Half-Sandwich Chiral Ruthenium Complexes

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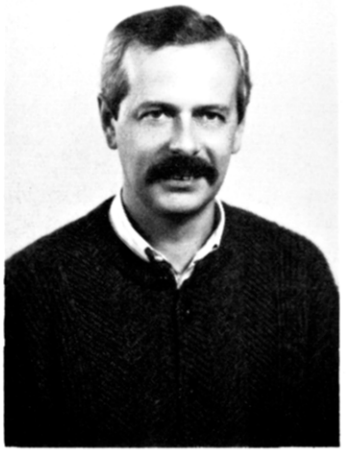
Contents

Giambattista Consiglio was born in Foggia, Italy, and received his doctoral degree in industrial chemistry at the University of Pisa in 1965. He is now Privat Dozent for industrial chemistry at the Swiss Federal Institute of Technology in Zürich. His research interests have developed in the area of homogeneous and asymmetric homogeneous catalysis by transition-metal complexes and in the stereochemistry of organotransition-metal compounds.



Franco Morandini was born in Rome in 1948 and received his doctoral degree at the University of Padua in 1972. After a 3-year stay in the laboratories of Prof. P. Pino at the E.T.H. in Zürich, he moved to Padua where he is now research associate of inorganic chemistry. His current research interests are in the field of organometallic chemistry and asymmetric catalysis.

I. Introduction

Among the many interesting developments in the field of transition-metal chemistry of the past years, the use of organometallic compounds in organic synthesis,[1,2] both as stoichiometric and catalytic reagents, is experiencing a burst of activity. Reactions involving such reagents often display unique chemoselectivities, allowing simple paths to some chemical transformations that would involve many steps via more classical organic chemistry.[3,4] Furthermore, the control of the stereoselectivity appears more facile when organotransition-metal templates are used.[5] Asymmetric catalysis by transition-metal complexes represents one of the most appealing ways to reach the goal of good chemo- and stereocontrol.[6] However, despite some exciting successes,[1,6,7] examples of asymmetric catalysis still remain to be exploited, due to the lack of criteria that would permit generalization and extrapolation of results.[6] The chiral transition-metal complexes acting as catalysts do interact within the catalytic cycle with a "prochiral" (or sometimes with a chiral) substrate, resulting in dia-

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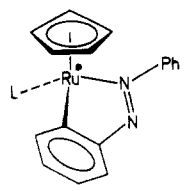
stereomeric intermediates; these, in turn, will form through diastereomeric transition states. The factors influencing energy differences between diastereomeric intermediates and diastereomeric transition states have scarcely been investigated. For instance, although chiral platinum(II)–olefin complexes (containing either chiral amines or chiral olefin ligands) have been studied for some years[8,9] as models for catalytic sites in stereospecific[10] and stereoelective[11] olefin polymerization, it is now widely accepted[10,12,13] that stereogenic[14] metal centers are responsible for the stereospecific polymerization of olefins over Ziegler–Natta catalysts. The remarkable stereoselectivities obtained in the polymerization of α-olefins using chiral homogeneous Ziegler–Natta catalysts[15,16] provide strong support for this proposal. It is likely that, due to the geometric requirements of transition-metal complexes, stereogenic metal atoms could be a common feature in asymmetric catalysis.[17-20] During catalysis, ligands coordinated to a metal atom can participate in a number of stereochemically significant transformations, including substitution, migration, and insertion reactions (among others). Investigation of the stereochemical course of simple reactions at transition-metal centers provides detailed information regarding the identification and definition of catalytic cycles.[21,22] Despite the wealth of information provided by such studies, this approach has not been fully exploited until recently.[21-23] For example, in the past few years diastereomeric ruthenium complexes (the subject of the present review) and chiral enantiomeric rhenium complexes[24] have been extensively investigated. In addition, experiments on the transfer of a methylcarbene moiety to styrene by diastereomeric cyclopentadienyl iron complexes[25] containing a stereogenic metal atom and a chirality center on the phosphino ligand ($[(\eta\text{-}C_5H_5)Fe(CO)\{PPh_2CH_2CH(CH_3)C_2H_5\}(CHCH_3)]OSO_2CF_3$) revealed that the chirality at the metal center was primarily (if not exclusively) responsible for the asymmetric synthesis of cyclopropanes. In spite of these studies, the role of the stereogenic metal atom in addition to that of the chiral ligand in asymmetric induction phenomena in model compounds remains poorly understood, particularly with regard to chiral ligands that are actually used in asymmetric synthesis. The recent development of the organometallic chemistry of ruthenium,[26] especially the preparation of chiral ruthenium complexes, has provided a unique opportunity to address these important stereochemical questions. This review summarizes studies of the stereochemical course of selected metallorganic reactions and the diastereomeric equilibria of compounds containing prochiral ligands carried out by using monometallic half-sandwich chiral ruthenium complexes. Some references to related results obtained with different metallic systems are also presented when appropriate.

II. Types of Chiral Half-Sandwich Ruthenium Complexes

A number of monometallic ruthenium half-sandwich complexes have been synthesized; these will be discussed according to the number of chirality elements present.

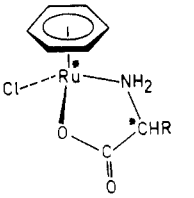
For complexes containing only one chiral element, chirality is due to the presence of a chirality center either at the metal or at the ligand(s). In addition, chirality can arise from the presence of a coordinated prochiral ligand (such as an alkylidenecarbene, an olefin, or an allyl).

The first ruthenium complexes (**1a,b**) containing a chiral metal center were synthesized long ago[26,27] but only as racemates. The fact that **1a** was isolated as a



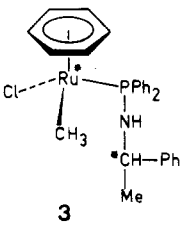
L = CO **1a**

L = PPh_3 **1b**



R = H **2a**

R = CH_3 **2b**



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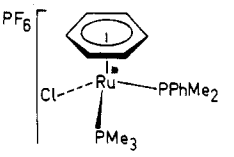

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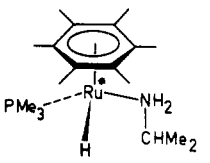
red oil was attributed to the presence of optical isomers.[27] Attempts to resolve this racemic mixture did not succeed. Moreover, the stereochemical stability at the metal center was not investigated. The question of stereochemical stability was first studied by using complexes **2b** and **3**, in which two chiral centers are present, one at the ruthenium atom and one at the ligands.[28,29] Stereochemical stability at a stereogenic metal resulted for complex **4**[30] (and the hexamethylbenzene analogue[31]) and complex **5**[32] containing the η^6-benzene ligand. It was shown that the two methyl



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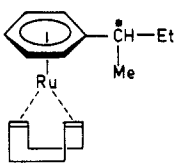

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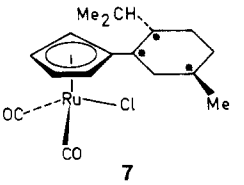
groups on the phenyldimethylphosphine ligand in complex **4** and in its hexamethylbenzene analogue give two sets of doublets in the ^1H NMR spectrum. This anisochrony is due to diastereotopicity[33] of the two methyl groups and suggests some optical stability at the metal, at least on the NMR time scale. Analogously, the two methyl groups of the isopropylamine ligand of complex **5** are diastereotopic, as shown by ^{13}C NMR.

Complexes containing chirality center(s) on the polyhapto ligand **6**[34] and **7**[35,36] or on one of the two-electron ligands[37,38] **8** and **9** were recently synthesized. Com-



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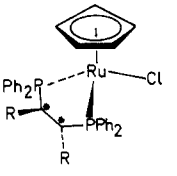
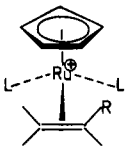


R = CH_3 **8**

R,R = $-(CH_2)_5-$ **9**

plexes 7–9 were used as starting materials for the synthesis of compounds having more than one chiral element (vide infra).

Half-sandwich ruthenium olefin complexes containing prochiral olefins[39–42] (as in 10) have been investigated far less than the analogous iron complexes.[42,43] Pre-



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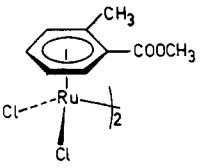

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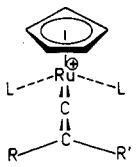
liminary results have been communicated concerning the chiral ruthenium complex 11, in which chirality is due to the presence of two different substituents on the polyhapto ligand.[44,45] In addition, complexes of type 12, having two different substituents on the alkylidene carbon atom, are chiral due to their preferred conformation[46] and have been reported.[40,47–52]

Most diastereomeric half-sandwich ruthenium complexes containing two elements of chirality have been synthesized for mechanistic studies of reactions in-



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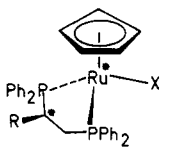

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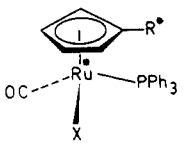

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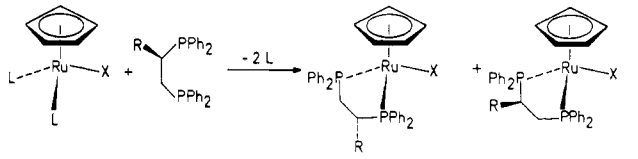
SCHEME 1

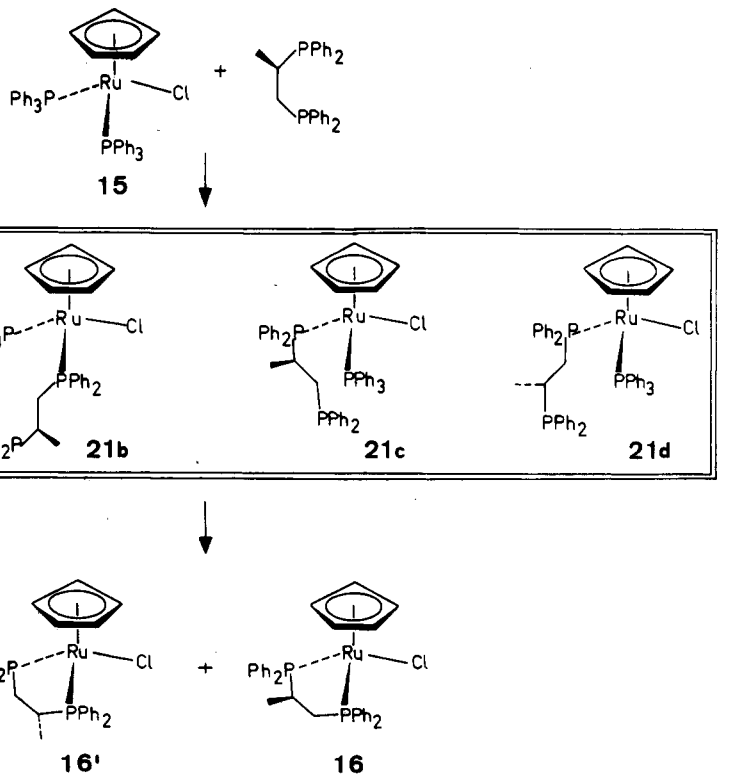


L=PPh_3, X=Cl	R=CH_3	$(R)_{Ru}$,$(R)_C$ 16'	$(S)_{Ru}$,$(R)_C$ 16
15	R=cyclo-C_6H_{11}	17'	17
	R=C_6H_5	18'	18
L=CO, X=H	R=CH_3	20'	20
19			

volving possible stereochemical changes at the metal atom. For these compounds, the metal center is chiral; another chiral center is present in one of the ligands. Compounds **2b** and **3** were the first reported[28,29] examples that allowed the determination of the stereochemical stability at the metal atom. The most thoroughly studied compounds contain chiral chelating diphosphines of type **13**[53] or monosubstituted chiral cyclopentadienyl ligands of type **14**.[35]

