Synthesis and Coordination Chemistry of Novel Chiral P,S-Ligands with a Xylofuranose Backbone: Use in Asymmetric Hydroformylation and Hydrogenation

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A series of novel chiral thioether-phosphite ligands derived from 1,2-*O*-isopropylidenexylofuranose have been synthesized. Reaction of these chiral ligands with $[M(cod)_2]BF_4$ (M = Ir, Rh; cod = 1,5-cyclooctadiene) yielded the complexes $[M(cod)(P-S)]BF_4$ **10**−**15**. The addition of H_2 to iridium complexes **12**−**15** gave the *cis*-dihydridoiridium(III) complexes $[IrH_2(cod)(P-S)]BF_4$ **19**−**21**, which are present in only one diastereoisomeric form. Iridium complexes are active in the hydrogenation of itaconic acid and produce enantioselectivities of up to 51% under atmospheric pressure. They have also been tested in the Rh-catalyzed hydroformylation of styrene. We discuss hydroformylation results according to the solution structure of the species formed under hydroformylation conditions.

Introduction

Chiral chelating ligands are widely employed in transition metal-catalyzed reactions.[1] Although the use of numerous chiral diphosphines has been successfully reported,[1,2] the design and synthesis of new chiral ligands is still a research subject of great significance in the field of asymmetric catalysis.

In the past few years, chiral bidentate ligands in which only one of the donor atoms is phosphorus have been of great interest with proven advantages in some cases. The advantage of these mixed ligands can be explained by the lack of symmetry of the intermediates in a catalytic cycle. Consequently, two electronically different donor atoms can match the two different coordination sites better and therefore influence both the stability and reactivity of the intermediates. While mixed (P,O)-[3] and (P,N)[4]-donor ligands have been widely applied in enantioselective catalysis, chiral (P,S)-donor ligands have been less studied,[5] although remarkable results in asymmetric allylic alkylation[5d,g,h,k] and hydrosilylation of ketones[5j] have been obtained with this type of ligand.

Most P,S-ligands applied in asymmetric catalysis contain phosphine and thioether moieties, although other combinations such as phosphinite and thioether have also been reported.[5d,f,k] Usually, chirality is exclusively associated with the sulfur moiety. To our knowledge, ligands containing both thioether and phosphite have never been used in asymmetric catalysis, although the potential utility of diphosphite and dithioether ligands in asymmetric catalysis is well-known. Diphosphites are particularly well suited for enantioselective hydroformylation[6] and the hydrogenation of acrylic acid derivatives.[7] Moreover, good results have been obtained

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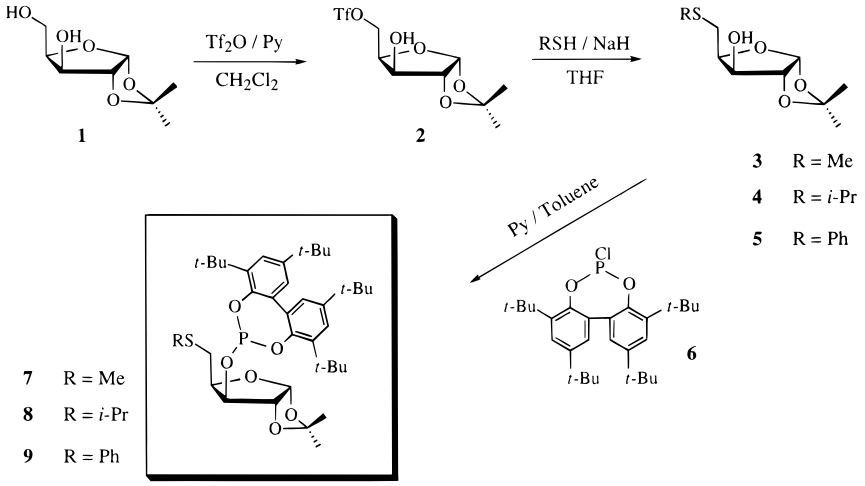
Scheme 1. Preparation of Thioether-Phosphite Ligands



using iridium cationic complexes containing dithioether ligands in the asymmetric hydrogenation under mild conditions.[8] Dithioethers have also been used in the asymmetric hydroformylation of styrene, but enantiomeric excesses were low.[9]

In the last few decades, carbohydrates have been widely used in asymmetric synthesis.[10] Nevertheless, their full potential in providing chiral ligands has hardly been studied.[11] As far as we know, only Vasella et al.,[5a] and more recently Pregosin et al.,[5d,f,g] have reported the coordination chemistry and use of sugar derivative P,S-ligands in asymmetric catalysis. Oehme et al.[5e] have also described a P,S-ligand derived from carbohydrates, but their use in asymmetric catalysis has not been reported.

In this paper, we report the synthesis of novel thioether-phosphite ligands derived from carbohydrates, the chirality of which is associated with the phosphite-thioether backbone, their Rh(I) and Ir(I) complexes, and the use of these new ligands in the asymmetric Rh-catalyzed hydroformylation and Ir-catalyzed hydrogenation of olefins. Hydroformylation results are discussed according to the solution structure of the species formed under hydroformylation conditions. We also describe the reactivity of Ir(I) complexes toward H_2 and the solution structures for the hydridoiridium(III) complexes formed.

Results and Discussion

Synthesis of Thioether-Phosphite Ligands

The new thioether-phosphite ligands **7**−**9** were accessible from 1,2-*O*-isopropylidene-α-D-xylofuranose **1** (Scheme 1). Compound **1** was converted into monotriflate **2** by adding triflic anhydride and pyridine to a dichloromethane solution of **1**. Triflate **2** was isolated as a white solid and characterized by NMR spectroscopy. The ^{13}C NMR spectrum showed a quadruplet at 118.1 ppm ($^1J_{C-F}$ = 324 Hz), which confirms the presence of the triflate group. Treating compound **2** with NaH and methanethiol, 2-propanethiol, or benzenethiol at −78 °C afforded the corresponding thioethers **3**, **4**, and **5**, which are stable to air at room temperature.

The desired thioether phosphite ligands **7**−**9** were obtained from the corresponding thioether **3**−**5** and (3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphorochloridite **6** in the presence of base. Compounds **7**−**9** were isolated in moderate yields (50%) as white solids by purification on neutral silica gel under an atmosphere of argon. They are stable at room temperature and very stable to hydrolysis. The ^1H and ^{13}C NMR spectra agree with those expected for these C_1 ligands. One singlet was observed in the ^{31}P NMR spectrum. Rapid ring inversions (atropoisomerization) in the bisphenol-phosphorus moieties occurred on the NMR time scale since the expected diastereoisomers were not detected by low-temperature phosphorus NMR.[12]

Synthesis of Olefinic Complexes. The reaction of the corresponding chiral thioether-phosphite ligands **7**−**9** with $[M(cod)_2]BF_4$ (M = Rh, Ir) in dichloromethane solution proceeded with the displacement of one molecule of 1,5-cyclooctadiene ligand to afford the cationic mononuclear complexes $[M(cod)(P-S)]BF_4$ (Scheme 2). The olefinic complexes **10**−**15** were isolated by precipitation with hexane as air-stable solids. These complexes are also stable in solution. The complexes were characterized by elemental analysis, FT-IR, ^1H, ^{13}C, and ^{31}P NMR spectroscopy, and FAB mass spectrometry (see Experimental Section).

As expected for C_1-symmetrical complexes, the ^{13}C NMR spectra of complexes **10**−**13** and **15** showed four

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Scheme 2. Synthesis of Rh and Ir Olefinic Complexes

$[M(cod)_2]BF_4$ + P-S ⟶ $[M(cod)(P\text{-}S)]BF_4$

	M	P-S		M	P-S
10	Rh	**7**	**13**	Ir	**7**
11	Rh	**8**	**14**	Ir	**8**
12	Rh	**9**	**15**	Ir	**9**

signals for the methylenic carbon atoms and four signals for the olefinic carbon atoms of the coordinated cyclooctadiene. For compound **14**, only two broad signals for methylenic carbons have been observed. Two of the four signals of the olefinic carbons of the cyclooctadiene, i.e., those located trans to the sulfur atom, appear high-field shifted.[5d]

In the ^{1}H NMR spectra of complexes **10**−**15**, the eight methylenic protons appeared as a unique broad signal. This phenomenon has also been reported for related asymmetric compounds with a similar ligand backbone.[7b] The ^{1}H NMR spectra are in agreement with the expected coordinated pattern for the xylofuranoside protons. The thioether signals are significantly more downfield shifted than the free ligands, which agrees with the coordination of the thioether to the metal center.[8]

The ambient-temperature ^{31}P NMR spectra for the rhodium complexes **10**−**12** showed one sharp doublet due to the ^{103}Rh coupling. Iridium complexes **13**−**15** showed one sharp signal. When the temperature was lowered, the presence of two sets of signals in the ^{31}P NMR spectra has been observed in different proportions for complexes **11**, **12**, **14**, and **15**. These results are consistent with the presence of two isomeric forms in fast exchange on the NMR time scale at room temperature for these complexes. These different isomers may be attributed to the two possible diastereoisomers formed when the thioether coordinates to the metal atom (note that the coordinated S atom is a stereogenic center), to different conformers for the seven-membered chelate ring, or to both.

