemical pathways for the formation of diastereo- and enantiomerically enriched olefinic and allylic tetracarbonyl iron complexes. These organometallics represent key intermediates in our iron-mediated allylic substitution reactions with self-reproduction of chirality ("chirality transfer"). Although this "chirality transfer process" in allylic substitution reactions is of stoichiometric nature with respect to the (η^3-allyl)tetracarbonyliron(1+) complexes employed, the high variability in substitution pattern of the allylic unit, the broad range of nucleophiles employable, and the possibility of preparing easily both enantiomers of a highly functionalized and stereochemically well-defined optically pure target molecule display the great synthetic potential of this protocol. The methodology presented should be regarded as a useful alternative for acylic stereocontrol in comparison to catalytic variants of

(57) Enders, D.; Jandeleit, B.; von Berg, S. *J. Organomet. Chem.* **1997**, *533*, 219.

(58) Enders, D.; Jandeleit, B. University of Technology Aachen, 1995, unpublished results.

allylic substitution reactions, which are often limited in their range of nucleophilic components and allylic substrates. The mechanistic insight and understanding thus obtained allow for a rational extension of this methodology. A general use of these planar chiral iron complexes as synthetic equivalents of a^4-synthons for homologous (1,5) conjugate addition reactions is of interest both as a form of Umpolung of classical d^4-chemistry and as a method of considerable synthetic potential.[30]

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry argon or carbon monoxide using standard Schlenk or vacuum line techniques unless otherwise stated. Solvents were dried and purified by conventional methods prior to use. Diethyl ether (Et_2O) was freshly distilled from sodium benzophenone ketyl, and ethanol-free dichloromethane (CH_2Cl_2), acetonitrile, *n*-pentane, and *n*-hexane were distilled from calcium hydride under an atmosphere of argon. Toluene was distilled from molten sodium under an atmosphere of argon. Light petroleum refers to the fraction with bp 40−80 °C. Reagents of commercial quality were obtained from commercial suppliers and were used from freshly opened containers without further purification unless otherwise stated.

Analytical precoated glass-backed TLC plates (silica gel 60 F_{254}) and silica gel 60 (230−400 mesh, i.e., particle size 0.040−0.063 mm) were purchased from Merck, Darmstadt, Germany. Melting points are uncorrected and were measured on a Dr. Tottoli apparatus. Analytical GLC was performed on Siemens Sichromat 2 and 3 equipped with an SE-54-CB or an OV-1-CB column (both 25 m × 0.25 mm), carrier gas: nitrogen, FID. Optical rotations were measured using a Perkin-Elmer P 241 polarimeter and chloroform of Merck UVASOL quality. Analytical HPLC for the determination of enantiomeric purities was conducted on a Hewlett-Packard 1050 equipped with chiral stationary phase (Daicel OD), UV-detector. Preparative HPLC was performed on Gilson Abimed; Merck-LiCrosorb-column (25 cm × 25 mm, silica 60, particle size 0.007 mm), UV-detector. ^{1}H NMR (500/300 MHz) and ^{13}C NMR (125/75 MHz) spectroscopy were conducted on a Varian Unity 500 and a Varian VXR 300 spectrometer using tetramethylsilane (TMS) as internal standard. Resonances in the ^{1}H NMR spectra of compounds containing the phenylsulfonyl group are indicated as *ortho*-, *meta*-, or *para*-C−H. Resonances in the ^{13}C NMR spectra of compounds containing the phenylsulfonyl group are indicated as *ortho*-, *meta*-, or *para*-C. IR spectra (film on NaCl, KBr) were recorded on a Perkin-Elmer FT/IR 1750 spectrophotometer. Mass spectra were measured on a Varian MAT 212 (EI 70 eV, 1 mA). Microanalyses were obtained with a Heraëus CHN-O-RAPID elemental analyzer. High-resolution mass spectra were performed on a Finnigan MAT 95.

O-Benzyl-2,2,2-trichloroacetimidate was synthesized by sodium hydride-catalyzed addition of benzyl alcohol to trichloroacetonitrile and was used without further purification.[59] Aliquots of commercially available solutions of Red-Al (Red-Al: sodium bis(2-methoxyethoxy)aluminum hydride) in toluene (ca. 3.5 mol L^{-1}) were diluted with anhydrous toluene to a concentration of ca. 0.5−1.5 mol L^{-1}) *prior* to use. Diethyl (phenylsulfonyl)methylphosphonate (**5**) was prepared in 59% overall yield from thiophenol by successive chloromethylation with paraformaldehydehydrochloric acid (73%), Michaelis-Arbuzov rearrangement of the resulting thiophenyl chloro methyl ether to the corresponding phosphonate with triethyl phosphite (91%), and its oxidation to the sulfone (90%) according to a literature procedure.[35] Methyl diethyl phosphonato acetate (**7**) was synthesized in 93% yield from triethyl phosphite and methyl bromoacetate by Michaelis−Arbuzov rearrangement.[36] Alkene (*S*)-**8** can now also be purchased from ACROS Chimica, Belgium.[37] Nonacarbonyldiiron (**13**) was photochemically synthesized by irradiation of pentacarbonyliron in a mixture of glacial acetic acid/acetic acid anhydride using a Philips HPK 125 W or TQ 150 W medium-pressure mercury lamp and a Dema irradiation apparatus.[41] Silyl enol ether **20** and silyl ketene acetal **21** were prepared from their corresponding carbonyl precursors and trimethylchlorosilane via the lithium enolates according to literature procedures.[55] The nucleophiles **20** and **21** were stored and handled with exclusion of moisture and air.

Safety note: Most reactions with compounds containing the iron carbonyl moiety lead to variable amounts of iron carbonyl, especially pentacarbonyl iron. These compounds are volatile and presumably toxic and must be handled with utmost care. They can be oxidatively decomposed with either KOH/H_2O_2, diluted HNO_3, or Br_2/H_2O.