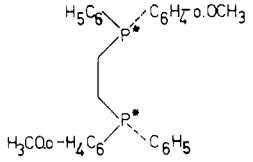
Complexes of type **13** are prepared by displacement of two two-electron-donor ligands by the appropriate diphosphine ligand (Scheme 1).[53–55] For the cyclopentadienylchlorobis(triphenylphosphine)ruthenium complex[56] **15** with the chiral prophos[57] (1-methyl-1,2-ethanediylbis[diphenylphosphine]), cycphos[58] (1-cyclohexyl-1,2-ethanediylbis[diphenylphosphine]), and phenphos[59] (1-phenyl-1,2-ethanediylbis[diphenylphosphine]), two diastereomers (**16** and **16'**, **17** and **17'**, and **18** and **18'**, respectively) form in approximately equimolar ratios.[37] Although the mechanism of this displacement reaction has not been thoroughly investigated, ^1H and ^{31}P NMR studies indicate a stepwise displacement of triphenylphosphine from **15**. Since the two triphenylphosphine ligands in **15** are enantiotopic,

SCHEME 2



they should dissociate with equal probability if a dissociative mechanism is involved (as it is likely on the basis of analogy with other 18-electron complexes[60]). This implies the formation of four possible diastereomeric intermediates (Scheme 2, **21a–d**), the presence of which is inferred from the ^{31}P NMR spectrum of the reaction mixture at different reaction times.[37]

The displacement reaction by a chiral diphosphine having C_2 symmetry such as (*R,R*)-ethanediylbis[*o*-anisylphenylphosphine][61] (dipamp) (**22**) was also monitored by ^{31}P NMR.[62] In this case only two diaste-



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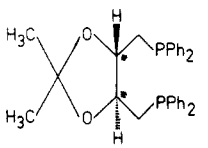

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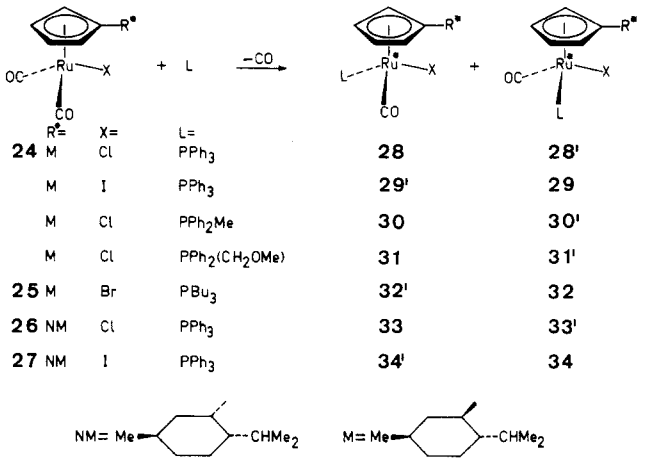
reomeric reaction intermediates can form. At the beginning of the reaction, only a small amount of the chelate complex is formed and two doublets having nearly equal intensities are present in the spectral region of the uncoordinated diphosphine (δ −19.6, J_{P-P} 7 Hz and δ −20.5, J_{P-P} 3 Hz). Similarly, when the diphosphine is (*R,R*)-[(2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene)]bis[diphenylphosphine] (diop)[17] (**23**), two singlets having similar intensities (δ −19.6 and −21.4) are observed in the region of the uncoordinated diphosphine. These signals (as well as the previous ones) are assigned to the uncoordinated phosphorus atom of the coordinated monodentate diphosphine. A similar complex containing monodentate bis(diphenylphosphino)methane was isolated and its crystal structure determined by X-ray diffraction.[63]

On this basis it can be assumed that the two pairs of intermediate species in Scheme 2, which have opposite configuration at the ruthenium atom, form equally. The fact that the two diastereomeric chelate complexes form in an almost equimolar ratio implies that chelate formation is stereospecific. However, at the beginning of the reaction one diastereomeric chelate complex prevails (e.g., **16′** in the case of the complexes containing the prophos ligand). The ratios of the diastereomeric ruthenium complexes do not correspond to the equilibrium ratio. Epimerization at the metal center occurs for these diastereomeric complexes at high temperature and in polar solvents, leading to the following diastereomeric composition (80 °C in chlorobenzene): **16**/**16′** = 2.4/1; **17**/**17′** = 2.4/1; **18**/**18′** = 1/1.8 (for the last two diastereomeric pairs, the stereochemical assignment is arbitrary[53]).

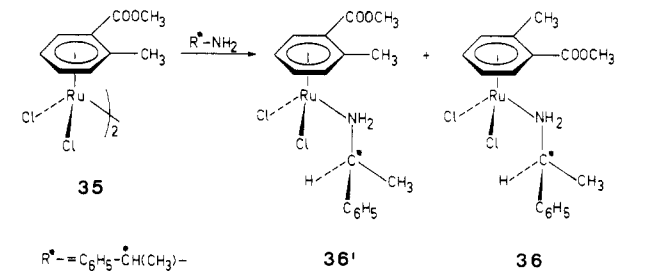
In contrast with the stereochemical outcome of the aforementioned displacement reaction, there is some asymmetric induction in the formation of the $(S)_{Ru}$-$(R)_C$-**20** and $(R)_{Ru}(R)_C$-**20′** diphosphine complexes (Scheme 1) in the displacement of CO from (η-cyclopentadienyl)dicarbonylrutheniumhydride (**19**).[55] In boiling heptane the two diastereomers **20** and **20′** form in a 1/4.6 molar ratio.[55] The equilibrium composition of the two diastereomeric complexes is 1/1.5 at room temperature in benzene.[64] The origin of the reported asymmetric induction is not clear. Again, dissociation of either enantiotopic carbon monoxide ligand should be equally probable (vide supra), unless assisted by the chiral ligand. In the absence of ligand assistance

SCHEME 3



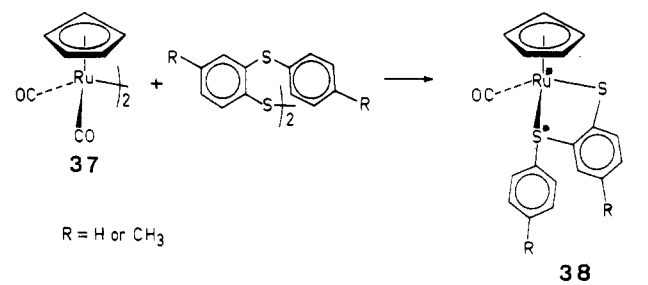
	R=	X=	L=		
24	M	Cl	PPh_3	**28**	**28′**
	M	I	PPh_3	**29′**	**29**
	M	Cl	PPh_2Me	**30**	**30′**
	M	Cl	$PPh_2(CH_2OMe)$	**31**	**31′**
25	M	Br	PBu_3	**32′**	**32**
26	NM	Cl	PPh_3	**33**	**33′**
27	NM	I	PPh_3	**34′**	**34**

SCHEME 4



35 **36′** **36**

SCHEME 5



37

R = H or CH_3

38

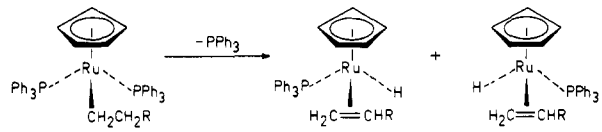
asymmetric induction should be determined at the level of the second substitution, probably due to a stereochemically labile 16-electron intermediate[125] (vide infra).

Complexes containing a chiral substituent on the cyclopentadienyl ligand where the metal is a chiral center have been prepared by displacement of either diastereotopic carbonyl ligand, starting from complexes **24–27** with the appropriate phosphine ligand (Scheme 3). Asymmetric induction by the neomenthylcyclopentadienyl ligand is low in this displacement reaction, yielding a diastereomeric excess of 19% and 9% for X = I and Cl, respectively.[36] No data are available concerning the equilibrium composition for these complexes.

Chiral complexes having a planar element of chirality were prepared as shown in Scheme 4.[44,45] Fractional crystallization allows the separation of the two diastereomers **36** and **36′**. However, no data are published on the stereochemical course of the synthesis (Scheme 4) or on the physicochemical properties of these complexes.

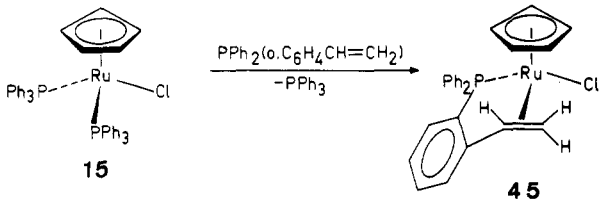
Some other complexes having two chirality elements have been prepared but only as racemate. Disulfides of the type reported in Scheme 5 react with [(η-C_5H_5)$Ru(CO)_2]_2$ (**37**) to give diastereomeric sulfidothiolato complexes **38**.[65]

SCHEME 6



R = CH_3	39	42	42'
R = C_2H_5	40	43	43'
R = C_6H_5	41	44	44'

SCHEME 7

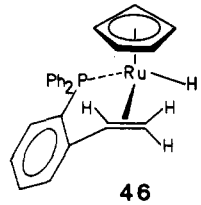


15 45

Epimerization of these complexes is facile. The diastereomeric ratio at equilibrium (−60 °C) in $CDCl_3$ is 7.5/1[65] for R = H. Interconversion of the two diastereomers is assumed to involve inversion at the sulfur atom of the sulfido ligand.

Complexes of the type $(\eta\text{-}C_5H_5)Ru(PPh_3)_2R$ (**39–41**) (where R is an alkyl group containing available β-hydrogens) are thermally labile (Scheme 6). They decompose to the hydrido–olefin complexes[66–68] having two chiral elements: a chiral center at the metal atom and a plane of chirality due to the complexed prochiral olefin. The diastereomeric ratio is 1.7/1 for the propylene and ~5.7/1 for the butene complexes. The complex $(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl$ (**15**) reacts with diphenyl(*o*-vinylphenyl)phosphine[69] to give **45**, which has two similar chiral elements (Scheme 7). In contrast to the analogous osmium complex $(\eta\text{-}C_5H_5)Os\{Ph_2P(o\text{-}CH_2{=}CHC_6H_4)\}Br$, only one of the possible diastereomers apparently forms. The structure of the ruthenium complexes has not been determined but is assumed to be the same as that found for the prevailing isomer (9/1) of the bromo osmium derivative.[69]

The reaction of **45** with sodium methoxide in methanol leading to the corresponding hydrido complex **46** is not stereospecific. Two diastereomeric complexes



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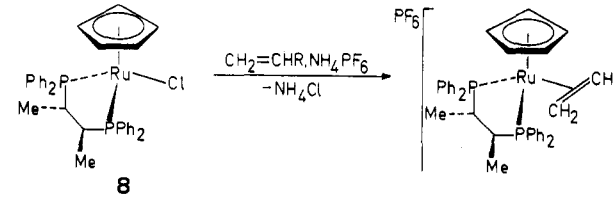
form in a molar ratio of 1.75/1. It is unclear whether this complex is optically stable at the metal atom. Complex **8**, containing the chiral diphosphine ligand (*S,S*)-1,2-dimethyl-1,2-ethanediylbis[diphenylphosphine] (chiraphos[57]), has been used as a starting material for compounds containing prochiral ligands such as olefins[70] and alkylidenecarbenes[71] in the presence of a halogen scavenger (Schemes 8 and 9).

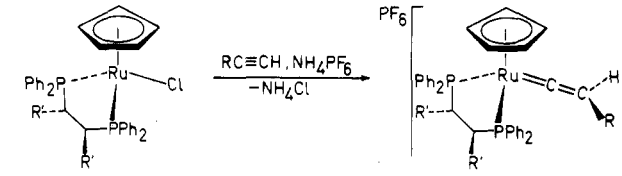
Analogously compounds having three elements of chirality[38,72] are prepared in a similar manner starting with diastereomers **16** and **16'** (Charts I and II). These complexes were prepared in order to address the effect of both the chiral ligand and the stereochemistry at the metal center on asymmetric induction.