Molecular mechanics calculations were performed for complexes **11**, **12**, **14**, and **15**. Two different diastereoisomers, which differ in the configuration of the sulfur atom and in the conformation of the seven-membered chelate ring, were minimized for each complex. For all complexes, the most stable diastereoisomer has its thioether group in an axial position with an *R* configuration for the sulfur atom, and the chelate ring is in a twist-boat conformation. The less stable diastereoisomers have a boat conformation for the chelate ring and the thioether group is in equatorial position with the sulfur in an *S* configuration.

The rate constants (k) for the fluxional process have been determined from the observed and calculated variable-temperature ^{31}P NMR spectra of complexes **11**, **12**, **14**, and **15**.

The enthalpies of activation ($\Delta H^{\ddagger}$) and entropies of activation ($\Delta S^{\ddagger}$) were calculated from the Eyring equation[13] and the Eyring plots,[14] while Gibbs free energies ($\Delta G^{\ddagger}$) of activation were also calculated from the equation $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ (Table 1). The small values calculated for the entropy of activation are characteristic of an intramolecular rearrangement process and make $\Delta G^{\ddagger}$ relatively insensitive to temperature changes.[6c] From these values we can conclude that, for this fluxional process, complexes **11** and **14** show a higher energy barrier than complexes **12** and **15**.

Table 1. Thermodynamic Data Obtained from VT ^{31}P NMR Spectroscopy

complex	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta G^{\ddagger}_{273K}$ (kJ mol^{-1})
11	37.4 ± 4.0	27.4 ± 4.9	29.9 ± 4.6
12	31.9 ± 3.2	25.8 ± 5.1	24.8 ± 4.5
14	38.7 ± 4.3	28.6 ± 6.2	30.9 ± 5.1
15	32.6 ± 3.7	26.4 ± 5.8	25.4 ± 4.8

Asymmetric Hydroformylation of Styrene. Thioether-phosphite ligands **7**−**9** were tested in the rhodium-catalyzed asymmetric hydroformylation of styrene. The catalysts were prepared in situ for 16 h by adding the corresponding thioether-phosphite to $[Rh(acac)(CO)_2]$ as catalyst precursor (acac = acetylacetonate, T = 313 K, P = 5 and 25 bar of syn gas, toluene as a solvent).[6c,d] Excess ligand was always added to avoid the formation of achiral active species $HRh(CO)_4$.[15] Good conversions (>99% in 5 h) and excellent regioselectivities in 2-phenylpropanal (94%) but practically null enantiomeric excesses were found for all ligands.

Solution Structure of the Species Formed during the Reaction of $[Rh(acac)(CO)_2]$ with 7 under Hydroformylation Conditions. High-pressure spectroscopic studies have revealed that Rh-thiolate-based catalyst precursors evolve under hydroformylation conditions to form thiolate-free mononuclear rhodium catalysts.[16,17] With chiral Rh-dithioether systems the low enantioselectivities have been attributed to the formation of an unfavorable mixture of diastereoisomers.[18] However, the presence of the dithioether ligand coordinated to rhodium during all the intermediates of the catalytic cycle has been questioned. Recent studies in our group[19] suggested the presence of dithioether-free mononuclear rhodium catalysts. Nevertheless, no spectroscopic evidence has been reported. In this context, an important question is the role of the chiral thioether moiety in the Rh-thioether systems. Phosphite-thioether ligands used in this work offer the possibility of using ^{31}P NMR spectroscopy to answer this question.

To obtain information about the intermediate species formed during the hydroformylation process, we made a spectroscopic study of the solutions produced when 5 and 25 bar of syn gas were added to a solution of $[Rh(acac)(CO)_2]$/**7** in toluene-d_8 in two different P−S/Rh ratios: (a) P−S/Rh = 1.1 and (b) P−S/Rh = 2.

(13) (a) The assumption is used that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are constant over the temperature range (293−203 K) employed. (b) Eyring equation: $kT^{-1} = k_B h^{-1} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$ with $k_B = 1.38 \times 10^{-23}$ J K^{-1} and $h = 6.63 \times 10^{-34}$ J s.

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Table 2. Selected NMR Data of the Species Formed in the Reaction of [Rh(acac)(CO)$_2$]/7 with CO/H$_2$[a]

	^{31}P{^{1}H}		^{1}H		
complex	δ	J_{Rh-P} (Hz)	δ_{Me-S}	δ_H	J_{P-H} (Hz)
16	154.3 (8)	208.8	2.14 (8)	−9.63 (33)	76.0
17	154.6 (17)	240.5	2.11 (17)	−9.84[c](67)	
18[b]	143.8 (75)	194	2.62[c] (75)		

[a] Experimental relative abundance in parentheses. [b] $J_{P-P} = 5.5$ Hz; $^1J_{Rh-Rh} = 286.6$ Hz. [c] Broad signal.

The ^{31}P{^{1}H} NMR spectrum of solution (a) shows three sets of signals at 154.3, 154.6, and 143.8 ppm at a ratio of 8:17:75 (Table 2). The ^{1}H NMR of solution (a) shows three sets of signals, in the low-field region, for the SMe protons at a ratio of 8:17:75, and in the high-field region there are two hydride signals at a ratio of 33:67 (Table 2). The ^{31}P{^{1}H} NMR spectrum of solution (b) shows signals only at 154.6 and 143.8 ppm. In the hydride region of the ^{1}H NMR spectrum of solution (b) only the broad signal at −9.84 ppm is observed, which could not be resolved by lowering the temperature.

The phosphorus signal at 143.8 ppm (Figure 1a) exhibits a complex pattern typical for an AA′XX′ spin system. Simulation for this species (Figure 1b) proves that the two phosphorus atoms are chemically equivalent on the NMR time scale at 40 °C. In the ^{1}H NMR spectrum the MeS protons appear at 2.62 ppm as a broad band, which indicates that the thioether groups are coordinated to the rhodium atoms.[8] These NMR data are consistent for an inactive dimeric species **18** (Scheme 3, Table 2).[16] Surprisingly the rhodium−rhodium coupling constant ($^1J_{Rh-Rh} = 286.6$ Hz) is larger than with the related carbonyl diphosphine and diphosphite dimers [Rh$_2$(CO)$_{8-x}$L$_x$] reported in the literature.[16] It has been reported that under synthesis gas atmosphere these dimer complexes are in equilibrium with the monomeric rhodium hydride complexes (see below), the position of which depends on the hydrogen concentration, and can be shifted to the dinuclear species by increasing the CO/H$_2$ ratio.[16] For further information about this species, we recorded the FT-IR spectrum of the final solution under atmospheric conditions (after depressurization, at a ratio CO/H$_2$ = 4, where the ^{31}P NMR shows only the signal at 143.8 ppm). This shows several strong bands in the bridging carbonyl (1799 and 1832 cm^{-1}) and terminal carbonyl (2008 and 2020 cm^{-1}) regions. This is in agreement with the nature of species **18**.[16]

The ^{31}P doublet at 154.3 ppm ($^1J_{Rh-P} = 208.8$ Hz) and the hydride signal at −9.63 ppm ($^2J_{P-H} = 76$ Hz) were attributed to the mononuclear hydride-rhodium complex **16** (Scheme 3). Small cis phosphorus−hydride coupling constants (between 1 and 30 Hz) are reported in [HRhPP(CO)$_2$] complexes with bisequatorially coordinating diphosphite ligands.[6c,d] In contrast, relatively large phosphorus−hydride coupling constants are found for fluxional [HRh{P(OCH$_2$)$_3$CPr^n}$_4$] and [HRh{P(OC$_2$H$_5$)$_3$}$_4$] complexes in the slow exchange. The trans relationship is responsible for the large $^2J_{Pax-H}$ (152 and 179, respectively) found for these complexes.[20] The intermediate phosphorus−hydride coupling constant for complex **16** (Table 2) suggests a time-averaged cis−trans relationship between the phosphorus and hydride nuclei. It is important to note that the methyl protons of the thioether group appear more high-field shifted (Table 2) than the coordinated ones and are very similar to the corresponding protons in the free ligand **7**, which indicates that the thioether is replaced by CO and agrees with the nature of species **16**.