Tetracarbonyl[(1−2η)-(*E*,1*R*,2*S*,3*S*)-3-phenylmethoxy-1-(phenylsulfonyl)but-1-en]iron(0) [(1*R*,2*S*,3*S*)-14a, 14a′, ψ-*exo*-14a] and Tetracarbonyl[(1−2η)-(*E*,1*S*,2*R*,3*S*)-3-phenylmethoxy-1-(phenylsulfonyl)but-1-ene]iron(0) [(1*S*,2*R*,3*S*)-14a, 14a″, ψ-*endo*-14a]. Representative procedure: 3.03 g (10.0 mmol) of alkenyl sulfone (*S*)-**6a** and 4.73 g (13.0 mmol) of nonacarbonyldiiron [$Fe_2(CO)_9$] (**13**) were placed in a 250 mL Schlenk flask and were suspended in anhydrous *n*-hexane (150 mL).[21g,42] The reaction mixture was stirred at room temperature for 3 days under an atmosphere of carbon monoxide and with exclusion of sunlight. After dilution with anhydrous diethyl ether (100 mL), filtration over Celite/sea sand, and washings with anhydrous diethyl ether a clear yellow filtrate was obtained. Removal of the solvents under reduced pressure, filtration of an ether solution (anhydrous diethyl ether) of the crude reaction product under argon by means of a PTFE-syringe filter device (pore size, 0.45 μm), and evaporation to dryness in a Schlenk flask yielded 4.70 g (quant.) of a yellowish solid, which was obtained in spectroscopic and analytical pure form. In general, a crude mixture of olefinic tetracarbonyliron complexes can be further purified by inert gas column chromatography (collection of the yellow fraction) employing previously dried and degassed silica gel and degassed and argon-saturated solvents (light petroleum/diethyl ether mixtures as indicated), which may lead to a slight enrichment of one of the diastereomers. Diastereo- and enantiomerically pure complex (1*R*,2*S*,3*S*)-**14a** (**14a**′, Ψ-*exo*-**14a**) (de = ee > 99%) was obtained after the first filtration by fractional crystallization from the partly evaporated filtrate (*n*-hexane/diethyl ether mixture) at −25 °C in a freezer to furnish 1.88−3.06 g (40−64%) of a bright yellow solid or crystals. Small amounts of highly diastereo- and enantiomerically enriched minor diastereomer (1*S*,2*R*,3*S*)-**14a** (**14a**″, Ψ-*endo*-**14a**) (de = ee > 99%) were obtained by fractional crystallization from remaining concentrated mother liquors. Screening of the different reaction conditions for complexation of ligand (*S*)-**6a** (solvent, temperature) was operationally identically performed. (1*R*,2*S*,3*S*)-**14a** mp 103 °C, dec; 1*S*,2*R*,3*S*)-**14a** mp 110 °C, dec. R_f: 0.43 (light petroleum/diethyl ether = 2:1). de = 70% (crude), de = ee > 99% (after fractional crystallization determined by ^{1}H NMR spectroscopy, 500 MHz, signals: CHC*H*$_3$, *ortho*-C−H). (1*R*,2*S*,3*S*)-**14a**: $[\alpha]_D^{26}$ +171.8 (*c* 1.05, C_6H_6). (1*S*,2*R*,3*S*)-**14a**: $[\alpha]_D^{26}$ +198.5 (*c* 0.46, C_6H_6). NMR spectroscopic data for the major diastereomer (1*R*,2*S*,3*S*)-**14a** (**14a**′, Ψ-*exo*-**14a**): ^{1}H NMR (500 MHz, C_6D_6) δ 0.91 (d, 3H, J = 6.1 Hz, CHC*H*$_3$), 3.04 (qdd, 1H, J = 6.1, 5.8, 0.3 Hz, C*H*CH$_3$), 3.29 (dd, 1H, J = 10.4, 5.8 Hz, C*H*=CHSO$_2$), 3.79 (d, 1H, J = 12.1 Hz, OC*H*HC$_6$H$_5$), 3.86 (dd, 1H, J = 10.2, 0.3 Hz, CH=C*H*SO$_2$), 3.93 (d, 1H, J = 12.1 Hz, OCH*H*C$_6$H$_5$), 6.87−7.13 (m, superimposed, 8H, OCH$_2$C$_6$*H*$_5$, *meta*-, -*para*-C−

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H), 7.85−7.91 (m, 2H, *ortho*-C−H) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 21.73 (CH*C*H$_3$), 57.96 (*C*H=CHSO$_2$), 66.70 (CH=*C*HSO$_2$), 70.15 (OCH$_2$), 76.31 (*C*HCH$_3$), 127.84 (*ortho*-C, superimposed with C_6D_6), 128.04, 128.23, 128.47 (OCH$_2$*C*$_6$H$_5$), 129.13 (*meta*-C), 132.54 (*para*-C), 137.97 (*ipso*-OCH$_2$*C*$_6$H$_5$), 142.66 (*ipso*-C), 207.25 (br, superimposed with major diastereomer, Fe−CO) ppm. NMR spectroscopic data for the minor diastereomer (1*S*,2*R*,3*S*)-**14a** (**14a**″, Ψ-*endo*-**14a**): ^{1}H NMR (500 MHz, C_6D_6) δ 0.86 (d, 3H, J = 6.1 Hz, CHC*H*$_3$), 3.11 (qd, br., 1H, J = 6.1, 5.5 Hz, C*H*CH$_3$), 3.29 (dd, 1H, J = 10.4, 5.2 Hz, C*H*=CHSO$_2$), 3.76 (d, 1H, J = 10.4 Hz, CH=C*H*SO$_2$), 3.83 (d, 1H, J = 11.9 Hz, OC*H*HC$_6$H$_5$), 4.12 (d, 1H, J = 11.9 Hz, OCH*H*C$_6$H$_5$), 6.87−7.13 (m, superimposed, 8H, OCH$_2$C$_6$*H*$_5$, *meta*-, *para*-C−H), 7.80−7.84 (m, 2H, *ortho*-C−H) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 21.86 (CH*C*H$_3$), 59.23 (*C*H=CHSO$_2$), 65.52 (CH=*C*HSO$_2$), 70.07 (OCH$_2$), 74.52 (*C*HCH$_3$), 127.45 (*ortho*-C), 127.94, 128.32, 128.53 (OCH$_2$*C*$_6$H$_5$), 129.24 (*meta*-C), 132.43 (*para*-C), 137.97 (*ipso*-OCH$_2$*C*$_6$H$_5$), 143.23 (*ipso*-C, superimposed with major diastereomer), 207.25 (br, superimposed with major diastereomer, Fe−CO) ppm. All additional spectroscopic and analytical data correspond with those reported in the literature.[21g,42]