SCHEME 8



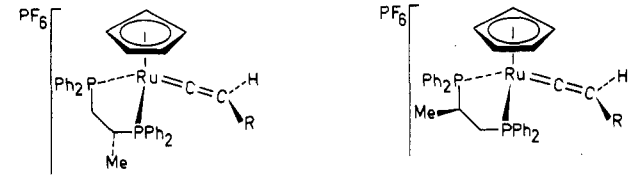
R = $-CH_3$	47
R = $-CH(CH_3)_2$	48
R = $-C_6H_5$	49
R = $-COOCH_3$	50
R = $-CH_2OCH_3$	51
R = $-COCH_2CH_3$	52

SCHEME 9



8	R' = CH_3	R = t.C_4H_9	53
		R = C_6H_5	54
9	R',R' = $-(CH_2)_5-$	R = t.C_4H_9	55
		R = C_6H_5	56

CHART I



$(R)_{Ru},(R)_C$ 57'	R = Me	$(S)_{Ru},(R)_C$ 57
58'	R = Ph	58

CHART II

$(R)_{Ru},(R)_C$ 59'	R = H	$(S)_{Ru},(R)_C$ 59
60'	R = CH_3	60
61'	R = C_6H_5	61
62'	R = $COOCH_3$	62

III. Determination of the Stereochemistry of the Chiral Complexes

The half-sandwich complexes discussed previously have pseudooctahedral geometries.[73] However, sterically, they are best considered as having pseudotetrahedral geometries.[22] Information concerning the geometry of ligands and their disposition around the metal atom is obtained by using three different spectroscopic methods: X-ray diffraction,[74] circular dichroism (and

optical rotatory dispersion),[75] and multinuclear NMR spectroscopy.[33]

A. X-ray Diffraction

In order to determine unambiguously the stereochemical course of reactions involving ligands around the metal atom, X-ray structure determination of reagents and products appears in most cases necessary[78] and has indeed been carried out.[53,64,76-79] In some cases the absolute configuration at the metal center was determined by taking into account the anomalous scattering effects.[77] The absolute configuration at the metal was, however, determined in most cases by taking advantage of the known absolute configuration of the chiral ligand present in the diastereomeric complexes under examination.[76,78,79] We shall not discuss the structure of the diastereomeric half-sandwich chiral ruthenium complexes in more detail because (a) they reveal nothing particular with respect to analogous achiral or optically inactive complexes[71,76,77,80-82] and (b) they provide little information concerning the conformations of ligands in solution. For conformational effects circular dichroism and especially NMR spectroscopy are more informative.

B. Chiroptical Methods

It has been recognized[22,83] that most diastereomeric organometallic complexes which differ only in the configuration at the metal (normally specified according to a modification[84] of Baird's proposal[85]) exhibit CD spectra that are almost mirror images, at least in the visible region. These spectra appear to be primarily influenced by the metal chromophore, the chirality at the ligand usually making only minor contributions.[83] Problems arise when correlations are made between the chiroptical properties and configurations at the metal for complexes in which one or more ligands are changed.

For pseudotetrahedral iron complexes of the general formula (η-C_5H_5)Fe(CO)(L)X (similar to the ruthenium complexes discussed in the present paper) when the X groups are similar and when the morphology of the corresponding CD curves are also very similar, tentative conclusions about absolute configurations appear possible.[86] In addition, it was found that for some enantiomerically pure (or enriched) (η-C_5H_5)Re(NO)(PPh_3)X complexes there is a relationship between the sign of the CD spectra and the absolute configuration at the rhenium atom; however, exceptions to this relationship are possible.[24c,d]

For ruthenium complexes **3** and for the trichlorostannato derivative (η-C_6H_6)Ru{$Ph_2PNHCH(CH_3)Ph$}(CH_3)$SnCl_3$ (**63**) it proved impossible[74,87] to correlate the CD spectra with the absolute configurations of the ruthenium atom as the two complexes give completely different CD curves. Nevertheless, a similar approach has been followed[36] for a series of diastereomeric complexes having the general formula (η-R*-C_5H_4)Ru(CO)LX (**28** and **28'**, **30–33**, and **30'–33'**) and the analogous diastereomeric (η-MC_5H_5)Ru(CO)[P($OPh)_3$]Br (M = menthyl) **64** and **64'**. On the basis of an apparent correlation between transitions observed in CD, UV, and visible spectra (305–325, 350–380, and over 400 nm) and on the similarity of these spectra, it has been proposed that the two short-wavelength bands (particularly that at 305–325 nm) are diagnostic of the absolute configuration at the metal. In light of the poor correlation found for the analogous iron series, the aforementioned relationship between the CD spectra and configuration for the ruthenium complexes is most likely due to the low number of complexes investigated.

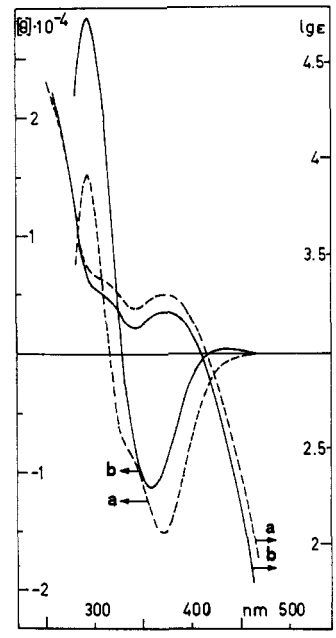


Figure 1. CD and UV–vis spectra of $(S)_{Ru},(R)_C$-**65** (a) and $(R)_{Ru},(R)_C$-(η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}$SnCl_3$ (**65'**) (b).

The chiroptical properties of complexes of type **13** containing chelate diphosphine ligand are even less diagnostic for stereochemical assignments. As an example Figure 1 shows the CD and the UV–vis spectra of the two diastereomeric $(S)_{Ru},(R)_C$-**65** and $(R)_{Ru},(R)_C$-(η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}$SnCl_3$-**65'** complexes.[77] Only relatively small differences are observed. Other complexes of this type[53,88] exhibit a similar behavior as well as the related iron complexes [(η-$C_5H_5Fe(CO)$){(−)norphos}]PF_6 (**66**) (where norphos is bicyclo[2.2.1]hept-5,6-ene-3,4-diylbis[diphenylphosphine]).[83] The similarity in the chiroptical properties for diastereomeric complexes differing only in the absolute configuration at the metal has been ascribed to the puckered conformation of the chelation ring. This conformation depends (at least mostly) on the absolute configuration of the chiral ligand and strongly influences the CD spectra of the complexes. This assumption finds strong support in the observation that the CD spectra of (*S,S*)-(η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}Cl (**8**) and of $(S)_{Ru},(R)_C$-(η-C_5H_5)Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}Cl (**16**) are virtually mirror images of each other even though the metal atom is stereogenic in the latter complex but not in the former (Figure 2). Due to the heterochirality[14] of the two diphosphine ligands in these complexes, the chelation ring is expected to assume the δ conformation for the *S,S* ligand but the λ for the *R* ligand. This difference therefore is expected to cause CD spectra that are almost mirror images. It is again worth noting that the differences in the CD spectra of **16** and of the alternative diastereomer **16'** are not very large.

C. Multinuclear NMR Spectroscopy

For the tremendous potential of NMR spectroscopy in stereochemical investigations, particularly in the

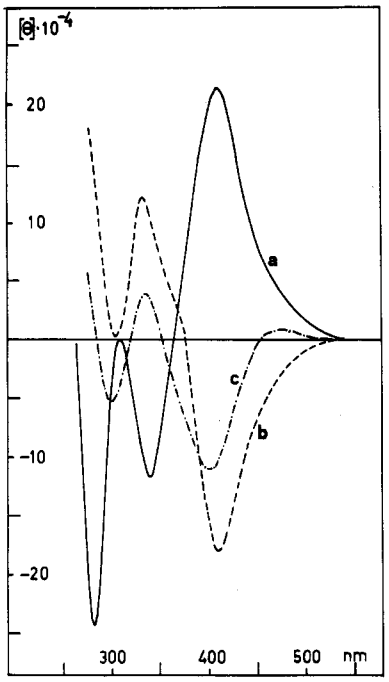


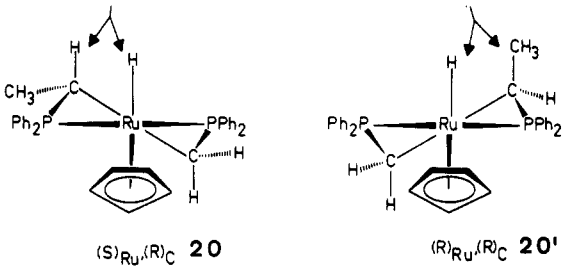
Figure 2. CD spectra of (S,S)-$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH(CH_3)$}Cl (**8**) (a), $(S)_{Ru},(R)_C$-**16** (b), and $(S)_{Ru},(R)_C$-$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}Cl (**16'**) (c).

organometallic field, we refer to the specialized literature.[89] We shall discuss here only some applications that have been reported for the complexes under examination.

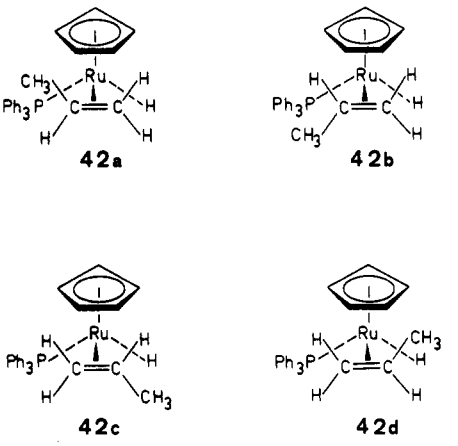
In dealing with chiral complexes, anisochrony due to diastereotopicity is commonly observed in the NMR spectra of all nuclei. Anisochrony of the diastereotopic ortho (and meta) protons has been observed in complex **6**[34] and in similar complexes containing different chiral substituents on the benzene ring.[90] Differences of up to 1.2 ppm have been reported. No anisochrony was observed for the dimeric complex $[RuCl_2[C_6H_5CH(CH_3)C_2H_5]]_2$.[34] In this dimer containing two homochiral 2-phenylbutene rings, the rather small difference in size between methyl and ethyl substituents might simulate a center of symmetry, leading to an apparent isochrony, as observed.

Anisochrony due to internal or external diastereotopicity[33] is normally more marked for nuclei that display a larger range of chemical shifts. Thus the differences in chemical shifts for the two diastereotopic phosphorus atoms in complexes **8** and **9** is 18 and 21 ppm, respectively.[37,38] These large differences make NMR a powerful tool for the determination of diastereomeric purities. NMR spectroscopy cannot be used for the determination of the absolute configuration. However, in diastereomeric metal complexes containing two elements of chirality, the relative configurations can sometimes be determined. In this way a complete stereochemical assignment is possible if the configuration of either chirality element is already known. The stereochemical assignment for the diastereomeric hydrido complexes[88] $(S)_{Ru},(R)_C$-**20** and $(R)_{Ru},(R)_C$-$(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH_2PPh_2$}H (**20'**), which contain the (*R*)-1-methyl-1,2-ethanediylbis[diphenylphosphine] ligand[57] and for which crystals of good quality for X-ray diffraction could not be obtained, was determined in this manner. Among other pieces of evidence,[88] the determination of the absolute configuration at the ruthenium in **20** and **20'** is based on the recognition of NOE between the hydrido hydrogen and the methyl substituent of the diphosphine and between the hydrido and the hydrogen atom bound to the chiral carbon atom of the diphosphine, respectively (Scheme 10). The former interaction is only possible for the δ conformer of the R_{Ru},R_C diastereomer (a conformation which therefore must have a significant population); the second one, by contrast, is only possible for the alternative diastereomer (Scheme 10).