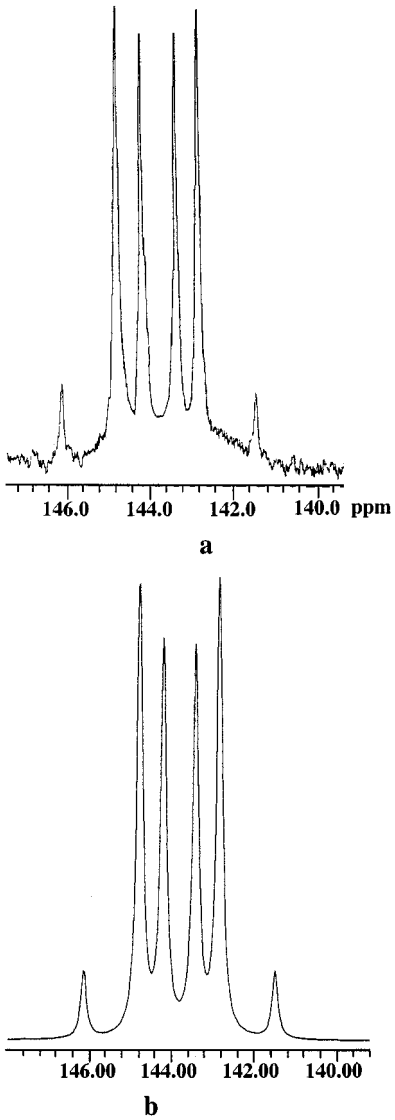

Figure 1. Observed (a) and calculated (b) 121.4 MHz ^{31}P-{^{1}H} NMR spectra for species **17** at 40 °C.

The phosphorus doublet at 154.6 ppm ($^1J_{Rh-P} = 240.5$ Hz) and the hydride signal at −9.84 ppm were attributed to the mononuclear species **17**. The fact that there is only one doublet for this AA′X spin system in the ^{31}P NMR spectra indicates a rapid exchange between both monodentate ligands. The average rhodium−phosphorus coupling constant of 240.5 Hz is characteristic of bisequatorially diphosphite [HRh(CO)$_2$(PP)] complexes.[6c,d,11c] Also the methyl protons of the thioether group appear more high-field shifted than the coordinated ones, which indicates that the thioether is replaced by CO and agrees with the nature of species **17**.

In summary, these HP NMR results show that under hydroformylation conditions the thioether moiety is not coordinated to rhodium in the mononuclear hydride-

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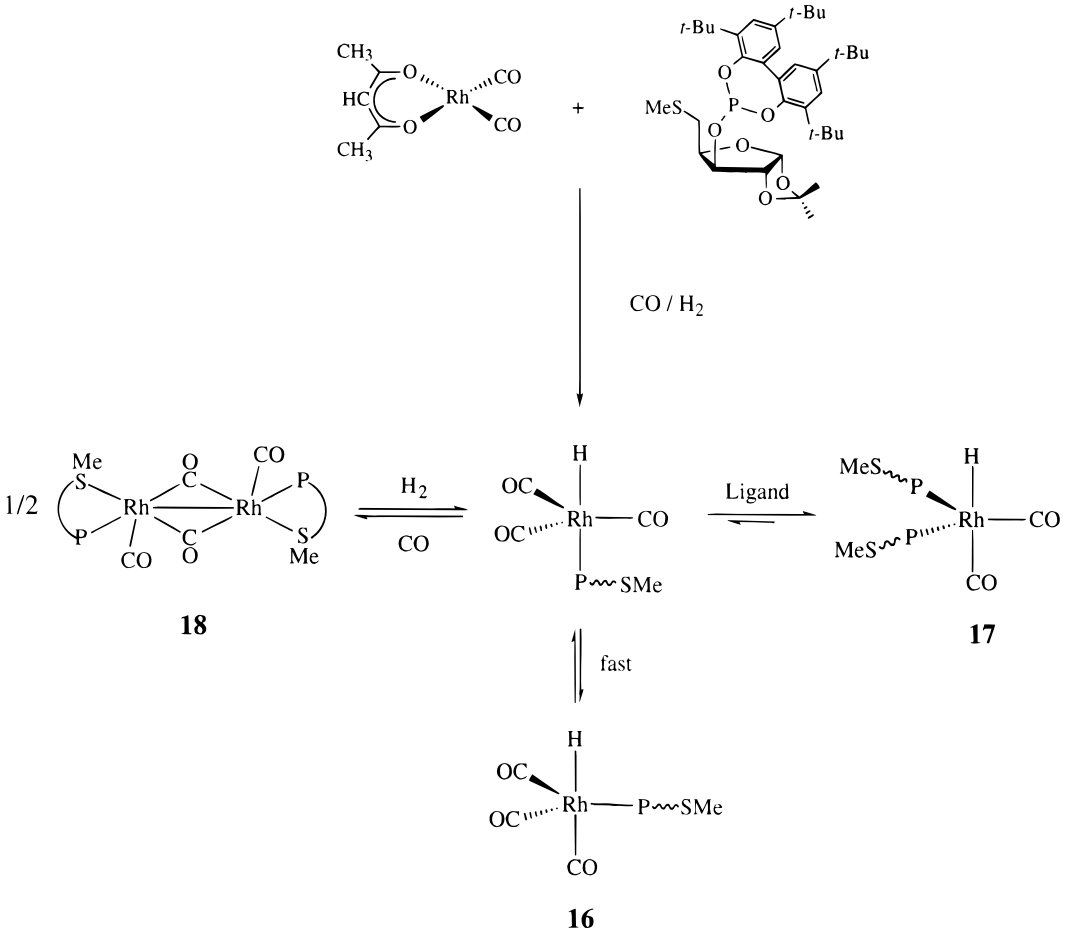
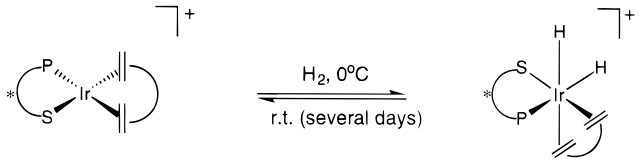
Scheme 3



Scheme 4. Preparation of *cis*-Dihydrido Iridium Complexes 19−21.



19 P-S = **7**

20 P-S = **8**

21 P-S = **9**

rhodium complexes. This could explain the low enantiomeric excesses obtained with thioether systems.[5b,9]

Synthesis of *cis*-Dihydridoiridium Complexes. Bubbling H_2 at 0 °C through CD_2Cl_2 solutions of Ir(I) complexes **13**−**15** afforded the corresponding *cis*-dihydridoolefin species **19**−**21** in quantitative yield. (Scheme 4).

These complexes were isolated by precipitation with hexane as pale yellow moderately air-stable solids. They were characterized by elemental analysis, IR spectroscopy, and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The FT-IR spectra in KBr pellets show the two expected asymmetric absorption bands ν_{Ir-H} (see Experimental Section) for a *cis*-dihydridoiridium(III) compound.[8a,21]

The nature of these hydrido ligands was confirmed by measuring T_{1min} with ^{1}H relaxation rates.[22] For all complexes the hydride resonances have T_{1min} values of around 300 ms in CD_2Cl_2 at −70 °C and 300 MHz, which are consistent with classical hydrides.[22]

The ^{31}P{^{1}H} NMR spectra consist of one sharp signal for these complexes, which do not show any splitting when the temperature is lowered to −90 °C and raised to 40 °C.

In the high-field region of the ^{1}H NMR spectra of the CD_2Cl_2 solutions of **19**−**21** there are two doublets due to ^{31}P coupling. The phosphorus−hydride coupling constants are in agreement with a structure in which the phosphorus atom is located trans to one hydride, and there is no interconversion between the two hydride atoms.[23]

The expected NMR pattern for the furanoside nucleus has been observed (Table 3).

The shapes of the ^{1}H and the ^{13}C NMR spectra for all the complexes do not change when their solutions are cooled to −90 °C. In particular, hydride, methyl, isopropyl, and phenyl resonances do not split, which indicates that only one diastereoisomer is present.