Tetracarbonyl[(1−2η)-(*E*,1*R*,3*S*)-3-(phenylmethoxy)-methoxy-1-(phenylsulfonyl)-but-1-ene]iron(0) [(1*R*,2*S*,3*S*)-14b, **14b**′**, Ψ-*exo*-14b] and Tetracarbonyl[(1−2η)-(*E*,1*R*,3*S*)-3-(phenylmethoxy)methoxy-1-(phenylsulfonyl)but-1-ene]iron(0) [(1*S*,2*R*,3*S*)-14b**, **14b**″**, ψ-endo-14b].** By analogy to the procedure for **14a**′/**a**″, 838 mg (2.50 mmol) of alkenyl sulfone (*S*)-**6b** was reacted with Fe$_2$(CO)$_9$ (**13**) (1.164 g, 3.20 mmol) in anhydrous diethyl ether or *n*-hexane (40 mL) to yield 900 mg (72%) of an orange-colored viscous oil after purification by inert gas column chromatography (silica gel, light petroleum/diethyl ether = 4:1).[21g,42] R_f: 0.13 (light petroleum/diethyl ether = 4:1). de: 18% (after purification by inert gas column chromatography determined by ^{1}H NMR spectroscopy, 300 MHz, signals C*H*CH$_3$, CH=C*H*SO$_2$). NMR spectroscopic data for the major diastereomer (1*R*,2*S*,3*S*)-**14b** (**14b**′, Ψ-*exo*-**14b**): ^{1}H NMR (300 MHz, C_6D_6) δ 0.95 (d, 3H, J = 6.1 Hz, CHC*H*$_3$), 3.27 (dd, 1H, J = 10.6, 5.5 Hz, C*H*=CHSO$_2$), 3.44 (quint., br, 1H, $J \approx$ 6.0 Hz, C*H*CH$_3$), 3.84 (d, 1H, J = 10.2 Hz, CH=C*H*SO$_2$), 4.08−4.17 (m, superimposed with minor diastereomer, 2H, OC*H*$_2$C$_6$H$_5$), 4.30 (d, 1H, J = 7.1 Hz, OC*H*HO), 4.34 (d, 1H, J = 6.9 Hz, OCH*H*O), 6.89−7.15 (m, superimposed with minor diastereomer, 8H, OCH$_2$C$_6$*H*$_5$, *meta*-, *para*-C−H), 7.81−7.91 (m, superimposed with minor diastereomer, 2H, *ortho*-C−H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 22.38 (CH*C*H$_3$), 57.60 (*C*H=CHSO$_2$), 66.50 (CH=*C*HSO$_2$), 69.49 (O*C*H$_2$C$_6$H$_5$), 74.73 (*C*HCH$_3$), 92.22 (OCH$_2$O), 127.34, 127.84, 128.54, 129.11 (*ortho*-C, OCH$_2$*C*$_6$H$_5$, superimposed with minor diastereomer and C_6D_6), 129.17 (*meta*-C), 132.59 (*para*-C), 138.15 (*ipso*-OCH$_2$*C*$_6$H$_5$), 142.49 (*ipso*-C), 207.08 (br, superimposed with major diastereomer, Fe−CO) ppm. NMR spectroscopic data for the minor diastereomer (1*S*,2*R*,3*S*)-**14b** (**14b**″, Ψ-*endo*-**14b**): ^{1}H NMR (300 MHz, C_6D_6) δ 0.90 (d, 3H, J = 6.1 Hz, CHC*H*$_3$), 3.35 (dd, 1H, J = 10.6 Hz, 5.0 Hz, C*H*=CHSO$_2$), 3.58 (quint., br, 1H, J = 5.6 Hz, C*H*CH$_3$), 3.79 (d, 1H, J = 10.6 Hz, CH=C*H*SO$_2$), 4.08−4.17 (m, superimposed with major diastereomer, 2H, OC*H*$_2$C$_6$H$_5$), 4.19 (d, 1H, J = 6.5 Hz, OC*H*HO), 4.23 (d, 1H, J = 6.9 Hz, OCH*H*O), 6.89−7.15 (m, superimposed with major diastereomer, 8H, OCH$_2$C$_6$*H*$_5$, *meta*-, *para*-C−H), 7.81−7.91 (m, superimposed with major diastereomer, 2H, *ortho*-C−H) ppm; ^{13}C NMR (125 MHz, C_6D_6) δ 22.69 (CH*C*H$_3$), 59.48 (*C*H=CHSO$_2$), 65.22 (CH=*C*HSO$_2$), 69.49 (O*C*H$_2$C$_6$H$_5$), 73.18 (*C*HCH$_3$), 91.99 (OCH$_2$O), 127.79, 127.84, 128.54, 129.11 (*ortho*-C, OCH$_2$*C*$_6$H$_5$, superimposed with major diastereomer and C_6D_6), 129.25 (*meta*-C), 132.54 (*para*-C), 137.98 (*ipso*-OCH$_2$*C*$_6$H$_5$), 143.01 (*ipso*-C), 207.08 (br, superimposed with major diastereomer, Fe−CO) ppm; IR (film on NaCl) ν 3067 (w), 3056 (m), 3020 (w, Ar−C−H), 2964, 2933, 2894 (w, CH, CH$_2$, CH$_3$), 2105 (vs, *axial*-Fe−CO), 2032, 2005 (vs, Fe−CO), 1498 (vw, C=C, Ar−C=C), 1448 (m), 1381 (w, CH$_3$), 1304 (s, S=O), 1262 (s), 1165 (w), 1145 (s, S=O), 1084 (s, C−O−C), 1039, 1026 (s, br, C−O−C), 927 (w), 628 (vs), 591, 566 (m) cm^{-1}; MS (70 eV) *m*/*z* (relative intensity) 416 (6) [M$^{\bullet+}$ − 3CO], 389 (15), 388 (56) [M$^{\bullet+}$ − 4CO], 359 (18), 358 (77) [M$^{\bullet+}$ − SO$_2$C$_6$H$_5$], 268 (15), 267 (100) [388 − CH$_2$OCH$_2$C$_6$H$_5$], 250 (16), 239 (15), 196 (7), 161 (14), 143 (7) [H$_2$SO$_2$C$_6$H$_5$+], 134 (8), 133 (37), 112 (8), 107 (5) [C$_7$H$_8$O$^+$], 91 (61) [C$_7$H$_7^+$], 84 (19), 77 (14) [C$_6$H$_5^+$], 65 (12) [C$_5$H$_5^+$], 56 (53) [Fe$^+$], 55 (10), 53 (11) [C$_4$H$_3^+$], 51 (10), 45 (10), 43 (13), 41 (12). Anal. Calcd for $C_{22}H_{20}FeSO_8$ (M_r 500.30): C, 52.82; H, 4.03. Found: C, 52.69; H 4.37.