SCHEME 10



SCHEME 11



The relative stereochemistry of the metal atom and of the olefin ligand was determined in a similar manner for the complexes $(\eta$-$C_5H_5)Ru(PPh_3)(CH_2{=}CHCH_3)H$ (**42** and **42'**), prepared in racemic form according to Scheme 6. For each configuration at the metal atom, four different diastereomeric species are in principle possible (Scheme 11 refers to species **42**). However, only species **42a** and **42d** are present in substantial concentrations. The *ul*[91] diastereomer **42a** is preferred in a 2/1 molar ratio with respect to the *lk* diastereomer **42d**, which is expected on steric grounds. However, the observed preference for the geometries in which the methyl substituent on the double bond points toward the C_5H_5 ligand (Scheme 11) is unexpected.

Together with the investigation of the relative stereochemistry of different chirality elements in chiral complexes, NMR analysis permits the identification of the prevailing conformation of the complexes in solution through identification of coupling constants and applications of the Karplus relationship. Recently the complex $(\eta$-$C_5H_5)$Ru{$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}-$CH_2CH_2C_6H_5$ (**67**) has been investigated through multinuclear NMR and through a two-dimensional *J*-resolved experiment.[92] The proton-decoupled proton spectrum allows the identification of the $^3J_{P-H}$ coupling constants for the two diastereotopic methylenic protons (3.0 and 8.8 and 4.4 and 7.6 Hz, respectively). Furthermore, vicinal $^3J_{H-H}$ coupling constants for the

TABLE I. ^{31}P NMR Parameters for Some Diastereomeric Neutral Complexes of the Type $(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}X$

X	S_{Ru}, R_C diastereomer			R_{Ru}, R_C diastereomer		
	P_A	P_B	J_{P-P}	P_A	P_B	J_{P-P}
H	98.1	77.2	30.0	104.3	85.7	22.9
CH_3	100.0	74.1	35.2	93.6	85.0	32.2
C_2H_5	99.1	72.3	36.4	88.3	81.6	37.1
$C_6H_5CH_2$	97.5	72.9	34.2	93.0	81.9	32.7
$C_6H_5CH_2CH_2$	100.4	74.3	35.7	89.6	82.4	36.3
$C_6H_5C{\equiv}C$	91.7	68.8	31.1	89.0	79.4	24.7
Cl	86.4	61.3	30.3	80.9	74.1	36.7
$SnCl_3$[a]	81.7	59.5	30.6	81.8	64.7	29.0

[a] Because of the convention applied in this case the descriptors must be interchanged even though the geometry of the complexes in the two series is the same.[84,85]

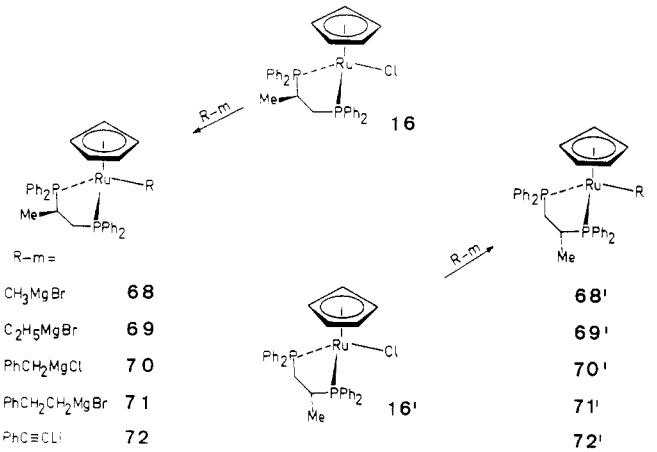
TABLE II. ^{31}P NMR Parameters for Some Cationic Diastereomeric Complexes of the Type $[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}L]PF_6$

L	S_{Ru}, R_C diastereomer			R_{Ru}, R_C diastereomer		
	P_A	P_B	J_{P-P}	P_A	P_B	J_{P-P}
CH_3CN	87.3	63.1	32.9	88.1	75.7	25.6
$CH_2{=}CH_2$	88.2	61.9	31.1	82.4	58.9	38.5
$C(OCH_3)CH_2C_6H_5$	92.2	67.6	32.8	84.0	76.6	33.1
$C{=}CHC_6H_5$	80.0	61.0	27.9	83.7	63.5	29.3
$C{=}CHCH_3$	83.1	67.9	25.8	90.7	74.1	23.8

proton of the two methylenic groups can be easily extracted from the second dimension of the spectrum (~4 and 14 Hz). Both results suggest an antiperiplanar conformation for the largest substituents on the C–C bond of the 1-phenylethylgroup and a similar conformation around the Ru–C bond of the η-C_5H_5 ligand on the ruthenium atom and of the benzylic substituent on the carbon atom.[93]

As previously pointed out, the determination of the absolute configuration normally requires an X-ray crystal structure determination. However, the comparison of the ^{31}P NMR parameters (Table I) for some complexes of the general formula $(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}X$ for which the absolute configuration at the metal is known[64,72,77-79] suggests a possible empirical rule. For these complexes the diastereomers having the S_{Ru},R_C configuration exhibit differences in ^{31}P chemical shifts for the two phosphorus atoms which are always larger than those for the R_{Ru},R_C diastereomers. Furthermore, with the exception of the trichlorostannato and the hydride derivatives, the ^{31}P NMR resonances of the R_{Ru},R_C diastereomers fall within the range of the resonances corresponding to the S_{Ru},R_C diastereomer. The correlation of ^{31}P shifts seems to be valid also for cationic complexes of the type $[(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}L]PF_6$ (where L = CH_3CN,[79] $CH_2{=}CH_2$,[72] or $C(OCH_3)CH_2C_6H_5$[71]) (Table II). However, this correlation does not extend to the cationic complexes containing the ethylidenecarbene ($CH_3CH{=}C$) or the benzylidenecarbene ($C_6H_5CH{=}C$) ligand, for which the alkylidene carbene ligand for the complexes can assume two different orientations (vide infra), each with its own population.[38] The ^{31}P NMR chemical shift differences observed between diastereomeric pairs of the complexes $(\eta\text{-}C_5H_5)Ru\{Ph_2PCHRCH_2PPh_2\}X$[37,53] (R = C_6H_5, 18′ δ 90.2 and 58.1 and 18 δ 83.9 and 66.4; R = c-C_6H_{11}, 17′ δ 90.0 and 61.9 and 17 δ 71.1 and 67.4) suggest that this empirical rule regarding the range of ^{31}P chemical shifts might be more generally applied. For these last four complexes, however, no crystal structure determination has been carried out.

SCHEME 12



IV. Stereochemical Course of Simple Metallorganic Reactions

The stereochemical course of simple reactions involving organometallic transition-metal complexes has only recently been investigated. Two different approaches have been followed: (a) investigation of reactions carried out on enantiomerically enriched (or pure) organometallic complexes having no chiral ligands[22,24] and (b) investigation of reactions carried out on diastereomeric metal complexes, which have a chiral center at the metal and a chiral ligand.

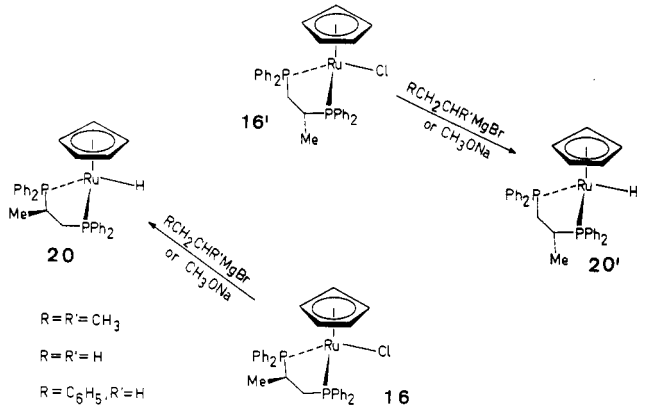
The first system requires a method for the determination of the optical purity of both reagent and reaction product, which is not always trivial.[24] By contrast, diastereomeric purities are much more easily determined. However, for the identification of the stereochemical course of the reaction, both diastereomers must be used in order to recognize the possible asymmetric bias of the chiral ligand present in the complexes under investigation. Only this second method was followed in the investigation of chiral ruthenium complexes. These studies have been carried out mostly by using complexes containing chiral diphosphine ligands of type 13.

A. Alkylation Reactions

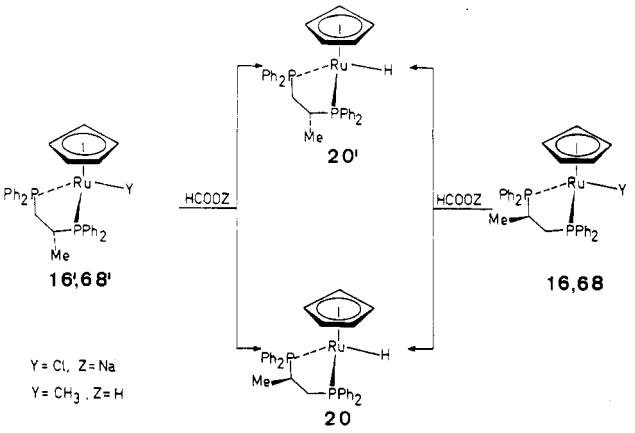
Transition-metal alkyl complexes are involved as intermediates in many catalytic reactions such as hydrogenation, hydroformylation, etc.[94] Furthermore, transalkylation of transition-metal complexes by organometallic derivatives of the main-group elements represents an important step in the cross-coupling reaction of those organometallic reagents with different electrophiles.[20,95]

Starting with the diastereomeric complexes $(S)_{Ru}$-$(R)_C$-16 and $(R)_{Ru},(R)_C$-$(\eta\text{-}C_5H_5)Ru\{Ph_2PCH(CH_3)CH_2PPh_2\}Cl$ (16′) different alkylation reactions have been carried out (Scheme 12). The diastereomeric composition of the reaction products can be very easily determined through NMR analysis using the $(\eta\text{-}C_5H_5)$ signal in the ^1H NMR spectrum or the ^{31}P NMR, which gives in all cases very simple spectra (a doublet of

SCHEME 13



SCHEME 14



doublets for each complex; compare the chemical shift data in Table I). The reaction was found to be stereospecific in each case;[78,80,88,92,96] in fact, the diastereomeric purity of the reaction products was always equal to the diastereomeric purity of the starting material, within the limits of the NMR detection (evaluated to be ±2%). In the case of Grignard reagents or lithium alkyls not having β-hydrogen atoms, the reaction appears to be completely chemoselective with only the alkylation product being recognizable in the crude reaction mixture. The similarity of the NMR parameters for the series of homochiral alkylation products has already been stressed (section III.C). The retention of the stereochemistry at the chiral ruthenium atom was established through comparison of the crystal structure of the starting material and of the corresponding methylation product for the S_{Ru},R_C diastereomer **68**.[78]

B. Formation of Hydrido Complexes

When alkylation reagents are used, which do contain β-hydrogen atoms (C_2H_5MgBr or $C_6H_5CH_2CH_2MgBr$ in Scheme 12), the alkylation reactions compete with formation of the hydrido complexes,[88,92] as found for the parent compound $(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl$.[67]