In the 2D-NOESY spectrum of complex **19** there is close contact between the H-9 and the methyl protons of the MeS group, which is consistent with an equatorial

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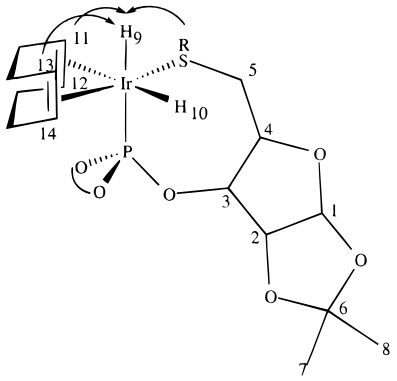
Table 3. Selected ^{1}H and ^{13}C NMR Data for *cis*-Dihydridoiridium Complexes 19−21[a]



	19		20		21	
position	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	5.83 (d) $^3J_{1-2}=3.3$	104.9	5.81 (d) $^3J_{1-2}=3.3$	105.2	5.77 (d) $^3J_{1-2}=3.6$	104.9
2	4.73 (d)	84.0 (d) $^3J_{P-C}=6.1$	4.66 (d)	83.7 (d) $^3J_{P-C}=6.9$	4.73 (d)	84.0 (d) $^3J_{P-C}=7.5$
3	5.26 (dd) $^3J_{3-P}=11.7$ $^3J_{3-4}=2.1$	80.0	5.15 (d) $^3J_{3-P}=13.2$	80.5	5.30(dd) $^3J_{3-P}=10.8$ $^3J_{3-4}=1.8$	81.1
4	4.67 (ddd)	75.8	4.63 (m)	78.1	4.55 (m)	76.4
5	3.93 (dd) $^3J_{5-4}=3.3$ $^2J_{5-5'}=13.8$	28.5	4.07 (dd) $^3J_{5-4}=1.8$ $^2J_{5-5'}=14.7$	31.9	4.01 (dd) $^3J_{5-4}=2.1$ $^2J_{5-5'}=15$	31.7
5′	3.08 (dd) $^3J_{5'-4}=10.8$		3.00 (dd) $^3J_{5'-4}=14.7$		3.21 (dd) $^3J_{5'-4}=11.7$	
6		113.7		113.4		113.6
7	1.11 (s)	26.4	1.13 (s)	26.0	1.24 (s)	26.5
8	1.32 (s)	26.9	1.36 (s)	26.3	1.38 (s)	26.7
9	−13.34 (d) $^2J_{9-P}=19.5$		−13.21 (d) $^2J_{9-P}=18.3$		−12.95 (d) $^2J_{9-P}=18.9$	
10	−14.09 (d) $^2J_{9-P}=9$		−14.18 (d) $^2J_{9-P}=6$		−13.91 (d) $^2J_{9-P}=9.9$	
11	4.30 (m)	96.3 (d) $J_{P-C}=12.1$	3.95 (m)	95.8 (d) $J_{P-C}=11.9$	4.21 (m)	96.1(d) $J_{P-C}=12.0$
12	5.42 (m)	89.3 (d) $J_{P-C}=19.9$	5.43 (m)	87.7 (d) $J_{P-C}=20.5$	5.39 (m)	92.2 (d) $J_{P-C}=18.9$
13	4.54 (m)	79.9 (m)	4.44 (m)	76.7 (m)	4.50 (m)	77.5 (m)
14	4.54 (m)	72.3 (m)	4.44 (m)	71.6 (m)	4.44 (m)	73.4 (m)

[a] In CD_2Cl_2 solvent at 293 K. Chemical shifts in ppm. Coupling constants in Hz. Abbreviations: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublets of doublets; m, multiplet.

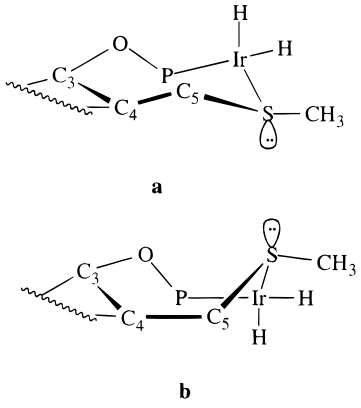


Figure 2. Two possible diastereoisomers, **a** and **b**, with the thioether group located in equatorial position for complex **19**.

location of this group. H-9 also shows close contact with the olefinic protons H-11 and H-13. Figure 2 shows the two possible diastereoisomers, **a** and **b**, with the thioether group located in equatorial position for complex **19**.

The high value of the coupling constant $^3J_{4-5'}$ indicates that the dihedral angle between protons H-4 and H-5′ is nearly 180°, while the low value of the $^3J_{4-5}$ indicates that the dihedral angle between H-4 and H-5 is nearly 90°.[24] When these results are compared with the relative positions of protons H-4, H-5, and H-5′ in the different diastereoisomers **a** and **b**, we can see that the diastereoisomer **a**, with an *S* configuration for the sulfur atom and with a chelate ring in a chair conformation, is present. Molecular mechanics calculations also show that the most stable diastereoisomer is **a**.

There are similar cross-peaks in the 2D-NOESY spectrum of complexes **20** and **21**.

In summary, the NMR study shows that compounds $[IrH_2(cod)(L)]BF_4$ **19**−**21** are present in only one diastereoisomeric form. It is important to note that this behavior is unusual since there are generally several diastereoisomers for these types of complexes.[5c,8] This unprecedented result (note that the coordinated S atom

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and the metal center are stereogenic centers) encouraged the use of these complexes in asymmetric hydrogenation.

Asymmetric Hydrogenation of Itaconic Acid. The iridium complexes containing the thioether-phosphite ligands **7**−**9** were tested in the asymmetric hydrogenation of itaconic acid at 1 bar of H_2 and 40 °C. The catalytic system was generated in situ from $[Ir(cod)_2]BF_4$ and the corresponding ligand.

Good conversions (100% in 12 h) were achieved in these hydrogenation reactions.

Enantioselectivities were higher when the catalyst precursors containing ligands **8** and **9** were used (51% and 47% with ligands **8** and **9**, respectively, vs 22% with **7**).

Enantiomeric excesses were moderate, but under milder conditions they were similar to the best ones for other mixed P,S-donor ligand systems reported in the literature.[5i,l]

Experimental Section

General Comments. All syntheses were performed using standard Schlenk techniques under argon atmosphere. The compounds $[Rh(cod)_2]BF_4$,[25] $[Ir(cod)_2]BF_4$,[25] 1,2-*O*-isopropylidene-α-D-xylofuranose **1**[26] and phosphorochloridite **6**[27] were prepared by previously described methods. Solvents were purified by standard procedures. All other reagents were used as commercially available. Elemental analyses were performed on a Carlo Erba EA-1108 instrument. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ (^1H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. All assignments in NMR spectra were determined by COSY and HETCOR spectra. Standard-pulse sequences were employed for the ^1H-2D-NOESY.[28] The phase-sensitive NOESY experiments used mixing times of 0.4 s. Proton T_1 studies were performed using the standard inversion recovery 180°−τ−90° pulse sequence method.[22] VG-Autospect equipment was used for FAB mass spectral analyses. The matrix was *m*-nitrobenzyl alcohol. Gas chromatographic analyses were run on a Hewlett-Packard HP 5890A instrument (split/splitless injector, J&W Scientific, Ultra-2 25 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas 150 kPa He, FID detector) equipped with a Hewlett-Packard HP 3396 series II integrator. Hydroformylation reactions were carried out in a homemade 100 mL stainless steel autoclave. Enantiomeric excesses were measured after oxidation of the aldehydes to the corresponding carboxylic acids on a Hewlett-Packard HP 5890A gas chromatograph (split/splitless injector, J&W Scientific, FS-Cyclodex β-I/P 50 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas 100 kPa He, FID detector). Absolute configuration was determined by comparing the retention times with optical pure (*S*)-(+)-2-phenylpropionic and (*R*)-(−)-2-phenylpropionic acids. Infrared spectra were recorded on a Midac Grams/386 spectrophotometer. Optical rotations were measured at 25 °C on a Perkin-Elmer 241 MC polarimeter. Hydrogenation reactions were performed in a previously described hydrogen-vacuum line.[29] Enantiomeric excesses were measured by polarimetry.[30] Molecular mechanics calculations were carried out with the program CERIUS[31] developed by Molecular Simulations (MSI) and the force field UFF developed by Rappe.[32] The electrostatic interactions were taken into account from the atomic changes generated by Qeq method.[33]