Tetracarbonyl[(1−2η)-(*E*,1*R*,2*S*,3*S*)-3-(*tert*-butyldimethylsiloxy)-1-(phenylsulfon-yl)but-1-ene]iron(0) [(1*R*,2*S*,3*S*)-14c, **14c**′**, Ψ-*exo*-14c] and Tetracarbonyl[(1−2η)-(*E*,1*S*,2*R*,3*S*)-3-(*tert*-butyldimethylsiloxy)-1-(phenylsulfonyl)but-1-ene]iron(0) [(1*S*,2*R*,3*S*)-14c**, **14c**″**, ψ-endo-14c].** By analogy with the procedure for **14a**′/**a**″, 1.47 g (4.50 mmol) of alkenyl sulfone (*S*)-**6c** was reacted with Fe$_2$(CO)$_9$ (**13**) (2.13 g, 5.85 mmol) in anhydrous diethyl ether (50 mL) to yield 2.00 g (90%) of a yellow viscous oil after purification by inert gas column chromatography (silica gel, light petroleum/diethyl ether = 4:1) and filtration by a PTFE-filter.[21g,42] R_f: 0.53 and 0.43 (light petroleum/diethyl ether = 2:1). de: 15−16% (after purification by inert gas column chromatography determined by ^{1}H NMR spectroscopy, 300 MHz, signals: CH=C*H*SO$_2$, CHC*H*$_3$, C(CH$_3$)$_3$, Si(CH$_3$)$_2$. NMR spectroscopic data for the major diastereomer (1*R*,2*S*,3*S*)-**14c** (**14c**′, Ψ-*exo*-**14c**): ^{1}H NMR (300 MHz, C_6D_6) δ −0.38 (s, 3H, SiCH$_3$), −0.21 (s, 3H, SiCH$_3$), 0.71 (s, 9H, C(CH$_3$)$_3$), 1.07 (d, 3H, J = 5.8 Hz, CHC*H*$_3$), 3.33−3.45 (m, 2H, C*H*CH$_3$, C*H*=CHSO$_2$), 3.78 (d, 1H, J = 9.9 Hz, CH=C*H*SO$_2$), 6.96−7.04 (m, superimposed with minor diastereomer, 3H, *meta*-, *para*-C−H), 7.85−7.93 (m, superimposed with minor diastereomer, 2H, *ortho*-C−H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ −4.83 (SiCH$_3$), −4.17 (SiCH$_3$), 18.24 (*C*(CH$_3$)$_3$), 25.83 (C(*C*H$_3$)$_3$), 26.06 (CH*C*H$_3$), 60.09 (*C*H=CHSO$_2$), 68.00 (CH=*C*HSO$_2$), 73.04 (*C*HCH$_3$), 127.99 (*ortho*-C), 129.24 (*meta*-C), 132.57 (*para*-C), 142.36 (*ipso*-C), 207.19 br, superimposed with minor diastereomer, Fe−CO) ppm. NMR spectroscopic data for the minor diastereomer (1*S*,2*R*,3*S*)-**14c** (**14c**″, Ψ-*endo*-**14c**): ^{1}H NMR (300 MHz, C_6D_6) δ −0.41 (s, 3H, SiCH$_3$), −0.33 (s, 3H, Si(CH$_3$), 0.65 [s, 9H, C(CH$_3$)$_3$], 0.96 (d, 3H, J = 6.1 Hz, CHC*H*$_3$), 3.50 (dd, 1H, J = 10.2, 3.8 Hz, C*H*=CHSO$_2$), 3.84 (d, 1H, J = 10.2 Hz, CH=C*H*SO$_2$), 4.00 (qd, 1H, J = 5.8, 3.8 Hz, C*H*CH$_3$), 6.96−7.04 (m, superimposed with major diastereomer, 3H, *meta*-, *para*-C−H), 7.85−7.93 (m, superimposed with major diastereomer, 2H, *ortho*-C−H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ −5.19 (SiCH$_3$), −5.02 (SiCH$_3$), 18.24 (*C*(CH$_3$)$_3$), 25.79 (C(*C*H$_3$)$_3$), 27.29 (CH*C*H$_3$), 62.89 (*C*H=CHSO$_2$), 64.89 (CH=*C*HSO$_2$), 68.63 (*C*HCH$_3$), 127.55 (*ortho*-C), 129.30 (*meta*-C), 132.48 (*para*-C), 143.34 (*ipso*-C), 207.19 (br, superimposed with major diastereomer, Fe−CO) ppm. IR (KBr): ν 2955, 2931, 2896, 2858 (w, CH, CH$_3$), 2107 (vs, *axial*-Fe−CO), 2061, 2042, 2028, 2000 (vs, Fe−CO), 1471, 1463 (vw, Ar−C=C), 1448 (m), 1385 (s, CH$_3$), 1319, 1304 (s, S=O), 1254 (m), 1145, (s, S=O), 1121(s, C−O−Si), 1084, 1036, 992, 963, 880, 837, 804, 777, 754, 710, 688 (m), 630 (s), 585, 565 (m) cm^{-1}; MS (70 eV) *m*/*z* (relative intesity) 494 (0.5) [M$^{\bullet+}$], 466 (6) [M$^{\bullet+}$ − CO], 438 (4) [M$^{\bullet+}$ − 2CO], 411 (11), 410 (32) [M$^{\bullet+}$ − 3CO], 384 (12), 383 (27) [438 − C$_4$H$_9$], 382 (100) [M$^{\bullet+}$ − 4CO], 325 (7) [382-C$_4$H$_9$], 314 (33), 299 (22), 271 (28), 257 (16), 250 (27), 243 (24), 239 (20), 208 (11), 207 (69) 145 (10), 143 (1) [H$_2$SO$_2$C$_6$H$_5^+$], 133 (13), 131 (17), 130 (10), 127 (12), 115 (2) [OSi(CH$_3$)$_2$C(CH$_3$)$_3^+$], 91 (5), 77 (5) [C$_6$H$_5^+$], 75 (24) [HO=Si(CH$_3$)$_2^+$], 73 (17), 57 (1) [C$_4$H$_9^+$], 56 (15) [Fe$^+$]. Anal. Calcd for $C_{20}H_{26}FeSSiO_7$ (M_r 494.41): C, 48.59; H, 5.30. Found: C, 48.56; H 5.33.

Tetracarbonyl[(1−2η)-(*E*,1*R*,2*S*,3*S*)-3-{(2-naphthyl)-methoxy}-1-(phenylsulfonyl)but-1-ene]iron(0) [(1*R*,2*S*,3*S*)-14d, **14d**′**, Ψ-*exo*-14d] and Tetracarbonyl[(1−2η)-(*E*,1*S*,2*R*,3*S*)-3-{(2-naphthyl)methoxy}-1-(phenylsulfonyl)but-1-ene]iron(0) [(1*S*,2*R*,3*S*)-14d, 14d**″**, ψ-endo-14d].** By analogy with the procedure for **14a**′/**a**″, 1.06 g (3.00 mmol) of alkenyl sulfone

(*S*)-**6d** was reacted with $Fe_2(CO)_9$ (**13**) (1.41 g, 3.90 mmol) in anhydrous diethyl ether (45 mL) to yield 740 mg (48%) of a beige-colored solid after purification by inert gas column chromatography (silica gel, light petroleum/diethyl ether = 4:1).[21g,42] Mp: 108 °C (dec). R_f: 0.17 (light petroleum/diethyl ether = 4:1). de: 45% (after purification by inert gas column chromatography determined by ^{1}H NMR spectroscopy, 300 MHz, $CHCH_3$). NMR spectroscopic data for the major diastereomer (1*R*,2*S*,3*S*)-**14d** (**14d′**, Ψ-*exo*-**14d**): ^{1}H NMR (300 MHz, C_6D_6) δ 0.94 (d, 3H, J = 6.2 Hz, $CHCH_3$), 3.10 (quint., br, 1H, $J \approx$ 6.0 Hz, $CHCH_3$), 3.32 (dd, 1H, J = 10.2, 5.5 Hz, $CH{=}CHSO_2$), 3.92 (d, 1H, J = 10.6 Hz, $CH{=}CHSO_2$), 3.96 (d, 1H, J = 12.3 Hz, $OCHHC_{10}H_7$), 4.09 (d, 1H, J = 12.3 Hz, $OCHHC_{10}H_7$), 6.83−7.93 (m, superimposed with minor diastereomer, 12H, $OCH_2C_{10}H_7$, *meta*-, *para*-, *ortho*-C−H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 21.85 ($CHCH_3$), 57.91 ($CH{=}CHSO_2$), 66.69 ($CH{=}CHSO_2$), 70.30 (OCH_2), 76.44 ($CHCH_3$), 126.04−129.09 ($OCH_2C_{10}H_7$, superimposed with minor diastereomer and C_6D_6), 132.51 (*para*-C), 133.42−133.62 ($OCH_2C_{10}H_7$), 135.39 (*ipso*-$OCH_2C_{10}H_7$), 142.60 (*ipso*-C), 207.08 (br, superimposed with minor diastereomer, Fe−CO) ppm. NMR spectroscopic for the minor diastereomer (1*S*,2*R*,3*S*)-**14d** (**14d″**, Ψ-*endo*-**14d**): ^{1}H NMR (300 MHz, C_6D_6) δ 0.90 (d, 3H, J = 6.1 Hz, $CHCH_3$), 3.18 (quint., br, 1H, J = 5.8 Hz, $CHCH_3$), 3.34 (dd, 1H, J = 10.2, 5.0 Hz, $CH{=}CHSO_2$), 3.77 (d, 1H, J = 10.6 Hz, $CH{=}CHSO_2$), 3.96 (d, 1H, J = 12.3 Hz, $OCHHC_{10}H_7$), 4.25 (d, 1H, J = 12.3 Hz, $OCHHC_{10}H_7$), 6.83−7.93 (m, superimposed with major diastereomer, 12H, $OCH_2C_{10}H_7$, *meta*-, *para*-, *ortho*-C−H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 21.85 ($CHCH_3$), 59.30 ($CH{=}CHSO_2$), 65.32 ($CH{=}CHSO_2$), 70.07 (OCH_2), 74.07 ($CHCH_3$), 126.04−129.09 ($OCH_2C_{10}H_7$, *ortho*-, *para*-C, superimposed with major diastereomer and C_6D_6), 132.30 (*para*-C), 133.42−133.62 ($OCH_2C_{10}H_7$), 135.31 (*ipso*-$OCH_2C_{10}H_7$), 143.06 (*ipso*-C), 207.08 (br, superimposed with major diastereomer, Fe−CO) ppm; IR (KBr) ν 3057, 3014 (w, Ar−C−H), 2991, 2932, 2864 (w, CH, CH_2, CH_3), 2105 (vs, *axial*-Fe−CO), 2049, 2019 (vs), 1988 (vs, br, Fe−CO), 1601, 1583, 1508 (w, Ar−C=C), 1446 (m), 1385 (w, CH_3), 1330 (m), 1306 (s, S=O), 1262 (m), 1191 (s), 1140 (s, S=O), 1125 (s), 1084 (s, C−O−C), 1068, 1029 (s−m, br), 935, 902, 864 (m), 810, 751, 717, 689 (s−m), 630, 615 (vs), 587, 579, 563 (s−m) cm^{-1}. MS (70 eV): *m*/*z* (relative intesity) 436 (1.4) [$M^{\bullet+}$ − 3CO], 408 (18) [$M^{\bullet+}$ − 4CO], 352 (1.5) [408 − Fe], 289 (2.4), 267 (100) [408 − $CH_2C_{10}H_7$], 250 (1.6), 211 (6), 196 (6), 186 (10), 167 (6), 157 (2) [$OCH_2C_{10}H_7^+$], 143 (3) [$H_2SO_2C_6H_5^+$], 142 (21), 141 (100) [$C_{11}H_9^+$, $SO_2C_6H_5^+$], 133 (7), 129 (10), 127 (4) [$C_{10}H_7^+$], 115 (22), 107 (6) [$C_7H_8O^+$], 84 (25), 77 (6) [$C_6H_5^+$], 56 (63) [Fe^+], 44 (9). Anal. Calcd for $C_{25}H_{20}FeSO_7$ (M_r 520.34): C, 57.71; H, 3.87. Found: C, 57.36; H, 3.98.