The chemoselectivity depends on the reaction temperature used; however, even at −80 °C a consistent amount of the hydride complexes (~20%) still forms. When a secondary Grignard reagent (*sec*-C_4H_9MgBr or *i*-C_3H_7MgBr) is used, hydride formation predominates, even at very low temperature (Scheme 13); no trace of alkylation product was identified in the NMR spectra of the crude reaction mixture. Such NMR analysis shows that in every case the reaction is completely stereospecific within the limits of the NMR detection, independent of the Grignard reagent used. For these hydrido complexes the absolute configuration at the metal atom could be identified by reference to the known absolute configuration of the chiral diphosphine ligand through difference NOE[88] (section III.C, Scheme 10); retention of configuration during the formation of the hydrido complexes was thus established. On the basis of the previously known behavior of the alkyl complexes $(\eta\text{-}C_5H_5)Ru(PPh_3)_2CH_2CH_2R$[66,67] (Scheme 6), a clean stereospecific retention of the configuration at the metal atom in the formation of the hydrido complexes **20** and **20'** with Grignard reagents having available β-hydrogen atoms was unexpected.[88] For this reason other routes for the preparation of the aforementioned hydrido complexes were examined. The first reagent, which had also[97] been used for the parent $(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl$, was sodium methoxide in methanol. This reaction is presumed to give an intermediate methoxy complex, which then transforms to the hydrido complex.[97,98] Treatment of diastereomeric complexes **16** and **16'** with sodium methoxide in methanol (Scheme 13) results in the clean stereospecific formation of the hydrides, which takes place with retention of configuration, completely analogous to the reaction that occurs with Grignard reagents having available β-hydrogens. In contrast, when the diastereomeric chloro complexes **16** and **16'** are each reacted in methanol with sodium formate, they give with moderate stereoselectivity a mixture of the hydrido complexes **20** and **20'** in a 1/4 molar ratio independent of the geometry of the starting material (Scheme 14). The above ratio does not correspond to the equilibrium composition between the two diastereomeric hydrido complexes, which is 1/1.5.[64] Stereoselectivity was also observed (even if surprisingly in a somewhat lower 1/1.5 molar ratio) in the formation of the hydrido complexes by treatment of the diastereomerically pure methyl complexes with HCOOH (Scheme 14). It should be noted that excess HCOOH causes decomposition of the hydrido complexes but not their epimerization.

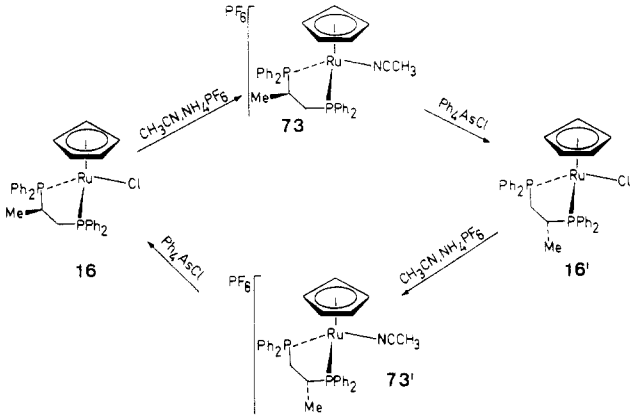
C. Other Substitution Reactions Involving the Halide Ligand. Formation of Cationic Complexes

1. Without Chemical Modification of the Incoming Ligand

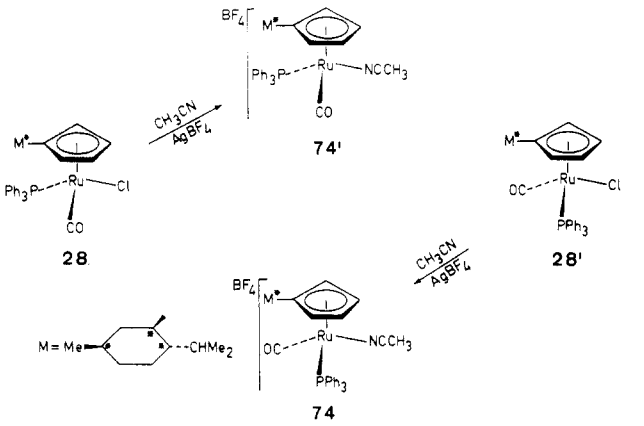
Substitution reactions involving halide abstraction for complexes of the type $(\eta\text{-}C_5H_5)MLL'X$ have been extensively used in preparative organometallic chemistry.[99] In the presence of a halogen scavenger (e.g., silver ions) a 16-electron intermediate is produced which is able (being a Lewis acid[24a]) to coordinate 2-electron donors such as olefins, acetylenes, phosphines, carbon monoxide, etc. The unsaturated intermediate has been postulated to be a solvate;[24a] for example, the isolation of $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2(CH_3OH)][B(C_6H_5)_4]$ has been reported.[100] The stereochemical outcome of such reactions is therefore related to the optical stability of the $(\eta\text{-}C_5H_5)MLL'$ fragment, to the rate of formation of the adduct with the two-electron donors, and to the lability of the bond in the adduct.

The displacement of the chlorine ligand with acetonitrile in methanol is stereospecific (≥95%) and takes place with retention of configuration at the ruthenium

SCHEME 15



SCHEME 16



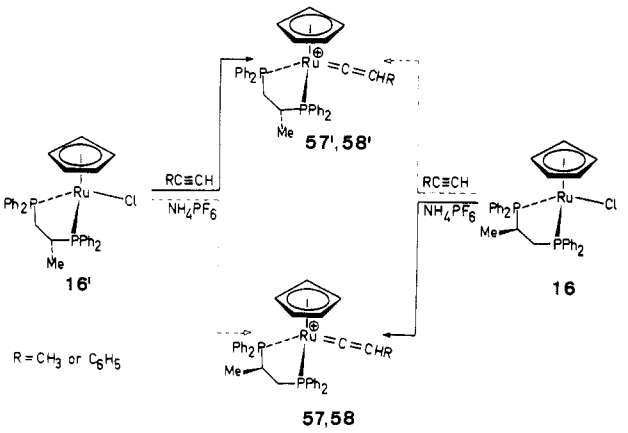
atom for the diastereomeric $(S)_{Ru},(R)_C$-**16** and $(R)_{Ru}$-$(R)_C$-**16′** complexes[88] (Scheme 15). The stereospecificities of the analogous reactions for $(S)_{Ru}$-**28** and $(R)_{Ru}$-$(\eta$-$MC_5H_4)Ru(CO)(PPh_3)Cl$ (**28′**) were in the range of 94–95% (Scheme 16) as in the case of $(R)_{Ru}$-$(\eta$-$NMC_5H_4)Ru(CO)(PPh_3)I$ (**34′**), which gives $(R)_{Ru}$-$[(\eta$-$NMC_5H_4)Ru(CO)(PPh_3)(CH_3CN)]BF_4$ (**75′**).

Contrary to the previous case, displacement of the chlorine atom with olefins is not completely (or even not at all) stereospecific.[72] The diastereomerically pure diphosphine chloride complexes **16** or **16′** yield the olefin complexes **59** and **59′** with diastereomeric purities of 62 and 80%, respectively. Complete epimerization at the metal was reached within 4 days at room temperature (molar ratio **59**/**59′** = 1/1.86). In the case of propylene or styrene (these substrates, being two-dimensional chiral simplexes,[14] give two complexes for each starting diastereomer (vide infra)) the reaction is not stereospecific. It is presumed that formation of the ethylene complex takes place with net retention of configuration at the ruthenium atom.[72]

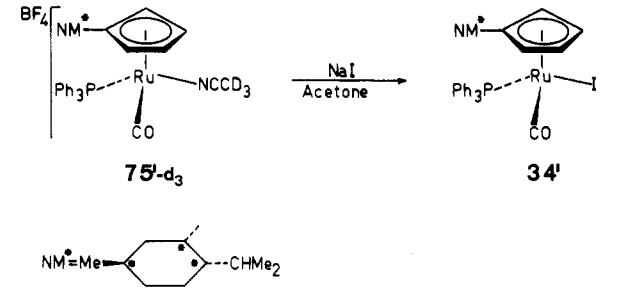
2. *With Chemical Modification of the Incoming Ligand*

Acetylenes have been reported[101] to give a reaction similar to that of the olefins with $(\eta$-$C_5H_5)MLL'X$ complexes. In the case of $(\eta$-$C_5H_5)RuL_2Cl$ (L_2 = $2PPh_3$ or diphos) when terminal acetylenes were used, formation of the alkylidenecarbene complexes was observed.[40,50,56] The reaction of the chloro complexes **16** and **16′** with phenylacetylene in boiling methanol (Scheme 17) is neither stereospecific nor stereoselective.[71] Complete epimerization at the ruthenium atom takes place independent of the starting material, and

SCHEME 17



SCHEME 18

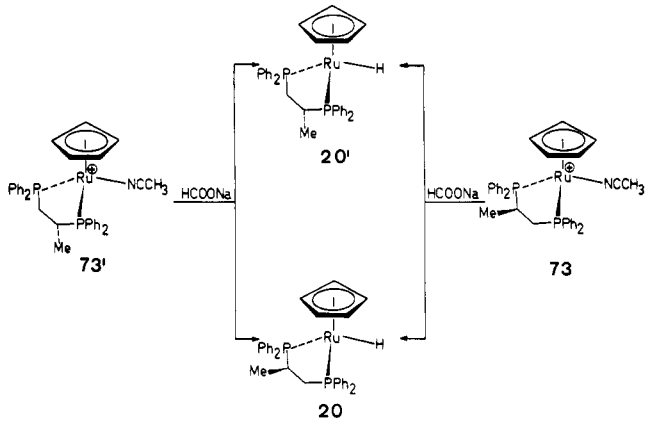


the two benzylidenecarbene complexes **58** and **58′** are formed in almost equimolar amounts. This is not due to the optical instability of **58** and **58′** in boiling methanol, since they separately convert to the methoxycarbene complexes (Scheme 24, see infra) in this medium with complete stereospecificity. The reaction is completely stereospecific when carried out at room temperature in methanol both for propyne (which gives **57** and **57′**) and for phenylacetylene. The determination of the stereochemical outcome of this reaction implying retention of the configuration at the metal follows from a crystal structure determination on $(S)_{Ru},(R)_C$-**57**.[71]

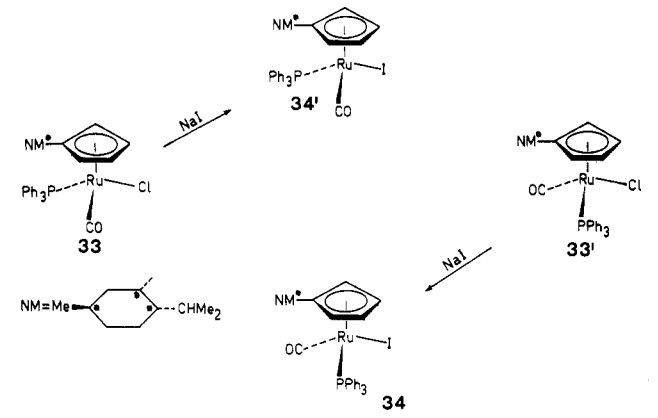
D. Substitution Reactions Involving the Acetonitrile Complexes

Complexes of the type $(\eta$-$C_5H_5)MLL'(CH_3CN)^+$ are useful precursors to other cyclopentadienyl metal complexes.[102] In fact they react with alkali salts, giving the corresponding halide complexes. Treatment of $(R)_{Ru}$-$[(\eta$-$NMC_5H_4)Ru(PPh_3)(CO)(CD_3CN)]BF_4$ (**75′**-d_3) (85% diastereomeric purity) with NaI gave the corresponding iodo complex **34′** having the same diastereomeric purity (Scheme 18). Retention of configuration at the metal atom was established on the basis of stereochemical correlations.[76] However, the reaction on the alternative diastereomer was not carried out nor was the diastereomeric equilibrium composition established for the iodo complex; thus, no conclusion can be drawn on the stereochemical course of the reaction, even though stereospecificity appears more probable than stereoselectivity. In fact, the aforementioned complex had been prepared by dissolving the $(R)_{Ru}$-$[(\eta$-$NMC_5H_4)Ru(CO)(PPh_3)(NCCH_3)]BF_4$ complex (**75′**) in CD_3CN and heating the solution at 85 °C for 8 h. During this time exchange of the coordinated acetonitrile with the labeled one was completed, whereas only 9% epimerization was observed. Therefore the ex-