1,2-*O*-Isopropylidene-5-*O*-trifluoromethanesulfonyl-α-D-(−)-xylofuranose (2). Anhydrous pyridine (0.3 mL, 3 mmol) was added to a solution of 1,2-*O*-isopropylidene-α-D-xylofuranose (0.57 g, 3 mmol) in dichloromethane (20 mL). After 10 min, trifluoromethanesulfonic anhydride (0.5 mL, 3 mmol) was added dropwise at −20 °C, and the mixture was allowed to react at room temperature for 20 min, after which the solvent evaporated. The residue was purified by column chromatography (hexane/ethyl acetate, 2:1) to produce the triflate (0.6 g, 65%) as a white solid (which decomposed after standing for 12 h at room temperature). Anal. Calcd for $C_9H_{13}F_3O_7S$: C, 33.54; H, 4.07; S, 9.95. Found: C, 34.09; H, 4.42; S, 9.08. ^1H NMR ($CDCl_3$): δ 1.31 (s, 3H, C*Me*), 1.49 (s, 3H, C*Me*), 2.21 (s, 1H, OH), 4.33 (m, 1H, H-3), 4.45 (ddd, 1H, H-4, $^3J_{4-5} = 6.1$ Hz, $^3J_{4-5'} = 6.0$ Hz, $^3J_{4-3} = 3.9$ Hz), 4.52 (d, 1H, H-2, $^3J_{2-1} = 3.3$ Hz), 4.67 (dd, 1H, H-5′, $^2J_{5-5'} = 10.8$ Hz, $^3J_{5'-4} = 6.0$ Hz), 4.77 (dd, 1H, H-5, $^2J_{5'-5} = 10.8$ Hz, $^3J_{5-4} = 6.1$ Hz), 5.96 (d, 1H, H-1, $^3J_{1-2} = 3.3$ Hz).^{13}C NMR ($CDCl_3$): δ 26.1 (C*Me*), 26.7 (C*Me*), 73.3 (C-5), 74.5 (C-3), 77.4 (C-4), 85.2 (C-2), 105.0 (C-1), 112.5 (*C*Me), 118.1 (q, CF_3, $^1J_{C-F} = 324$ Hz). $[\alpha]^{20}_D = -17.5$ ($c = 1$, $CHCl_3$).

1,2-*O*-Isopropylidene-5-methylsulfanyl-α-D-(−)-xylofuranose (3). A suspension of NaH (0.56 g, 23 mmol) in paraffin, cleaned twice in hexane, in THF (15 mL) was cooled to −78 °C, and methanethiol (0.5 mL, 9 mmol) at −78 °C was added. The resulting solution was stirred and the temperature raised to 0 °C. After 5 min the solution was cooled to −78 °C and a solution of compound **2** (1 g, 3.1 mmol) in THF (10 mL) was added. After 45 min, water (50 mL) was added, the solvent was evaporated, and the residue was extracted with dichloromethane (3 × 50 mL). The extract was dried over magnesium sulfate and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate, 2:1) to produce 0.5 g (71%) as a white solid. Anal. Calcd for $C_9H_{16}O_4S$: C, 49.07; H, 7.32; S, 14.55. Found: C, 49.12; H, 7.34; S, 13.99. ^1H NMR ($CDCl_3$): δ 1.32 (s, 3H, C*Me*), 1.50 (s, 3H, C*Me*), 2.21 (s, 3H, Me−S), 2.53 (d, 1H, OH, $J = 5.7$ Hz), 2.84 (m, 2H, H-5′, H-5), 4.26 (dd, 1H, H-3, $J = 5.7$ Hz, $^3J_{3-4} = 2.8$ Hz), 4.33 (m, 1H, H-4), 4.51 (d, 1H, H-2, $^3J_{2-1} = 3.9$ Hz), 5.93 (d, 1H, H-1, $^3J_{1-2} = 3.9$ Hz). ^{13}C NMR ($CDCl_3$), δ (ppm): 16.1 (Me−S), 25.9 (C*Me*), 26.5 (C*Me*), 31.2 (C-5), 75.0 (C-3), 79.3 (C-4), 85.1 (C-2), 104.7 (C-1), 111.7 (*C*Me). $[\alpha]^{20}_D = -59.4$ ($c = 1$, $CHCl_3$).

1,2-*O*-Isopropylidene-5-isopropylsulfanyl-α-D-(−)-xylofuranose (4). A solution of 2-propanethiol (0.52 mL, 5.6 mmol) in THF (6 mL) was added to a suspension of NaH (0.56 g, 23 mmol) in paraffin, cleaned twice in hexane, in THF (8 mL). After 30 min at room temperature, the suspension was cooled to 78 °C, and a solution of **2** (1 g, 3.1 mmol) in THF (10 mL) was added. After 20 min, water (50 mL) was added, the solvent was evaporated, and the residue was extracted with dichloromethane (3 × 50 mL). The extract was dried over magnesium sulfate and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate, 2:1) to produce 0.55 g (72%) as a white solid. Anal. Calcd for $C_{11}H_{20}O_4S$: C, 53.20; H, 8.12; S, 12.91. Found: C, 53.04; H, 8.31; S, 12.78. ^1H NMR ($CDCl_3$): δ 1.30 (m, 9H, C*Me*, Me), 1.50 (s, 3H, C*Me*), 2.85 (m, 2H, H-5′, H-5), 3.1 (m, 1H, CH−S), 4.29 (m, 1H, H-3), 4.33

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(m, 1H, H-4), 4.53 (d, 1H, H-2, $^3J_{2-1}$ = 3.9 Hz), 5.93 (d, 1H, H-1, $^3J_{1-2}$ = 3.9 Hz). ^{13}C NMR ($CDCl_3$): δ 23.3 (Me), 26.1 (C*Me*), 26.7 (C*Me*), 27.8 (C-5), 35.6 (CH−S), 75. (C-3), 79.5 (C-4), 85.1 (C-2), 104.8 (C-1), 111.7 (*C*Me). $[\alpha]^{20}_D = -44.2$ (c = 1, $CHCl_3$).

1,2-*O*-Isopropylidene-5-phenylsulfanyl-α-D-(−)-xylofuranose (5). Treatment of benzenethiol (0.5 mL, 4.9 mmol) and compound **2** as described for compound **4** afforded compound **5**, which was purified by column chromatography (hexane/ethyl acetate, 2:1). Yield: 0.62 g (72%) of a white solid. Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43; S, 11.35. Found: C, 59.39; H, 6.51; S, 11.01. ^{1}H NMR ($CDCl_3$): δ 1.29 (m, 3H, C*Me*), 1.42 (s, 3H, C*Me*), 1.78 (s, 1H, OH), 3.15 (dd, 1H, H-5′, $^2J_{5'-5}$ = 12.6 Hz, $^3J_{5'-4}$ = 9.2 Hz), 3.31 (dd, 1H, H-5, $^2J_{5-5'}$ = 12.6 Hz, $^3J_{5-4}$ = 4.8 Hz), 4.26 (m, 1H, H-3), 4.31 (m, 1H, H-4), 4.51 (d, 1H, H-2, $^3J_{2-1}$ = 3.6 Hz), 5.91 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 7.2−7.5 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 26.0 (C*Me*), 26.5 (C*Me*), 31.2 (C-5), 74.6 (C-4), 79.2 (C-3), 87.5 (C-2), 104.7 (C-1), 111.8 (*C*Me), 126.8, 129.1, 130.1, 135.2 (CH═, Ph). $[\alpha]^{20}_D$ = −59.9 (c = 1, $CHCl_3$).