Tetracarbonyl[(1−2η)-(*E*,1*R*,2*S*,3*S*)-1-(phenylsulfonyl)-but-1-en-3-ol]iron(0) [(1*R*,2*S*,3*S*)-14e, **14e′**, *ψ-exo*-**14e] and Tetracarbonyl[(1−2η)-(*E*,1*S*,2*R*,3*S*)-1-(phenylsulfonyl)-but-1-en-3-ol]iron(0) [(1*S*,2*R*,3*S*)-14e** (**14e″**, **Ψ-*endo*-14e].** By analogy with the procedure for **14a′**/**a″**, 424 mg (2.00 mmol) of alkenyl sulfone (*S*)-**6e** was reacted with $Fe_2(CO)_9$ (**13**) (946 mg, 2.60 mmol) in anhydrous diethyl ether (30 mL) to yield 920 mg (quant.) of a yellow, slightly greenish viscous oil after purification by filtration through a PTFE-filter (contains small amounts of $Fe(CO)_5$ and $Fe_3(CO)_{12}$).[21g,42] R_f: 0.17 (light petroleum/diethyl ether = 1:1). de: 35% (determined by ^{1}H NMR spectroscopy, 300 MHz, $CHCH_3$, OH, $=CHSO_2$). NMR spectroscopic data for the major diastereomer (1*R*,2*S*,3*S*)-**14e** (**14e′**, Ψ-*exo*-**14e**): ^{1}H NMR (300 MHz, C_6D_6) δ 0.79 (d, 3H, J = 6.3 Hz, $CHCH_3$), 1.44 (d, 1H, J = 4.7 Hz, OH), 3.24 (dd, 1H, J = 10.4, 4.1 Hz, $CH{=}CHSO_2$), 3.37−3.46 (m, 1H, $CHCH_3$), 3.86 (d, 1H, J = 10.2 Hz, $CH{=}CHSO_2$), 4.50 (dq, 1H, J = 9.1, 6.5 Hz, $CHCH_3$), 6.93−7.05 (m, superimposed with minor diastereomer, 3H, *meta*-, *para*-C−H), 7.79−7.89 (m, superimposed with minor diastereomer, 2H, *para*-C−H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 25.49 ($CHCH_3$), 60.13 ($CH{=}CHSO_2$), 65.13 ($CH{=}CHSO_2$), 69.83 ($CHCH_3$), 127.72−128.36 (*ortho*-C, superimposed with C_6D_6), 129.17 (*meta*-C), 132.62 (*para*-C), 142.51 (*ipso*-C), 207.25 (br, superimposed with minor diastereomer, Fe−CO) ppm. NMR spectroscopic data for the minor diastereomer (1*S*,2*R*,3*S*)-**14e** (**14e″**, Ψ-*endo*-**14e**): ^{1}H NMR (300 MHz, C_6D_6) δ 0.82 (d, 3H, J = 6.0 Hz, $CHCH_3$), 1.58 (d, 1H, J = 4.4 Hz, OH), 3.33 (dd, 1H, J = 10.2, 6.0 Hz, $CH{=}CHSO_2$), 3.37−3.46 (m, 1H, $CHCH_3$), 3.69 (d, 1H, J = 10.4 Hz, $CH{=}CHSO_2$), 6.93−7.05 (m, superimposed with major diastereomer, *meta*-, *para*-C−H), 7.79−7.89 (m, 2H, superimposed with major diastereomer, *ortho*-C−H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 26.07 ($CHCH_3$), 61.35 ($CH{=}CHSO_2$), 65.81 ($CH{=}CHSO_2$), 69.52 ($CHCH_3$), 127.47 (*ortho*-C), 129.28 (*meta*-C), 133.43 (*para*-C), 142.96 (*ipso*-C), 207.25 (br, superimposed with major diastereomer, Fe−CO) ppm; IR (film on NaCl) ν 3496 (w−m, br., OH), 3021 (w, Ar−C−H), 2970, 2927 (w, CH, CH_3), 2104 (vs, *axial*-Fe−CO), 2030, 2001 (vs, Fe−CO), 1585, 1479 (vw, Ar−C=C), 1447 (m), 1369 (w, CH_3), 1302 (s, S=O), 1217 (m), 1143 (s, S=O), 1084 (s), 808, 750, 719, 689 (m), 626 (s), 592 (w) cm^{-1}; MS (70 eV) *m*/*z* (relative intesity) 380 (0.1) [$M^{\bullet+}$], 352 (5) [$M^{\bullet+}$ − CO], 324 (14) [$M^{\bullet+}$ − 2CO], 296 (46) [$M^{\bullet+}$ − 3CO], 279 (4) [$M^{\bullet+}$ + 1 − 3CO − H_2O], 268 (31) [$M^{\bullet+}$ − 4CO], 251 (13), 250 (100) [268 − H_2O], 186 (27), 184 (48), 169 (29), 160 (23), 149 (16), 143 (3) [$H_2SO_2C_6H_5^+$], 133 (19), 125 (17), 78 (9), 77 (19) [$C_6H_5^+$], 73 (13), 71 (9), 56 (30) [Fe^+], 55 (21), 53 (8), 51 (15). Calcd for $^{12}C_{11}{}^1H_{12}{}^{56}Fe^{32}S^{16}O_4$ ($M^{\bullet+}$ − 3CO) *m*/*z* = 295.98057. Found *m*/*z* = 295.98050.