SCHEME 19



SCHEME 20



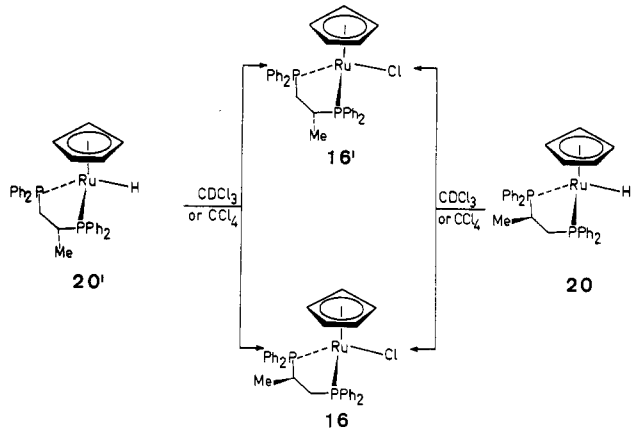
change reaction is assumed to be very stereospecific (≥95%). However, since no results on the alternative diastereomer were reported, it remains an open question whether the exchange reaction is indeed very stereospecific or if it is stereoselective and the final diastereomeric composition does correspond to the thermodynamic equilibrium. The acetonitrile complexes[88] $(S)_{Ru},(R)_C$-**73** and $(R)_{Ru},(R)_C$-**73′** react in methanol with excess of HCOONa to give, independent of the starting material, a mixture of the diastereomeric hydrides $(S)_{Ru},(R)_C$-**20** and $(R)_{Ru},(R)_C$-**20′** in a 1/1.5 molar ratio (Scheme 19). The reaction has therefore the same stereochemical outcome as the production of the same hydrido complexes from the chloro compounds and HCOONa (Scheme 14), but the degree of stereoselectivity is lower. In this case the ratio obtained corresponds to the equilibrium mixture between the two diastereomeric hydrides.

Particularly interesting in view of the uncommon stereochemical outcome is the reaction of the acetonitrile complexes **73** and **73′** with Ph_4AsCl (Scheme 15). In this reaction the chloro complexes **16′** and **16** form with prevailing inversion of configuration and with stereospecificities of ~30% for both diastereomers. Inversion of configuration at the metal is rather rare for reactions involving a chiral metal center; however, there are some precedents.[103] Kinetic experiments should lead to a better understanding of the above reaction.

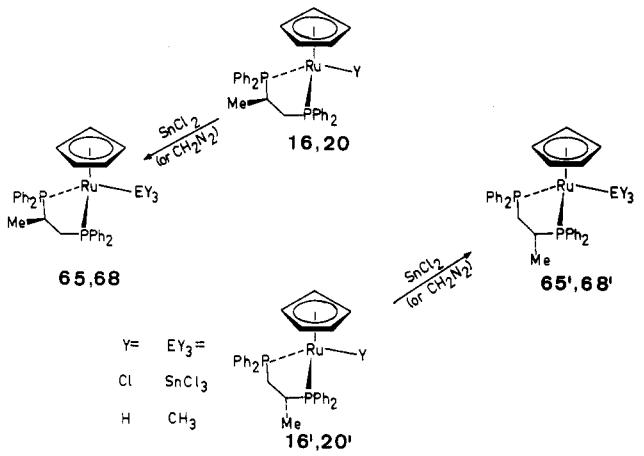
E. Exchange Reactions

The stereochemical outcome of halide ligand exchange has been investigated[76] in dichloromethane by treating the $(S)_{Ru}$-**33** and $(R)_{Ru}$-$(\eta$-$NMC_5H_4)$Ru-

SCHEME 21



SCHEME 22



$(PPh_3)(CO)Cl$ (**33′**) complexes with NaI (Scheme 20). The reaction is completely stereospecific for both diastereomers and takes place with retention of the configuration at the metal.

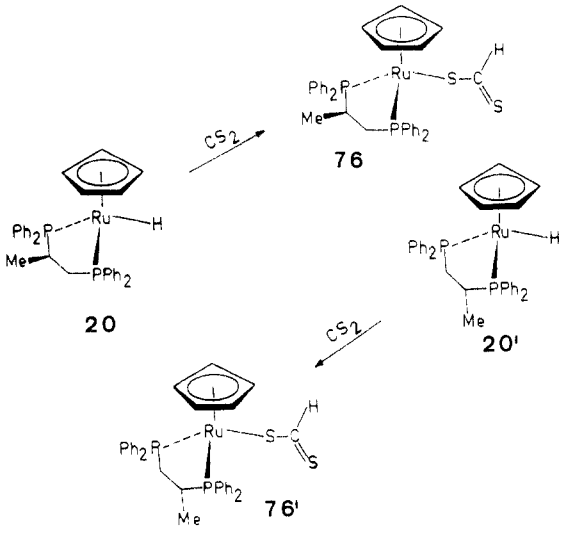
In contrast, the reaction of the diastereomeric hydrido complexes $(S)_{Ru},(R)_C$-**20** and $(R)_{Ru},(R)_C$-**20′** with chloroform or carbon tetrachloride, which yields the corresponding chloro complexes (Scheme 21), is not stereospecific. Complexes $(S)_{Ru},(R)_C$-**16** and $(R)_{Ru},(R)_C$-**16′** form in a molar ratio of 4/1 in chloroform and 1.5/1 in carbon tetrachloride[88] independent of the starting material. Coproducts in the reaction are methylene chloride and chloroform, respectively.

F. Insertion Reactions

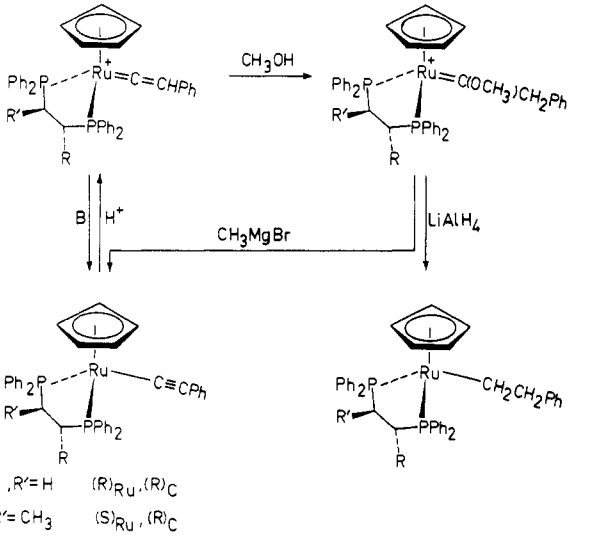
Insertion reactions are of widespread significance in organometallic chemistry.[94] The insertion reaction of $SnCl_2$ in a transition metal–chlorine bond is of particular interest in view of the importance of the trichlorostannato ligand in homogeneous catalysis.[104] This problem was first approached by reacting complex **3** in diastereomerically pure form with $SnCl_2$ in THF. Unfortunately, complex **3**, despite its optical stability in THF, was found to epimerize under the reaction conditions used.[87] Nevertheless the results imply that the reaction is stereospecific; however, no conclusion can be drawn about the stereochemical course, due to the difficulty in growing crystals of **3** suitable for crystal structure determination.[74]

The problem was solved later by using $(S)_{Ru},(R)_C$-**16** and $(R)_{Ru},(R)_C$-**16′** as the starting material (Scheme 22). The reaction was found to be completely stereospecific

SCHEME 23



SCHEME 24



in the formation of $(S)_{Ru},(R)_C$-**65**, whereas for the alternative diastereomer **65′** ~10% loss of stereochemistry was found. Retention of the geometry at the ruthenium atom (the chirality descriptor, however, changes because of the nomenclature used) was established through crystal structure determination on both starting material and product.[77]

A similar reaction to that above is the insertion of a methylene group (derived from palladium-catalyzed decomposition of diazomethane) into a ruthenium–hydrogen bond. Such reactions are of interest as model reactions for the reduction of CO to Fisher–Tropsch products;[105] furthermore, such insertions are increasingly applied in preparative organometallic chemistry.[106] The reaction (Scheme 22) was found to be completely stereospecific and to occur with retention of the configuration at the metal; however, in addition to ~50% methyl derivatives, other products form that have not been identified.[88]

Attempts to insert CO_2 in the diastereomeric $(S)_{Ru},(R)_C$-**20** and $(R)_{Ru},(R)_C$-**20′** hydrido complexes failed, even under high CO_2 pressure.[64] This was disappointing but not completely unexpected, as the hydrido complexes are formed (Schemes 14 and 19) in reactions involving ruthenium formato intermediates. The analogous reaction with CS_2, however, gives η^1-S-thioformato complexes as insertion products **76** and **76′** (Scheme 23). According to X-ray structure determination the reaction takes place with retention of the configuration at the metal atom. Furthermore the reaction is stereospecific for complex **20**, whereas for the alternative diastereomer **20′** ~10% loss of stereochemistry at the metal takes place. Curiously, COS does not insert in the hydrido complexes but, instead, causes complete epimerization at the metal, giving the $(S)_{Ru},(R)_C$-**20** and $(R)_{Ru},(R)_C$-**20′** hydrides in a 1/1.5 molar ratio independent of the diastereomeric composition of the starting hydride. It is assumed, therefore, that the 1/1.5 ratio corresponds to the equilibrium ratio for the hydrido complexes **20** and **20′**.

G. Some Reactions Not Directly Involving the Ruthenium Atom

It would appear unnecessary to investigate the stereochemistry at the metal atom for reactions involving only modifications at a coordinated ligand(s). Recent studies, however, suggest that the point of the kinetic attack of a particular reagent could be disguised by rearrangements to the thermodynamically stable product.[107] For this reason, stereochemical investigations of organometallic reactions for which a plausible mechanism cannot be proposed appear worthwhile.

It has been shown that in alkylidenecarbene complexes of the type $[(\eta\text{-}C_5H_5)RuL_2(C{=}CHR)]^+$ (L_2 = 2 PPh_3 or diphos) the hydrogen atom has quite acidic properties.[40,50,56] As a matter of fact, upon treatment with bases such complexes lead to the formation of alkynyl derivatives; these can in turn be protonated back to the alkylidenecarbene complexes. These reversible protonation reactions carried out on the $(S)_{Ru},(R)_C$-**58** and -**72** and $(R)_{Ru},(R)_C$-**58′** and -**72′** complexes (Scheme 24), take place stereospecifically with retention of the configuration at the metal atom.

The benzylidenecarbene complexes **58** and **58′** react with boiling methanol to give corresponding methoxycarbene complexes $(S)_{Ru},(R)_C$-**77** and $(R)_{Ru},(R)_C$-**77′** (Scheme 24). These reactions also take place stereospecifically with retention of configuration at the metal atom.