1,2-*O*-Isopropylidene-3-[(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite]-5-methylsulfanyl-D-(+)-xylofuranose (7). In situ formed **6** (2.2 mmol) was dissolved in toluene (5 mL), to which pyridine (0.36 mL, 4.6 mmol) was added. 1,2-*O*-Isopropylidene-5-methylsulfanyl-α-D-xylofuranose (0.44 g, 2 mmol) was azeotropically dried with toluene (3 × 1 mL) and dissolved in toluene (10 mmol), to which pyridine (0.36 mL, 4.6 mmol) was added. The 1,2-*O*-isopropylidene-5-methylsulfanyl-α-D-xylofuranose solution in toluene was added in 30 min to the solution of **6** at room temperature. The reaction mixture was stirred overnight at reflux, and the pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam, which was purified by flash column chromatography (eluent: toluene, R_f 0.35) to produce 0.7 g (53%) of a white powder (mp 81−82 °C). Anal. Calcd for $C_{37}H_{55}O_6S$: C, 67.45; H, 8.41; S, 4.87. Found: C, 67.75; H, 8.45; S, 4.98. ^{31}P NMR ($CDCl_3$): δ 145.4 (s, 1P). ^{1}H NMR ($CDCl_3$): δ 1.21 (s, 3H, C*Me*), 1.39 (s, 18H, *t*-Bu), 1.47 (s, 3H, C*Me*), 1.50 (s, 9H, *t*-Bu), 1.53 (s, 9H, *t*-Bu), 2.0 (Me-S), 2.59 (m, 2H, H-5, H-5′), 4.11 (m, 1H, H-2), 4.21 (m, 1H, H-4), 4.63 (dd, 1H, H-3, $^3J_{3-4}$ = 8.4 Hz, $^3J_{3-P}$ = 2.1 Hz), 5.62 (d, 1H, H-1, $^3J_{1-2}$ = 3.3 Hz), 7.0−7.4 (m, 4H, Ph).^{13}C NMR ($CDCl_3$): δ 16.1 (Me−S), 26.1 (C*Me*), 26.6 (C*Me*), 31.0 (CH_3, *t*-Bu), 31.2 (CH_3, *t*-Bu), 31.4 (CH_3, *t*-Bu), 31.6 (C-5), 34.5 (C, *t*-Bu), 35.2 (C, *t*-Bu), 76.6 (C-3), 79.8 (d, C-4, J_{C-P} = 4.6 Hz), 83.9 (d, C-2, J_{C-P} = 1.8 Hz), 104.7 (C-1), 111.6 (*C*Me), 124.2, 124.3, 126.7, 126.8 (CH═, Ph), 132.8, 140.0, 140.3, 146.8 (C, Ph). $[\alpha]^{20}_D$ = +85.2 (c = 1, $CHCl_3$).

1,2-*O*-Isopropylidene-3-[(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite]-5-isopropylsulfanyl-D-(+)-xylofuranose (8). Treatment of in situ formed **6** (2.2 mmol) and 1,2-*O*-isopropylidene-5-isopropylsulfanyl-α-D-xylofuranose (0.49 g, 2 mmol) as described for compound **7** afforded thioether-phosphite **8**, which was purified by flash column chromatography (eluent: toluene, R_f 0.55). Yield: 0.82 g (59%) of a white powder (mp 80−82 °C). Anal. Calcd for $C_{39}H_{59}O_6S$: C, 68.19; H, 8.66; S, 4.67. Found: C, 67.94; H, 8.55; S, 4.78. ^{31}P NMR ($CDCl_3$): δ 144.9 (s, 1P). ^{1}H NMR ($CDCl_3$): δ 1.17 (s, 3H, C*Me*), 1.24 (m, 6H, Me), 1.38 (s, 18H, *t*-Bu), 1.44 (s, 3H, C*Me*), 1.49 (s, 9H, *t*-Bu), 1.54 (s, 9H, *t*-Bu), 2.80 (m, 2H, H-5, H-5′), 2.99 (sp, 1H, CH−S, $^3J_{H-H}$ = 6.3 Hz), 4.14 (m, 1H, H-2), 4.29 (m, 1H, H-4), 4.77 (dd, 1H, H-3, $^3J_{3-4}$ = 8.4 Hz, $^3J_{3-P}$ = 2.4 Hz), 5.71 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 7.0−7.5 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 23.3 (Me), 23.4 (Me), 26.2 (C*Me*), 26.7 (C*Me*), 28.2 (C-5), 31.2 (CH_3, *t*-Bu), 31.3 (CH_3, *t*-Bu), 31.4 (CH_3, *t*-Bu), 31.5 (CH_3, *t*-Bu), 34.6 (C, *t*-Bu), 35.3 (CH−S), 35.4 (C, *t*-Bu), 76.8 (C-3), 79.9 (d, C-4, J_{C-P} = 4.8 Hz), 84.0 (C-2), 104.7 (C-1), 111.5 (*C*Me), 124.2, 124.3, 126.7, 126.8 (CH═, Ph), 132.7, 132.9, 140.0, 140.3, 145.4, 146.7 (C, Ph). $[\alpha]_D^{20}$ = +112.5 (c = 1, $CHCl_3$).

1,2-*O*-Isopropylidene-3-[(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite]-5-phenylsulfanyl-D-(+)-xylofuranose (9). Treatment of in situ formed **6** (2.2 mmol) and 1,2-*O*-isopropylidene-5-phenylsulfanyl-α-D-xylofuranose (0.56 g, 2 mmol) as described for compound **7** afforded thioether-phosphite **9**, which was purified by flash column chromatography (eluent: toluene, R_f 0.35). Yield: 0.65 g (43%) of a white powder (mp 82−84 °C). Anal. Calcd for $C_{37}H_{55}O_6S$: C, 67.45; H, 8.41; S, 4.87. Found: C, 67.75; H, 8.45; S, 4.98. ^{31}P NMR ($CDCl_3$): δ 145.1 (s, 1P). ^{1}H NMR ($CDCl_3$): δ 1.05 (s, 3H, C*Me*), 1.23 (m, 3H, C*Me*), 1.27 (s, 18H, *t*-Bu), 1.38 (s, 9H, *t*-Bu), 1.43 (s, 9H, *t*-Bu), 2.99 (m, 2H, H-5, H-5′), 4.08 (m, 1H, H-2), 4.15 (m, 1H, H-4), 4.66 (dd, 1H, H-3, $^3J_{3-4}$ = 8.4 Hz, $^3J_{3-P}$ = 2.7 Hz), 5.60 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 7.0−7.4 (m, 9H, Ph). ^{13}C NMR ($CDCl_3$): δ 26.2 (C*Me*), 26.5 (C*Me*), 31.15 (C-5, CH_3, *t*-Bu), 31.4 (CH_3, *t*-Bu), 34.5 (C, *t*-Bu), 35.3 (C, *t*-Bu), 76.5 (C-3), 78.5 (d, C-4, J_{C-P} = 4.6 Hz), 84.0 (d, C-2, J_{C-P} = 1.7 Hz), 104.7 (C-1), 111.7 (*C*Me), 124.2, 124.3, 126.7, 126.8, 129.0, 130.0 (CH═, Ph), 132.7, 132.9, 135.4, 140.0, 140.3, 146.8 (C, Ph). $[\alpha]^{20}_D$ = +49.1 (c = 1, $CHCl_3$).

Preparation of Olefinic Complexes. General Procedure. Thioether-phosphite ligand (0.1 mmol) was added to a solution of $[M(cod)_2]BF_4$ (0.1 mmol) in dichloromethane (2 mL). After 10 min, the desired products were obtained by precipitation with hexane.

[Rh(cod)(7)]BF_4 (10): 83 mg (86%) as a yellow solid. Anal. Calcd for $C_{45}H_{67}BF_4O_6PRhS$: C, 56.49; H, 7.06; S, 3.34. Found: C, 56.67; H, 7.21; S, 3.43. FAB *m*/*z*: 869 [M^+]. IR (KBr pellet, cm^{-1}): $\nu(BF_4)$ 1070 (s), 450 (m). ^{31}P NMR ($CDCl_3$): δ 139.8 (d, 1P, $^1J_{Rh-P}$ = 243.8 Hz).^{1}H NMR ($CDCl_3$): δ 1.21 (s, 3H, C*Me*), 1.33 (s, 9H, *t*-Bu), 1.34 (s, 9H, *t*-Bu), 1.40 (s, 3H, C*Me*), 1.51 (s, 9H, *t*-Bu), 1.62 (s, 9H, *t*-Bu), 2.34 (m, 8H, CH_2), 2.67 (Me−S), 3.12 (m, 1H, H-5′), 3.32 (m, 1H, H-5), 3.86 (d, 1H, H-2, $^3J_{2-1}$ = 3.3 Hz), 4.59 (m, 1H, H-4), 4.93 (m, 3H, H-3, CH═), 5.53 (m, 2H, CH═), 5.60 (d, 1H, H-1, $^3J_{1-2}$ = 3.3 Hz), 7.0−7.5 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 20.4 (Me−S), 26.0 (C*Me*), 26.5 (C*Me*), 28.0 (CH_2), 28.8 (CH_2), 30.6 (CH_3, *t*-Bu), 31.1 (CH_3, *t*-Bu), 31.2 (CH_3, *t*-Bu), 31.3 (C-5), 31.5 (CH_2), 31.9 (CH_2), 34.5 (C, *t*-Bu), 35.3 (C, *t*-Bu), 76.1 (C-4), 80.0 (m, CH═), 83.9 (d, C-2, J_{P-C} = 8.0 Hz), 85.1 (m, C-3), 87.1 (m, CH═), 104.8 (C-1), 110.8 (dd, CH═, J_{P-C} = 13.7 Hz, J_{Rh-C} = 5.1 Hz), 112.9 (*C*Me), 115.2 (dd, CH═, J_{P-C} = 12.6 Hz, J_{Rh-C} = 6.1 Hz), 124.8, 124.9, 127.2, 128.2 (CH═, Ph), 130.0, 130.8, 139.0, 139.4, 148.7, 148.9 (C, Ph).