Tetracarbonyl[(1−2η)-(*E*,1*R*,2*S*,3*S*)-3-acetoxy-1-(phenylsulfonyl)but-1-en]iron(0) [(1*R*,2*S*,3*S*)-14f, **14f′**, *ψ-exo*-**14f] and Tetracarbonyl[(1−2η)-(*E*,1*S*,2*R*,3*S*)-3-acetoxy-1-(phenylsulfonyl)but-1-en]iron(0) [(1*S*,2*R*,3*S*)-14f, 14f″**, ***ψ-endo*-**14f].** By analogy to the procedure for **14ai**/**aii**, 509 mg (2.00 mmol) of alkenyl sulfone (*S*)-**6d** was reacted with $Fe_2(CO)_9$ (**13**) (946 mg, 2.60 mmol) in anhydrous diethyl ether (30 mL) to yield 788 mg (93%) of a yellow-greenish viscous oil after purification by filtration through a PTFE-filter (contains small amounts of $Fe(CO)_5$ and $Fe_3(CO)_{12}$).[21g,42] R_f: 0.19 (light petroleum/diethyl ether = 2:1). de: 22% (determined by ^{1}H NMR spectroscopy, 300 MHz, signals: $CHCH_3$, $COCH_3$, $CH{=}CHSO_2$, $CHCH_3$). NMR spectroscopic data for the major diastereomer (1*R*,2*S*,3*S*)-**14f** (**14f′**, Ψ-*exo*-**14f**): ^{1}H NMR (300 MHz, C_6D_6) δ 1.11 (d, 3H, J = 6.3 Hz, $CHCH_3$), 1.20 (s, 3H, $COCH_3$), 3.15 (dd, 1H, J = 9.9, 9.3 Hz, $CH{=}CHSO_2$), 4.08 (d, 1H, J = 10.2 Hz, $CH{=}CHSO_2$), 4.50 (dq, 1H, J = 9.1, 6.5 Hz, $CHCH_3$), 6.90−7.03 (m, superimposed with minor diastereomer, 3H, *meta*-, *para*-C−H), 7.79−7.88 (m, superimposed with minor diastereomer, 2H, *ortho*-C−H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 20.47 ($CHCH_3$), 21.19 ($COCH_3$, superimposed with minor diastereomer), 53.33 ($CH{=}CHSO_2$), 67.84 ($CH{=}CHSO_2$), 74.17 ($CHCH_3$), 127.90 (*ortho*-C), 129.41 (*meta*-C), 132.52 (*para*-C), 142.19 (*ipso*-C), 169.33 ($COCH_3$), 206.37 (br, superimposed with minor diastereomer, Fe−CO) ppm. NMR spectroscopic data for the minor diastereomer (1*S*,2*R*,3*S*)-**14f** (**14f″**, Ψ-*endo*-**14f**): ^{1}H NMR (300 MHz, C_6D_6) δ 0.80 (d, 3H, J = 6.1 Hz, $CHCH_3$), 1.70 (s, 3H, $COCH_3$), 3.23 (dd, 1H, J = 10.3, 9.0 Hz, $CH{=}CHSO_2$), 3.52 (d, 1H, J = 10.4 Hz, $CH{=}CHSO_2$), 4.29 (dq, 1H, J = 8.9, 6.2 Hz, $CHCH_3$), 6.90−7.03 (m, superimposed with major diastereomer, 3H, *meta*-, *para*-C−H), 7.79−7.88 (m, superimposed with major diastereomer, 2H, *ortho*-C−H) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 21.19 ($COCH_3$, superimposed with major diastereomer), 23.26 ($CHCH_3$), 54.84 ($CH{=}CHSO_2$), 67.05 ($CH{=}CHSO_2$), 74.12 ($CHCH_3$), 127.66 (*ortho*-C), 129.26 (*meta*-C), 132.78 (*para*-C), 142.39 (*ipso*-C), 168.99 ($COCH_3$), 206.37 (br, superimposed with major diastereomer, Fe−CO) ppm; IR (film on NaCl) ν 3024 (w, Ar−C−H), 2980, 2937 (vw, CH, CH_3), 2107 (vs, *trans*-Fe−CO), 2032, 2007 (vs, Fe−CO), 1732 (s, C=O), 1585, 1479 (vw, Ar−C=C), 1447 (m), 1372 (m, CH_3), 1308 (s, S=O), 1238 (s, br, CO−O), 1148 (s, S=O), 1085, 1046 (m), 944 (w), 802, 753, 718, 689 (m), 628, 592 (s) cm^{-1}; MS (70 eV) *m*/*z* (relative intensity) 366 (4) [$M^{\bullet+}$ − 2CO], 338 (22) [$M^{\bullet+}$ − 3CO], 311 (16), 310 (100) [$M^{\bullet+}$ − 4CO], 279 (2) [338 − CH_3CO_2H], 267 (4) [$M^{\bullet+}$ − 4CO, − H_3CCO], 250 (42)

[310 − H_3CCO_2H], 230 (4), 220 (4), 203 (4), 186 (44), 184 (31), 160 (12), 150 (5), 141 (1.2) [$SO_2C_6H_5^+$], 133 (21), 125 (10), 115 (16), 77 (9) [$C_6H_5^+$], 56 (30) [Fe^+], 53 (12). HRMS: calcd for $^{12}C_{13}1H_{14}56Fe^{16}O_5 32S$ ($M^{\bullet+}$ − 3CO) *m*/*z* 337.99113, found *m*/*z* 337.99087.