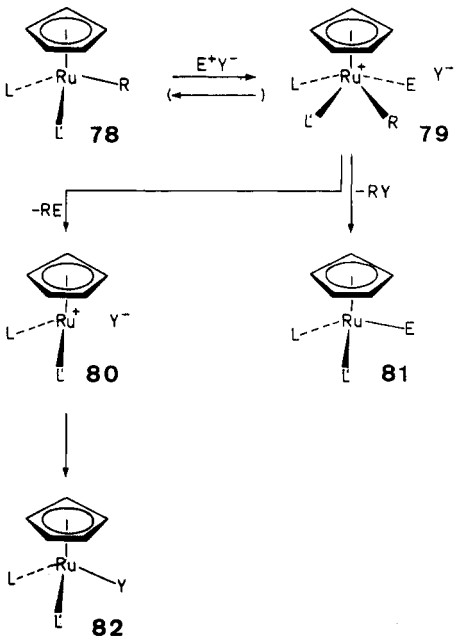
Less expected are the two other reactions in Scheme 24, particularly that of the methoxycarbene complex with methylmagnesium bromide, which leads to the formation of the phenylethynyl complexes.[80] This reaction is rather satisfying from the preparative point of view, yields being higher than 90%. Also the reaction of complexes **77** and **77′** with $LiAlH_4$ is rather chemoselective and allows us to prepare the 2-phenylethyl complexes **71** and **71′** free from contaminant hydrides.

Both reactions are stereospecific within the limits of NMR detection and take place with retention of the configuration at the ruthenium atom.

H. General Remarks on the Stereochemistry

As in organic chemistry[108] the interest for the investigation of the stereochemical course of the reactions resides in the possibility of achieving information about the mechanism. In dealing with pseudotetrahedral chiral complexes, the same possibilities encountered for asymmetric carbon atoms do exist: retention, inversion, or racemization. Therefore when transition-metal

SCHEME 25



complexes having an asymmetric metal atom and a chiral ligand are used as the starting material, we shall observe, at the level of the metal atom, retention or inversion or epimerization.

A summary survey of the literature on the stereochemistry of metallorganic reactions carried out on complexes having different metals but similar to those discussed here confirms that the most common stereochemical outcome involves retention of configuration at the metal. Epimerization (or racemization) is sometimes observed; net inversion of the configuration at the metal appears to be rare.[21,22,24,86,103,109]

The complexes discussed in this review are 18-electron species and can be considered as "electron-rich".[40] For example, $(\eta\text{-}C_5R_5)Ru\{PMe_3\}_2Cl$ (R = H or CH_3) is easily protonated, the latter even by NH_4PF_6.[110,111] Similarly, a triplet hydride is observed in the NMR spectrum of $(\eta\text{-}C_5H_5)Ru(PPh_3)_2Cl$ when treated with CF_3COOH in CD_2Cl_2.[96] This behavior suggests, in agreement with previous proposals,[109e,23] that the reaction of the complexes examined with electrophiles should give pentacoordinate intermediate **79** (Scheme 25). Cis and trans geometries for this intermediate both appear possible. Both intermediates **79** and **80** in Scheme 25 are susceptible to epimerization at the metal; intermediate **79** could epimerize through a trigonal bipyramidal species, whereas intermediate **80** could epimerize through a planar species (vide infra). In either case we would expect a higher stereochemical stability when L and L′ in Scheme 25 are part of a chelate ligand.

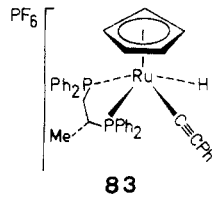
In fact, the reaction in Scheme 22 involving the chloride complexes $(S)_{Ru},(R)_C$-**16** and $(R)_{Ru},(R)_C$-**16′** and $SnCl_2$ is stereospecific (retention) for the first diastereomer, whereas ~10% epimerization was found for the second one.[77] In contrast, extensive epimerization of both starting material and reaction product was observed when complex **3** was treated with $SnCl_2$.[87] Epimerization at a reversibly formed intermediate adduct of the ruthenium complex with $SnCl_2$, having a structure similar to species **79** in Scheme 25, would rationalize the observed results. Similarly, the reaction of hydrido complexes $(S)_{Ru},(R)_C$-**20** and $(R)_{Ru},(R)_C$-**20′** with CS_2 (Scheme 23) proceeds stereospecifically with retention of configuration for the former diastereomer, whereas ~11% epimerization is observed[64] for the latter diastereomer. These results, as well as the epimerization of the aforementioned ruthenium complexes caused by COS, can again be rationalized on the basis of a similar reaction intermediate.

Complexes of the type $(\eta\text{-}C_5H_5)RuLL'Cl$ have been found to be stereochemically stable in hydrocarbon solvents. However, complexes **16–18** (and **16′-18′**) epimerize when more polar solvents such as chlorobenzene are used.[53] It should also be considered that for these complexes substitution of the chlorine ligand by other two-electron donors takes place in polar solvent like methanol in the presence of a halogen scavenger. Considering the 18-electron nature of the complexes under investigation, a dissociative mechanism is expected for those substitution reactions involving the formation of tricoordinated intermediates of type **80**. Mechanistic investigations of halide abstraction from $(\eta\text{-}C_5H_5)Fe(CO)_2I$ implies that the adduct $(\eta\text{-}C_5H_5)Fe(CO)_2IAg^+BF_4^-$ forms initially and subsequently dissociates to give $(\eta\text{-}C_5H_5)Fe(CO)_2^+$.[99] Independent of the first step of the reaction, the formation of the Lewis acid species is invoked, and has, in some cases, been observed.[24a] Due to its nature, species **80** can react with any available Lewis base or, competitively, can rearrange to the other form having opposite geometry at the metal atom. In fact, such $(\eta\text{-}C_5H_5)ML_1L_2$ 16-electron fragments should have a pyramidal geometry, with a reasonably high barrier to inversion.[112] On this basis, in nucleophilic substitution reactions, retention of configuration is expected, which, however, may be accompanied by some epimerization at the metal. Epimerization should depend on (a) the rate of the adduct formation between the unsaturated species and the Lewis base and (b) the position of the equilibrium for the adduct formation. Formation of an adduct with acetonitrile takes place with retention of configuration at the metal with stereospecificities equal to or higher than 95% for complexes of the type $(\eta\text{-}C_5H_5)Ru$(diphosphine)Cl (Scheme 15) and $(\eta\text{-}C_5H_4R^*)Ru(CO)(PPh_3)X$ (Scheme 16).

For complex **75**, which contains a substituted cyclopentadienyl ligand, exchange of the acetonitrile ligand takes place at 80 °C with stereospecificity higher than 95%. The formation of ethylene complexes **59** and **59′** is much less stereospecific, whereas for propylene (which gives **60** and **60′**) complete epimerization at the metal is observed.[72] Formation of the olefin complexes appears to be strongly influenced by steric factors. In fact, we[96] and others[113] were unable to prepare iron olefin complexes analogous to those reported in Scheme 8 and Chart II. Furthermore, the complex $[(\eta\text{-}C_5H_5)Ru(Ph_2PCH_2CH_2PPh_2)(3\text{-MP})]PF_6$ (3-MP = 3-methylpent-1-ene) could not be prepared,[96] even though the analogous propylene complex is known.[40] For this reason the lack of stereospecificity in the case of the formation of the propylene complexes can be ascribed to a higher (even if not detectable, e.g., through NMR) concentration of the unsaturated species of type **80**.

Complete epimerization at the metal atom in the formation of the benzylidenecarbene complexes (Scheme 17)[71] when the reaction is carried out in boiling

methanol could again be due to a relatively long-lived 16-electron intermediate of type **80** with respect to further reaction. However, in this case a possible 5-coordinate hydridoalkynyl[114] intermediate such as **83**



83

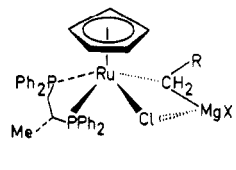
could also (vide supra) be responsible for the observed epimerization; note that no epimerization was observed at lower temperatures.

The difference in stereoselectivities in the nonstereospecific formation of hydrides complexes **20** and **20′** in the reactions in Schemes 14 and 19 implies these reactions go through different intermediates. In fact, electrophilic attack at the metal by HCOOH in the methyl complexes **68** and **68′** leading to pentacoordinate intermediates (which can epimerize) appears possible (vide supra). More difficult to understand at the moment are the different stereochemical outcomes for hydride formation in the reaction of HCOONa with either the chloride (**16** and **16′**) or the acetonitrile complexes (**73** and **73′**); also in this case, however, a different reaction intermediate must be involved. It appears appropriate to recall that the thermal decomposition of chiral rhenium formato complexes (η-C_5H_5)Re(PPh$_3$)(NO)OCOH can take place with extensive racemization at the metal, depending on the reaction conditions used.[24e]

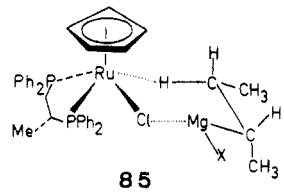
Exchange of iodide for chloride (Scheme 20) in the diastereomeric complexes $(S)_{Ru}$-**33** and $(R)_{Ru}$-(η-$C_5H_4R^*$)Ru(PPh$_3$)(CO)Cl (**33′**) is very stereospecific. This can be expected on the basis of a stronger coordination of iodide with respect to chloride.[115] In contrast, exchange of hydride for chloride implies that for complexes **20** and **20′** complete epimerization at the metal in the reaction with $CDCl_3$ or CCl_4 may be (Scheme 21) possibly connected with an electron-transfer mechanism.[88]

The net inversion of configuration in the reaction of acetonitrile complexes **73** and **73′** with Ph_4AsCl to give **16** and **16′** (Scheme 19) is unusual and warrants further investigation.

Stereospecific retention of configuration at the metal for complexes **16** and **16′** during alkylation with Grignard reagents or lithium compounds can be explained on the basis of a configurationally stable pyramidal 16-electron intermediate. However, the low polarity of the reaction medium makes this mechanism unlikely. A four-center transition state or an intermediate such as **84** appears more probable. The stereospecific for-



84



85

mation of the hydrido complexes from Grignard reagents with available β-hydrogens or sodium methoxide does not proceed via decomposition of the alkylation product, but from an independent pathway.[67,88] Since an olefin is released during hydride formation,[110] it is appealing to propose a six-center intermediate (or transition state) like **85**. Preference for a hydrido formation instead of for alkylation should be probably determined by steric reasons. Hydride formation, indeed, is the only reaction observed when a secondary Grignard reagent is used.[88]

It has already been noted that complex **45** does react with sodium methoxide to give the corresponding hydrido complex **46** in a nonstereospecific manner (diastereomeric ratio 1.8/1);[69] this contrasts with the results obtained for complexes **16** and **16′** if we assume that **46** is optically stable at the metal. Analogously to hydrides **20** and **21′** (Scheme 21), **46** gives back **45** when treated with $CDCl_3$; the reaction appears to be stereoselective,[69] similar to the case of **20** and **20′**.

V. Diastereomeric Equilibria for Complexes Containing Prochiral Ligands

The study of the factors that can influence the diastereomeric equilibria in complexes containing prochiral ligands (such as olefins, allyls, and carbenes) is of particular interest in view of the role played by the relative concentration of similar complexes for the stereochemical outcome of asymmetric catalytic reaction.[116] Complexes of type **13** and **28** can be used as precursors for these types of compounds and permit the study of the influence of opposite chiralities at the metal, in addition to that of the chiral ligands on asymmetric induction phenomena. Particularly interesting in this context is the pair of diastereomeric complexes **16** and **16′**. In fact, the CD spectrum (Figure 2) of **16** is virtually a mirror image to that of **8** due to the heterochirality of the diphosphine ligands. This can be taken as an indication of similar environments caused by the two chiral ligands around the metal. Therefore the investigation of complexes derived from **16** and a comparison with the corresponding complexes derived from **8** should give an idea of the possible influence of stereogenic metal atoms on diastereomeric equilibria connected with the presence of prochiral ligands.