[Rh(cod)(8)]BF_4 (11): 86 mg (87%) as a yellow solid. Anal. Calcd for $C_{47}H_{71}BF_4O_6PRhS$: C, 57.32; H, 7.27; S, 3.25. Found: C, 56.98; H, 7.41; S, 3.49. FAB *m*/*z*: 897 [M^+]. IR (KBr pellet, cm^{-1}): $\nu(BF_4)$ 1071 (s), 450 (m). ^{31}P NMR ($CDCl_3$): δ 131.3 (d, 1P, $^1J_{Rh-P}$ = 266.1 Hz). ^{1}H NMR ($CDCl_3$): δ 1.18 (s, 3H, C*Me*), 1.33 (s, 9H, *t*-Bu), 1.34 (s, 9H, *t*-Bu), 1.42 (s, 3H, C*Me*), 1.55 (m, 15H, *t*-Bu, Me), 1.59 (s, 9H, *t*-Bu), 2.46 (m, 8H, CH_2), 3.19 (m, 1H, H-5′), 3.44 (m, 2H, H-5, CH−S), 3.51 (d, 1H, H-2, $^3J_{2-1}$ = 3.3 Hz), 4.48 (m, 1H, H-4), 4.76 (m, 3H, H-3, CH═), 5.51 (d, 1H, H-1, $^3J_{1-2}$ = 3.3 Hz), 5.72 (m, 2H, CH═), 7.0−7.5 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 22.5 (Me), 22.9 (Me), 25.7 (C*Me*), 26.4 (C*Me*), 27.6 (C-5), 28.1 (CH_2), 28.7 (CH_2), 30.8 (CH_3, *t*-Bu), 31.1 (CH_3, *t*-Bu), 31.3 (CH_3, *t*-Bu), 31.5 (CH_2), 32.0 (CH_2), 34.6 (C, *t*-Bu), 35.2 (C, *t*-Bu), 41.3 (CH−S), 77.7 (C-4), 80.5 (m, CH═), 83.0 (d, C-2, J_{P-C} = 5.7 Hz), 84.7 (m, C-3), 86.1 (m, CH═), 104.8 (C-1), 111.98 (dd, CH═, J_{P-C} = 12.6 Hz, J_{Rh-C} = 5.1 Hz), 112.8 (*C*Me), 113.4 (dd, CH═, J_{P-C} = 12.6 Hz, J_{Rh-C} = 5.2 Hz), 124.8, 124.9, 127.5, 128.1 (CH═, Ph), 129.8, 130.8, 138.8, 139.5, 148.4, 148.8 (C, Ph). ^{31}P NMR ($CDCl_3$, 233 K): δ major isomer (65% according to ^{31}P NMR). ^{31}P NMR ($CDCl_3$, 233 K): major isomer 65% δ 135.2 (d, 1P, $^1J_{Rh-P}$ = 255.4 Hz), minor isomer 35% δ 127.8 (d, 1P, $^1J_{Rh-P}$ = 268.5 Hz).

[Rh(cod)(9)]BF_4 (12): 87 mg (88%) as a yellow solid. Anal. Calcd for $C_{50}H_{69}BF_4O_6PRhS$: C, 58.94; H, 6.83; S, 3.14. Found: C, 59.13; H, 7.11; S, 3.34. FAB *m*/*z*: 931 [M^+]. IR (KBr pellet, cm^{-1}): $\nu(BF_4)$ 1070 (s), 450 (m). ^{31}P NMR ($CDCl_3$): δ 131.2 (d, 1P, $^1J_{Rh-P}$ = 257.8 Hz). ^{1}H NMR ($CDCl_3$): δ 1.13 (s, 3H, C*Me*), 1.31 (s, 18H, *t*-Bu), 1.37 (s, 3H, C*Me*), 1.56 (s, 9H, *t*-Bu), 1.59 (s, 9H, *t*-Bu), 2.21 (m, 8H, CH_2), 3.48 (m, 1H, H-5′),

3.66 (m, 2H, H-5, H-2), 4.38 (m, 1H, H-4), 4.84 (m, 3H, H-3, CH═), 5.1 (m, 2H, CH═), 5.65 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 7.0−7.7 (m, 9H, Ph). ^{13}C NMR ($CDCl_3$): δ 25.7 (C*Me*), 26.2 (C*Me*), 27.1 (CH_2), 27.4 (CH_2), 28.0 (CH_2), 30.7 (CH_3, *t*-Bu), 30.9 (CH_3, *t*-Bu), 31.0 (CH_3, *t*-Bu), 31.2 (C-5), 32.3 (CH_2), 34.4 (C, *t*-Bu), 35.1 (C, *t*-Bu), 76.7 (C-4), 80.9 (m, CH═), 83.0 (d, C-2, J_{P-C} = 5.7 Hz), 83.5 (m, C-3), 86.0 (m, CH═), 104.5 (C-1), 112.7 (*C*Me), 113.6 (dd, CH═, J_{P-C} = 12.6 Hz, J_{Rh-C} = 5.1 Hz), 114.8 (dd, CH═, J_{P-C} = 13.7 Hz, J_{Rh-C} = 6.3 Hz), 124.9 (CH═, Ph), 127.0 (C, Ph), 127.3, 127.7 (CH═, Ph), 128.7 (C, Ph), 129.4 (CH═, Ph), 129.8, 130.2 (C, Ph), 130.6, 131.7, 132.7 (CH═, Ph), 138.9, 139.3, 148.4, 148.6 (C, Ph). ^{31}P NMR ($CDCl_3$, 233 K): major isomer 55% δ 127.3 (d, 1P, $^1J_{Rh-P}$ = 252 Hz), minor isomer 45% δ 137.4 (d, 1P, $^1J_{Rh-P}$ = 251 Hz).

[Ir(cod)(7)]BF_4 (13): 91 mg (87%) as an orange solid. Anal. Calcd for $C_{45}H_{67}BF_4O_6PIrS$: C, 51.67; H, 6.46; S, 3.06. Found: C, 52.01; H, 6.54; S, 3.31. FAB *m*/*z*: 959 [M^+]. IR (KBr pellet, cm^{-1}): $\nu(BF_4)$ 1072 (s), 450 (m). ^{31}P NMR ($CDCl_3$): δ 120.4 (s, 1P). ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 3H, C*Me*), 1.36 (s, 18H, *t*-Bu), 1.42 (s, 3H, C*Me*), 1.45 (s, 9H, *t*-Bu), 1.47 (s, 9H, *t*-Bu), 2.50 (m, 8H, CH_2), 2.86 (Me−S), 3.43 (m, 1H, H-5′), 3.91 (m, 1H, H-5), 4.01 (m, 1H, H-2), 4.51 (m, 2H, H-4, CH═), 4.62 (m, 2H, H-3, CH═), 5.18 (m, 2H, CH═), 5.71 (d, 1H, H-1, $^3J_{1-2}$ = 3.9 Hz), 7.1−7.5 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 21.8 (Me−S), 26.2 (C*Me*), 26.7 (C*Me*), 28.4 (C-5), 28.6 (d, CH_2, J = 3.4 Hz), 30.7 (d, CH_2, J = 2.4 Hz), 31.1 (CH_3, *t*-Bu), 31.5 (CH_3, *t*-Bu), 31.7 (CH_3, *t*-Bu), 31.9 (d, CH_2, J = 3.4 Hz), 33.7 (d, CH_2, J = 5.1 Hz), 35.1 (C, *t*-Bu), 35.3 (C, *t*-Bu), 35.9 (C, *t*-Bu), 73.3 (C-4), 74.9 (m, CH═), 76.6 (C-3), 80.6 (m, CH═), 84.6 (d, C-2, J_{P-C} = 9.1 Hz), 102.2 (d, CH═, J_{P-C} = 116.6 Hz), 105.6 (C-1), 106.7 (d, CH═, J_{P-C} = 13.8 Hz), 113.4 (*C*Me), 125.7, 127.8, 128.9 (CH═, Ph), 130.5, 131.3, 139.5, 139.9, 145.9, 148.9, 149.7 (C, Ph).