Tetracarbonyl[(1−2*η*)-(*E*,1*R*,2*S*,3*S*)-1-methoxycarbonyl-3-(phenylmethoxy)but-1-en]iron(0) [(1*R*,2*S*,3*S*)-15, **15′**, ***ψ*-*endo*-15] and Tetracarbonyl[(1−2*η*)-(*E*,1*S*,2*R*,3*S*)-1-methoxycarbonyl-3-(phenylmethoxy)but-1-en]iron(0) [(1*S*,2*R*,3*S*)-15**, **15″**, **Ψ*-*exo*-15].** By analogy with the procedure for **14a′**/**a″**, 441 mg (2.00 mmol) of ester (*S*)-**8** was reacted with $Fe_2(CO)_9$ (**13**) (1.46 g, 4.00 mmol) in anhydrous diethyl ether or *n*-hexane (15 mL) to yield 660 mg (85%) of a yellow, slightly greenish viscous oil, which solidifies to needles after purification by filtration through a PTFE-filter.[21b] Additional purification by inert gas column chromatography (silica gel, light petroleum/diethyl ether = 14:1) gave 477 g (62%) of yellow light-sensitive crystalline needles. R_f: 0.22 (light petroleum/diethyl ether = 14:1). de: 16% (determined by ^{1}H NMR spectroscopy, 300 MHz, signals: OCH_3). $CHCH_3$). NMR spectroscopic data of the major diastereomer (1*R*,2*S*,3*S*)-**15** (**15′**, Ψ-*endo*-**15**): ^{1}H NMR (300 MHz, C_6D_6) δ 1.09 (d, 3H, J = 6.1 Hz, $CHCH_3$), 3.23 (br. qd, J = 6.1, 5.2 Hz, $CHCH_3$), 3.40 (s, 3H, OCH_3), 3.85 (dd, 1H, J = 11.0, 5.2 Hz, $CH{=}CHCO_2$), 3.98 (d, 1H, J = 11.6 Hz, $OCHHC_6H_5$), 4.20 (br d, 1H, J = 11.9 Hz, $CH{=}CHCO_2$), 4.24 (d, 1H, J = 11.6 Hz, $OCHHC_6H_5$), 7.04−7.23 (m, superimposed with minor diastereomer, 5H, $OCH_2C_6H_5$) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 22.77 ($CHCH_3$), 42.95 ($CH{=}CHCO_2$), 51.25 (OCH_3), 66.29 ($CH{=}CHCO_2$), 70.55 ($OCH_2C_6H_5$), 75.60 ($CHCH_3$) 127.68−128.50 ($OCH_2C_6H_5$, superimposed with minor diastereomer and C_6D_6), 138.37 (*ipso*-$OCH_2C_6H_5$), 174.93 ($CH{=}CHCO_2$), 208.51 (br, Fe−CO) ppm. NMR spectroscopic data of the minor diastereomer (1*S*,2*R*,3*S*)-**15** (**15″**, Ψ-*exo*-**15**): ^{1}H NMR (300 MHz, C_6D_6) δ 1.23 (d, 3H, J = 6.1 Hz, $CHCH_3$), 3.33 (d, 1H, J = 11.3 Hz, $OCHHC_6H_5$), 3.34 (br quint., J = 6.0 Hz, $CHCH_3$), 3.37 (s, 3H, OCH_3), 3.80 (dd, 1H, J = 10.9, 6.0 Hz, $CH{=}CHCO_2$), 4.12 (br d, 1H, J = 11.9 Hz, $CH{=}CHCO_2$), 4.28 (d, 1H, J = 11.6 Hz, $OCHHC_6H_5$), 7.04−7.23 (m, superimposed with major diastereomer, 5H, $OCH_2C_6H_5$) ppm; ^{13}C NMR (75 MHz, C_6D_6) δ 22.24 ($CHCH_3$), 44.78 ($CH{=}CHCO_2$), 51.35 (OCH_3), 63.92 ($CH{=}CHCO_2$), 70.19 ($OCH_2C_6H_5$), 77.78 ($CHCH_3$), 127.68−128.50 ($OCH_2C_6H_5$, superimposed with major diastereomer and C_6D_6), 138.48 (*ipso*-$OCH_2C_6H_5$), 174.65 ($CH{=}CHCO$), 208.37 (br, Fe−CO) ppm; IR ($CHCl_3$) ν 3026, 3012 (w, Ar−C−H), 2952, 2868 (w, CH, CH_3), 2098 (vs, *axial*-Fe−CO), 2023, 1993 (vs, Fe−CO), 1701 (s, C=O), 1604, 1500, 1477 (w, Ar−C=C), 1455, 1435 (m), 1373 (w, CH_3), 1348 (w), 1265, 1193 (m), 1173 (s, C−O−C), 1062, 1027 (w), 908 (w), 699, 669 (m), 629 (vs) cm^{-1}; MS (70 eV) *m*/*z* (relative intensity) 388 (0.5) [$M^{\bullet+}$], 357 (1.0) [$M^{\bullet+}$ − OCH_3], 332 (2) [$M^{\bullet+}$ − 2CO], 304 (5) [$M^{\bullet+}$ − 3CO], 277 (13), 276 (55) [$M^{\bullet+}$ − 4CO], 218 (7), 193 (4), 185 (45) [276 − $CH_2C_6H_5$], 168 (26), 163 (8), 133 (5), 114 (12), 92 (16), 91 (100) [$C_7H_7^+$], 82 (11), 79 (9), 77 (9) [$C_6H_5^+$], 65 (12) [$C_5H_5^+$], 56 (26) [Fe^+], 53 (12), 39 (12). HRMS: calcd for $^{12}C_{14}1H_{16}56Fe^{16}O_4$ ($M^{\bullet+}$ − 3CO) *m*/*z* 304.03980, found *m*/*z* 304.04008.

Tetracarbonyl[(1−3*η*)-(1*R*,2*S*,3*R*)-1-(phenylsulfonyl)-but-1-en-3-yl]iron(1+) Tetrafluoroborate [(1*R*,2*S*,3*R*)-18, **18′**, ***syn*-Me,*syn*-SO_2Ph-18].** Representative procedure: 8.54 g (18.2 mmol) of complex (1*R*,2*S*,3*S*)-**14a** (**14a′**, Ψ-*exo*-**14a**; de = ee > 99%) was dissolved in 50 mL of anhydrous diethyl ether under an atmosphere of argon.[21g,42] The bright yellow solution was taken up into a syringe and filtered through a PTFE-syringe filter into a 500 mL Schlenk flask. The solution was diluted up to a total volume of 250−300 mL with anhydrous diethyl ether and then warmed carefully to 30 °C. A 3.0 mL (21.8 mmol) sample of a 54% solution of HBF_4 in diethyl ether was added dropwise to the solution. After 2 h, the precipitate was filtered off under an atmosphere of argon using an inert gas frit. The collected precipitate was washed with anhydrous diethyl ether until the filtrate remained colorless. The residue was dried for 12 h under reduced pressure at room temperature in high vacuum, yielding 7.84 g (96%) of a pale yellow solid. The complex was obtained in spectroscopic and analytical pure form and was used without further purification in nucleophilic addition reactions. Screening for *syn*-Me/*anti*-Me selectivity in the formation of complexes **18′**/**″** employing mixtures of complexes **14a′**/**a″** and **14f′**/**f″** was operationally identically performed. Mp: 153−155 °C (dec). de > 99% (*syn*-Me/*anti*-Me: > 99:1; determined by ^{1}H NMR spectroscopy, 500 MHz, signals: $CHCH_3$, $CH{-}CHSO_2$, $CHCH_3$). ee > 99%. $[\alpha]_D^{21}$: +158.3 (*c* 0.96, acetone). NMR spectroscopic data for the (1*R*,2*S*,3*R*)-**18**, (**18′**, *syn*-Me,*syn*-SO_2Ph-**18**) isomer: ^{1}H NMR (500 MHz, CD_3NO_2) δ 2.13 (d, 3H, J = 6.4 Hz, $CHCH_3$), 4.64 (dd, 1H, J = 10.1, 0.6 Hz, $CH{-}CHSO_2$), 4.93 (dqd, 1H, J = 12.4, 6.4, 0.6 Hz, $CHCH_3$), 6.23 (dd, 1H, J = 12.4, 10.1 Hz, $CH{-}CHSO_2$), 7.72−7.80 (m, 2H, *meta*-C−H), 7.82−7.91 (m, 1H, *para*-C−H), 8.07−8.14 (m, 2H, *ortho*-C−H) ppm; ^{13}C NMR (125 MHz, CD_3NO_2) δ 20.77 ($CHCH_3$), 73.73 ($CH{-}CHSO_2$), 90.58 ($CHCH_3$), 97.65 ($CH{-}CHSO_2$), 129.46 (*ortho*-C), 131.54 (*meta*-C), 136.61 (*para*-C), 139.57 (*ipso*-C), 195.35, 196.10, 197.43, 197.67 (Fe−CO) ppm. All additional spectroscopic and analytical data correspond with those reported in the literature.[21g,42]