A. Olefin Complexes

The half-sandwich ruthenium olefin complexes containing either the chiraphos (**47–52**)[70] or the prophos (**59–62** and **59′–62′**, respectively)[72] chiral ligand have been easily prepared according to Scheme 8. Complexes **47–52** show in the NMR spectra the presence of the two diastereomers due to enantioface selection. The equilibrium ratio is reached rapidly even at low temperatures for propylene (**47**), 3-methylbut-1-ene (**48**), or styrene (**49**) compounds. In the case of methyl acrylate (**50**) or ethyl vinyl ketone (**52**) epimerization is slower, taking 10–15 h to reach the thermodynamic equilibrium. Curiously, enantioface selection for these latter olefinic compounds is quite low (55/45 and 43/57, respectively), whereas it is rather high for the other olefins (89/11 for **47**, 23/77 for **48**, 95/5 for **50**, and 83/17 for **51**). Enantioface selection for the propylene complex **47** is much higher than for complex **42**. However, for **47** the exact geometry and the preferred enantioface could not be assigned. These results suggest that enantioface selection is determined not only by steric

factors but may also be influenced by electronic effects. In the ^1H NMR spectrum of complex **50** the signals corresponding to two protons in the phenyl region are clearly shifted to lower field by about 0.2 ppm; this shift might be indicative of an attractive interaction between the phenyl ring(s) of the diphosphine ligand and the carbonyl group of the olefinic ligand. If such an attractive interaction exists, it could be responsible both for the slower epimerization of the complex (due to stronger complexation of the olefin) and for the lower enantioface selection at the thermodynamic equilibrium. In fact, epimerization is expected to occur via dissociation of the olefin ligand and reassociation with the opposite enantioface. Unfortunately, the low stability of the complexes as well as the overlap of signals in the ^1H NMR spectra has hindered the identification and the comparison of the preferentially complexed enantioface for the different olefinic compounds.

The very rapid epimerization observed for the complexes **47–49** is most likely reflected in the apparent lack of stereospecificity (vide supra) in the preparation of the analogous complexes containing the prophos ligands **60**, **61**, **60′**, and **61′**. Therefore in this case even the identification of the absolute configuration at the metal is problematic. Due to the presence of three chirality elements, four diastereomeric species are in this case possible, without considering the alternative conformation of the olefinic ligand (compare Scheme 11). The four species appear in a 53/25/18/4 molar ratio for the propylene complex and in a 22/5/19/54 for the styrene complex. In spite of the difficulty in identifying the diastereomeric species with the same configuration at the ruthenium atom, the above figures (when compared with the diastereomeric ratios observed for complexes **47** and **49**) clearly show the importance of the chirality at the metal for the phenomena of enantioface selection. This is more obvious for the complexes containing methyl acrylate **62** and **62′**. In this case (in agreement with the behavior observed for **50**) epimerization at the olefinic enantioface and, related to that, epimerization at the ruthenium atom is much slower. Thus the diastereomeric ratio at the equilibrium of 22/5 for the $(S)_{Ru},(R)_C$-**62** compounds and of 19/54 for the $(R)_{Ru}$-$(R)_C$-**62′** complexes could be determined. Enantioface differentiation is different for the two epimers at the metal and also different to that (55/45) found for **50**.

B. Alkylidenecarbene Complexes

Alkylidenecarbene complexes of type **12**, in which the plane of the alkylidenecarbene ligand is orthogonal to the plane containing the centroid of the η-cyclopentadienyl ligand, the ruthenium atom and the carbene carbon atom, are chiral (compare **12** and **12a** in Scheme 26). The definition of the element of chirality[14] is ambiguous for these compounds; however, since an alkylidenecarbene ligand having two different substituents is a two-dimensional chiral simplex[14] (like an olefin), we can consider these complexes as having a plane of chirality. The first unambiguous identification of the conformation **12** or **12a** (Scheme 26) for such complexes in solution was possible through low-temperature ^{31}P NMR on $[(\eta\text{-}C_5H_5)Fe(Ph_2PCH_2CH_2PPh_2)(C{=}CHPh)]PF_6$, which gave the expected AB spectrum (since **12** and **12a** are enantiomers); this kind of experiment also permitted the

SCHEME 26

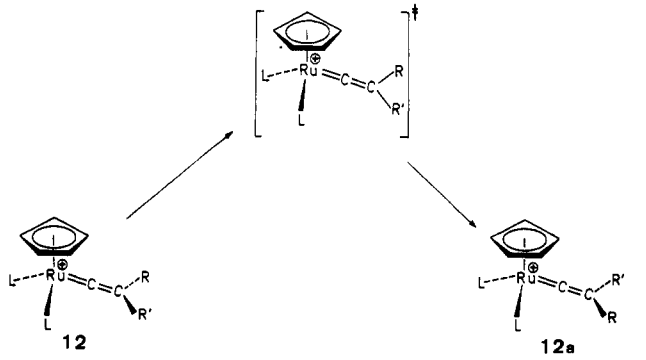


TABLE III. Diastereomeric Composition at ~160 K for the Alkylidene Complexes of the Type $[(\eta\text{-}C_5H_5)Ru(LL)(C{=}CHR)]PF_6$

	LL (absolute configuration)			
	chiraphos (*S*,*S*)	cypenphos[a] (*S*,*S*) or (*R*,*R*)	prophos (S_{Ru},R_C)	prophos (R_{Ru},R_C)
R = CH_3			78:22	50:50
R = *t*-C_4H_9	65:35	>90:10		
R = C_6H_5	50:50	>90:10	>90:10	90:10

[a] *trans*-1,2-Cyclopentanediylbis[diphenylphosphine] (ref 118).

evaluation of the energy barrier for enantiomerization (Scheme 26) of this complex, about 9.4 kcal/mol. A similar value (9.1 kcal/mol) was subsequently found for the analogous ruthenium complex.[38]

These results compared favorably with those obtained for the similar complexes $[(\eta\text{-}C_5H_5)M(Ph_2PCH_2CH_2PPh_2)(CH_2)]PF_6$ containing the methylene (=CH_2) ligand, for which an orientation orthogonal to that of the vinylidene ligand has been found,[117] according to theoretical predictions.[46] For complexes containing chiral diphosphine ligands having a C_2 symmetry (**53–56**), the two conformations of the vinylidene ligands (corresponding to **12** and **12a** in Scheme 26) give rise to two diastereomeric species. Low-temperature ^{31}P NMR spectroscopy is useful for recognizing and determining the differences in population for the diastereomeric conformation (Table III).

Contrary to the previously discussed olefin complexes, the alkylidenecarbene complexes in which the metal atom is a center of chirality (**57**, **58**, **57′** and **58′**) are optically stable at the metal and have been prepared in diastereomerically pure form (section IV.C.1). Their diastereomeric composition, as far as the alkylidene ligand is concerned, as derived from ^{31}P NMR spectra at low temperature, is reported in Table III. The exact geometry of the alkylidenecarbene ligand could not be determined. However, the data in Table III clearly show the influence of the chirality at the metal (when the metal is a stereogenic center) on asymmetric induction phenomena. Asymmetric induction is larger for the complexes having *S* absolute configuration at the ruthenium atom than for those having *R* absolute configuration (**57** vs. **57′** and **58** vs. **58′**). Furthermore, asymmetric induction is larger when the metal is a chiral center (**58** vs. **54**). The ligand cypenphos (*trans*-1,2-cyclopentanediylbis(diphenylphosphine)) induces higher asymmetric induction than chiraphos; that is most probably due to a more congested situation around the metal caused by the former ligand, as suggested by CPK molecular models. It is also worth

noting that for the iron complex analogous to **54** asymmetric induction is much higher (86/14) than it is for **54** (~50:50).[38]

VI. Conclusion

Interest in optically active half-sandwich ruthenium complexes developed for the most part because of two different but related reasons: their possible application as catalyst precursors in asymmetric reactions[34,35,44,45] and their use for the investigation of the stereochemical course at the metal atom of reactions involving organometallic compounds.[53,74,76] In this latter field, the research has complemented the work carried out on other metallorganic systems[23,24,103,109] as well as the studies involved with the stereochemistry of asymmetric carbon atoms bound to transition-metal complexes.[23] For instance, the intermediate (or transition state) **84** proposed for alkylation reactions in order to explain the retention of the configuration at the ruthenium atom could also account for the net inversion of the configuration observed at the carbon atom involved in transalkylation reactions.[119]

The importance of the chirality at the metal for the stereochemical course of reactions involving prochiral ligands has been shown in the case of the asymmetric cyclopropanation of olefins.[25] In fact, this has also been recognized in the case of olefin and vinylidenecarbene chiral ruthenium complexes. More detailed investigations (such as, e.g., NOE experiments) should help in defining the role of the chirality at the metal, thereby providing fundamental information about asymmetric induction phenomena in asymmetric reactions mediated by transition-metal complexes involving prochiral substrates.

The exploitation of the optically active half-sandwich ruthenium complexes as catalyst precursors in asymmetric reactions appears in principle possible. In fact, it seems that cyclopentadienyl complexes of type **7**,[35] when used in reactions such as hydroformylation or hydrogenation, do not lose their cyclopentadienyl ligand except under severe conditions.[120] Arene complexes of type **6** have also found application as hydrogenation catalysts.[121] Furthermore, it has been recently reported that complex **15** as well as the analogous complex **86** containing the 1,2-ethanediylbis[diphenylphosphine] ligand are selective hydrogenation catalysts for olefinic substrates showing high turnover numbers.[122] In this last case, however, the relatively high temperature required for hydrogenation does not appear to be favorable for the successful use of the analogous chiral complexes (**8**, **9**, **17–20**) in enantioselective reactions.

The investigation of chiral diphosphine cyclopentadienyl ruthenium complexes has furthermore pointed out some observations, which have suggested a rationalization or a more complete picture of the phenomena connected with catalytic reactions. Thus the investigation of the displacement reaction of triphenylphosphine from complex **15** by diphosphine has shown a remarkable difference in the chelate stability in complexes **8**, **16**, and **86**, the stability decreasing in this order. The ligand chiraphos less than prophos and this less than diphos tend to give species having the ligand in a monodentate fashion, thus depressing the reaction pathway involving ligand dissociation, like isomer formation in cross-coupling reactions.[95e] The dichotomy of reactions shown by the chloride complexes **16** and **16′** with Grignard reagents having available β-hydrogen atoms (i.e., formation of alkyl vs. hydrido complexes) suggests another possible mechanism for the competitive reduction of electrophiles during the transition-metal-catalyzed cross-coupling reaction of these reagents with organometallic derivatives of the main-group elements.[95a] This catalytic reduction could in fact take place through a sequence of reactions represented in the Schemes 13 and 21 without formation of an alkyl complex (compare intermediate **85**). Furthermore, the low level of asymmetric induction by the chiral ligand for the pairs of diastereomers **16** and **16′**, **17** and **17′**, and **18** and **18′** on the chiral center on the metal can account for the lower asymmetric induction obtained by using these chiral ligands in the nickel-catalyzed asymmetric allylation of Grignard reagents when compared with the chiraphos ligand, which has a C_2 symmetry. In these reactions in fact, the intermediates that determine the asymmetric induction have stereogenic metal centers.[20] The presence of different diastereomeric species having opposite chirality at the metal is unfavorable for the achievement of high optical yields.[25]

Other possible applications of the half-sandwich chiral complexes appear at the moment possible. Like the analogous iron complexes,[5e,25,73,123] olefin, carbene, and alkylidenecarbene complexes can be used for reactions of the prochiral ligands to give optically active organic materials. It has been pointed out that the halide complexes of type **8** behave as Lewis acids in polar solvents. These chiral Lewis acids could thus be used for the determination of the optical purity of chiral Lewis bases by taking advantage of the large differences in the chemical shifts for the phosphorus resonances in NMR for diastereomeric species. Furthermore, due to this peculiarity it appears possible to exploit these diastereomeric species (or particularly their indenyl analogues) as chiral catalysts for reactions catalyzed by Lewis acids.[124]

Registry No. Ru, 7440-18-8.

VII. References

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