[Ir(cod)(8)]BF_4 (14): 90 mg (84%) as an orange solid. Anal. Calcd for $C_{47}H_{71}BF_4IrO_6PS$: C, 52.56; H, 6.66; S, 2.98. Found: C, 52.76; H, 6.98; S, 3.12. FAB *m*/*z*: 987 [M^+]. IR (KBr pellet, cm^{-1}): $\nu(BF_4)$ 1070 (s), 450 (m). ^{31}P NMR ($CDCl_3$): δ 116.5 (s, 1P). ^{1}H NMR ($CDCl_3$), δ: 1.20 (s, 3H, C*Me*), 1.36 (s, 18H, *t*-Bu), 1.43 (s, 3H, C*Me*), 1.59 (m, 15H, *t*-Bu, Me), 1.61 (s, 9H, *t*-Bu), 2.36 (m, 8H, CH_2), 3.52 (m, 2H, H-5′, CH−S), 3.65 (d, 1H, H-2, $^3J_{2-1}$= 3.9 Hz), 3.81 (m, 1H, H-5), 4.33 (m, 1H, H-4), 4.50 (m, 2H, CH═), 4.83 (m, 1H, H-3), 5.39 (m, 2H, CH═), 5.64 (d, 1H, H-1, $^3J_{1-2}$ = 3.9 Hz), 7.0−7.5 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): δ 23.3 (Me), 26.2 (C*Me*), 26.8 (C*Me*), 28.5 (C-5), 29.6 (b, CH_2), 31.2 (CH_3, *t*-Bu), 31.5 (CH_3, *t*-Bu), 31.7 (CH_3, *t*-Bu), 32.8 (b, CH_2), 35.2 (C, *t*-Bu), 35.3 (C, *t*-Bu), 35.8 (C, *t*-Bu), 35.9 (C, *t*-Bu), 43.5 (CH−S), 71.7 (C-4), 74.1 (m, CH═), 78.2 (C-3), 80.5 (m, CH═), 83.8 (d, C-2, J_{P-C} = 7.4 Hz), 103.8 (m, CH═), 104.7 (d, CH═, J_{P-C} = 16 Hz), 105.6 (C-1), 113.4 (*C*Me), 125.8, 128.2, 128.9, 129.2 (CH═, Ph), 131.5, 139.4, 140.0, 146.2, 146.4, 149.1, 149.7 (C, Ph). ^{31}P NMR ($CDCl_3$, 233 K): major isomer 80% δ 119.0 (s, 1P), minor isomer 20% δ 113.2 (s, 1P).

[Ir(cod)(9)]BF_4 (15): 98 mg (83%) as an orange solid. Anal. Calcd for $C_{50}H_{69}BF_4IrO_6PS$: C, 47.08; H, 5.46; S, 2.51. Found: C, 47.23; H, 5.57; S, 2.89. FAB *m*/*z*: 1021 [M^+]. IR (KBr pellet, cm^{-1}): $\nu(BF_4)$ 1073 (s), 450 (m). ^{31}P NMR ($CDCl_3$): δ 113.1 (s, 1P). ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 3H, C*Me*), 1.31 (s, 18H, *t*-Bu), 1.45 (s, 3H, C*Me*), 1.50 (s, 9H, *t*-Bu), 1.59 (s, 9H, *t*-Bu), 2.28 (m, 8H, CH_2), 3.73 (d, 1H, H-2, $^3J_{2-1}$ = 3.6 Hz), 3.91 (m, 1H, H-5′), 4.23 (m, 1H, H-5), 4.41 (m, CH═), 4.55 (m, 1H, H-4), 4.74 (m, 1H, H-3), 4.94 (m, 2H, CH═), 5.67 (d, 1H, H-1, $^3J_{1-2}$ = 3.6 Hz), 7.0−7.8 (m, 9H, Ph). ^{13}C NMR ($CDCl_3$): δ 26.3 (C*Me*), 26.8 (C*Me*), 28.3 (d, CH_2, J_{P-C} = 2.9 Hz), 28.4 (C-5), 29.5 (d, CH_2, J_{P-C} = 3.4 Hz), 31.5 (CH_3, *t*-Bu), 31.8 (CH_3, *t*-Bu), 32.4 (d, CH_2, J_{P-C} = 3.4 Hz), 33.9 (d, CH_2, J_{P-C} = 3.9 Hz), 35.1 (C, *t*-Bu), 35.3 (C, *t*-Bu), 35.9 (C, *t*-Bu), 36.0 (C, *t*-Bu), 73.3 (C-4), 74.0 (m, CH═), 77.4 (C-3), 81.7 (m, CH═), 84.0 (d, C-2, J_{P-C} = 6.9 Hz), 105.5 (C-1), 106.4 (d, CH═, J_{C-P} = 15.5 Hz), 106.6 (d, CH═, J_{P-C} = 15.5 Hz), 113.6 (*C*Me), 125.9, 128.3, 128.8, 129.2 (CH═, Ph), 130.6, 131.2 (C, Ph), 133.3, 133.7 (CH═, Ph), 139.5, 140.1, 145.5, 146.1, 149.5, 149.7 (C, Ph). ^{31}P NMR ($CDCl_3$, 233 K): δ major isomer 65% 117.5 (s, 1P), minor isomer 35% δ 109.7 (s, 1P).

Preparation of *cis*-Dihydridoiridium(III) Complexes. Hydrogen was bubbled through a solution of $[Ir(cod)_2]BF_4$ (24.7 mg, 0.05 mmol) and ligand (0.05 mmol) in CD_2Cl_2 (0.5 mL) at 0 °C. After 15 min, the solution was either transferred to an NMR spectrometer tube (^{1}H NMR and ^{31}P NMR were recorded to the desired temperature) or precipitated with hexane.

[IrH_2(COD)(7)]BF_4 (19): Anal. Calcd for $C_{45}H_{69}BF_4IrO_6PS$: C, 51.57; H, 6.64; S, 3.05. Found: C, 51.34; H, 6.34; S, 2.98. ^{31}P NMR ($CDCl_3$): δ 110.1 (s, 1P). IR (KBr pellet, cm^{-1}): ν_{Ir-H} 2139 (m), 2202 (m).

[IrH_2(COD)(8)]BF_4 (20): Anal. Calcd for $C_{47}H_{73}BF_4IrO_6PS$: C, 52.46; H, 6.84; S, 2.98. Found: C, 52.28; H, 6.87; S, 3.11. ^{31}P NMR ($CDCl_3$): δ 109.0 (s, 1P). IR (KBr pellet, cm^{-1}): ν_{Ir-H} 2154 (m), 2201 (m).

[IrH_2(COD)(9)]BF_4 (21): Anal. Calcd for $C_{50}H_{71}BF_4IrO_6PS$: C, 54.10; H, 6.45; S, 2.88. Found: C, 54.65; H, 6.57; S, 3.00. ^{31}P NMR ($CDCl_3$): δ 107.9 (s, 1P). IR (KBr pellet, cm^{-1}): ν_{Ir-H} 2149 (m), 2198 (m).

Hydroformylation of Styrene. The autoclave was purged three times with CO. The solution was formed from [Rh(acac)-$(CO)_2$] (0.013 mmol) and thioether-phosphite (0.015 mmol) in toluene (10 mL). After pressurizing to the desired pressure with syn gas and heating the autoclave to the reaction temperature, the reaction mixture was stirred for 15 h to form the active catalyst. The autoclave was depressurized, and a solution of styrene (13 mmol) in toluene (5 mL) was brought into the autoclave and pressurized again. During the reaction several samples were taken from the autoclave. After the desired reaction time, the autoclave was cooled to room temperature and depressurized. The reaction mixture was analyzed by gas chromatography.

In Situ HP NMR Hydroformylation Experiments. In a typical experiment a sapphire tube (ϕ = 10 mm) was filled under argon with a solution of [Rh(acac)$(CO)_2$] (0.030 mmol) and ligand (molar ratio P/Rh = 1.1 and 2) in toluene-d_8 (1.5 mL). The HP NMR tube was purged twice with CO and pressurized to the appropriate pressure of CO/H_2. After a reaction time of 15 h shaking at the desired temperature, the solution was analyzed.

Hydrogenation of Itaconic Acid. In a typical run, a Schlenk tube was filled with a dichloromethane (6 mL) solution of substrate (1 mmol) and catalyst precursor (0.01 mmol). It was then purged three times with H_2 and vacuum. The reaction mixture was then shaken under H_2 (1 bar) at 313 K. After the desired reaction time, the solvent was removed. The conversion was measured by ^{1}H NMR.

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