rac*-Tetracarbonyl[(1−3*η*)-1-(phenylsulfonyl)but-1-en-3-yl]iron(1+) Tetrafluoroborate *rac*-18′ (*rac*-*syn*-Me,*syn*-SO_2Ph-18) and *rac*-18″ (*rac*-*anti*-Me,*syn*-SO_2Ph-18).** Representative procedure: By analogy with the conversion of (*S*)-**6f** to complexes **14*f′*/*f″, 12.7 g (50 mmol) of the racemic alkenyl sulfone *rac*-**6f** was reacted with $Fe_2(CO)_9$ (23.7 g, 75 mmol) (**13**) in anhydrous diethyl ether (300 mL).[21g,42] After completion of the reaction, filtration over Celite/sand, and several washings with anhydrous diethyl ether, the combined filtrate was partially evaporated under reduced pressure to yield a bright yellow clear solution of complex mixture *rac*-**14f′**/**f″**. By analogy with the procedure for the synthesis of complex **18′**, the solution was carefully warmed to 30 °C, and 8.9 mL (65 mmol) of a 54% solution of HBF_4 in diethyl ether was added dropwise. After 2 h, the precipitate was filtered off under an atmosphere of argon and washed with anhydrous diethyl ether until the filtrate was colorless. Drying in high vacuum yielded 21.2 g (94%) of a pale yellow solid. The complex mixture was obtained in spectroscopic and analytical pure form and was used without further purification in nucleophilic addition reactions. Mp: 153−155 °C (dec). de: 49% (*syn*-Me/*anti*-Me: 2.94:1; determined by ^{1}H NMR spectroscopy, 500 MHz, signals: $CHCH_3$, $CH{-}CHSO_2$, $CHCH_3$). NMR spectroscopic data for the minor diastereomer *rac*-**18″** (*rac*-*anti*-Me,*syn*-SO_2Ph-**18**): ^{1}H NMR (500 MHz, CD_3NO_2) δ 1.77 (d, 3H, J = 7.3 Hz, $CHCH_3$), 5.30 (d, 1H, J = 11.0 Hz, $CH{-}CHSO_2$), 5.85 (dq, br., 1H, J = 9.1, 7.2 Hz, $CHCH_3$), 6.12 (dd, br, 1H, J = 11.0, 9.0 Hz, $CH{-}CHSO_2$), 7.72−7.80 (m, 2H, *meta*-C−H, superimposed with major diastereomer), 7.82−7.91 (m, 1H, *para*-C−H, superimposed with major diastereomer), 8.07−8.14 (m, 2H, *ortho*-C−H, superimposed with major diastereomer) ppm; ^{13}C NMR (125 MHz, CD_3NO_2) δ 20.15 ($CHCH_3$), 77.73 ($CH{-}CHSO_2$), 92.56 ($CHCH_3$), 94.46 ($CH{-}CHSO_2$), 129.63 (*ortho*-C), 131.54 (*meta*-C, superimposed with major diastereomer), 136.61 (*para*-C, superimposed with major diastereomer), 139.33 (*ipso*-C), 195.05, 196.30, 197.44, 197.79 (Fe−CO) ppm. All additional spectroscopic and analytical data correspond with those of the major diastereomer *rac*-**18′** (*rac*-*syn*-Me,*syn*-SO_2Ph-**18**).[21g,42]

Tetracarbonyl[(1−3*η*)-(1*R*,2*S*,3*R*)-1-(methoxycarbonyl)but-1-en-3-yl]iron(1+) Tetrafluoroborate [(1*R*,2*S*,3*R*)-19, **19′**, ***anti*-Me,*syn*-CO_2Me-19] and Tetracarbonyl[(1−3*η*)-(1*S*,2*R*,3*R*)-1-(methoxycarbonyl)but-1-en-3-yl]iron-(1+) Tetrafluoroborate [(1*S*,2*R*,3*R*)-19**, **19″**, ***syn*-Me,*syn*-CO_2Me-19].** By analogy with the procedure for the synthesis of *rac*-**14f′**/**f″** and *rac*-**18′**/**″**, 440 mg (2.0 mmol) of the ester (*S*)-**8** was reacted with 1.46 g (4.0 mmol) of $Fe_2(CO)_9$ (**13**) in anhydrous diethyl ether (15 mL). The reaction mixture was

filtered twice, diluted with anhydrous diethyl ether to give a total volume of 20 mL, and warmed to 30 °C. A 0.33 mL (2.4 mmol) portion of a 54% solution of HBF_4 in diethyl ether was added dropwise. After 2 h, the precipitate was filtered off under an atmosphere of argon, washed with anhydrous diethyl ether, and dried in high vacuum to yield 640 mg (87%) of a pale yellow solid. The complex was obtained in spectroscopic and analytical pure form and was used without further purification in nucleophilic addition reactions. Mp: 89−90 °C (dec). de = 9% (*syn*-Me/*anti*-Me = 1.0:1.19; determined by ^{1}H NMR spectroscopy, 500 MHz, signals: C*H*CH_3, C*H*-C*H*CO_2CH_3). NMR spectroscopic data for the major (1*R*,2*S*,3*R*)-**19** (**19′**, *anti*-Me,*syn*-CO_2Me-**19**): ^{1}H NMR (500 MHz, CD_3NO_2) δ 1.85 (dd, 3H, J = 7.3, 0.9 Hz, CHCH_3), 3.93 (s, 3H, OCH_3), 4.27 (dd, 1H, J = 11.9, 0.9 Hz, CH−C*H*CO_2), 5.88 (dqd, 1H, J = 8.2, 7.0, 0.9 Hz, C*H*CH_3), 6.24 (ddd, 1H, J = 11.6, 8.2, 0.9 Hz, C*H*-CHCO_2) ppm; ^{13}C NMR (125 MHz, CD_3NO_2) δ 19.91 (CH*C*H_3), 54.59 (CO_2*C*H_3), 57.85 (CH-*C*CO_2), 90.60 (*C*CH_3), 97.53 (*C*H−CHCO_2), 171.08 (*C*O_2CH_3), 195.93, 197.17, 198.46, 198.60 (Fe−CO) ppm. NMR spectroscopic data for the minor diastereomer (1*S*,2*R*,3*R*)-**19** (**19″**, *syn*-Me,*syn*-CO_2Me-**19**): ^{1}H NMR (500 MHz, CD_3NO_2) δ 2.19 (d, br, 3H, J = 6.4 Hz, CHCH_3), 3.64 (d, 1H, J = 10.7 Hz, CH−C*H*CO_2), 3.90 (s, 3H, OCH_3), 4.97 (dqd, 1H, J = 12.5, 6.4, 0.9 Hz, C*H*CH_3), 6.35 (ddd, 1H, J = 12.5 Hz, 10.7 Hz, 0.9 Hz, C*H*-CHCO_2) ppm; ^{13}C NMR (125 MHz, CD_3NO_2) δ 21.11 (CH*C*H_3), 53.38 (CH-*C*CO_2), 54.53 (CO_2*C*H_3), 89.26 (*C*CH_3), 100.83 (*C*H−CHCO_2), 171.44 (*C*O_2-CH_3), 196.27, 196.92, 198.15, 198.73 (Fe−CO) ppm. All additional spectroscopic and analytical data correspond to those reported in the literature.[21b]

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Supporting Information Available: Synthetic procedures and full analytical data for compounds (*S*)-**2**, (*S*)-**3a**−**d**, (*S*)-**4a**−**d**, (*S*)-**6a**−**f**, (*S*)-**8**, (*R*)-**23**, and (*S*)-**24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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