Half-Sandwich Complexes with Aminocarboxylate Ligands and Their Use as Enantioselective Hydrogen Transfer Catalysts

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Keywords: Chiral-at-metal complexes / Asymmetric hydrogen transfer catalysis / Rhodium / Ruthenium / Iridium / Osmium / Aminocarboxylate ligands

Chiral-at-metal half-sandwich complexes of rhodium, iridium, ruthenium, or osmium of the general formula [(η^n-ring)M(Aa)Cl] [(η^n-ring)M = (η^5-C_5Me_5)Rh, (η^5-C_5Me_5)Ir, (η^6-*p*-MeC_6H_4*i*Pr)Ru, (η^6-*p*-MeC_6H_4*i*Pr)Os; Aa = L-α-aminocarboxylate] can readily be prepared from the corresponding dimers [{(η^n-ring)MCl}$_2$(μ-Cl)$_2$]. The compounds have been prepared as diastereomeric mixtures of the two epimers at the metal center. In general, alkynyl aminocarboxylate derivatives [(η^n-ring)M(Aa)(C≡CR)] are obtained by treating the aforementioned chlorides with the corresponding alkynes in basic media. However, the reaction of the (alaninato)rhodium chloride [(η^5-C_5Me_5)Rh(Ala)Cl] with the alkynes HC≡CR (R = Ph, *p*-tolyl) produced the alkynylcyclobutadiene complexes [(η^5-C_5Me_5)Rh(η^4-C_4HR_2C≡CR)] (R = Ph, *p*-tolyl). Treatment of the chlorides [(η^n-ring)M(Aa)Cl] with $AgBF_4$ afforded the cationic trimers [{(η^n-ring)M(Aa)}$_3$](BF_4)$_3$. Trimerization occurs with chiral self-recognition: only the (*R*,*R*,*R*) or (*S*,*S*,*S*) configuration at the metal trimers can be detected. The trimers [{(η^n-ring)M(Aa)}$_3$](BF_4)$_3$ reacted with tertiary phosphanes, leading to the cationic mononuclear complexes [(η^n-ring)M(Aa)(PR_3)](BF_4). The assignment of the configuration at the metal center was accomplished by X-ray diffraction, circular dichroism and NMR spectroscopy. Most of the aminocarboxylate derivatives epimerized at the metal center. On the basis of kinetic and spectroscopic data, a general mechanism is proposed for the epimerization process. Neutral [(η^n-ring)M(Aa)Cl] and cationic [{(η^n-ring)M(Aa)}$_3$](BF_4)$_3$ complexes are active catalysts for the hydrogen transfer reaction from 2-propanol to acetophenone. Conversions of up to 97% and enantioselectivities up to 75% were achieved. A proposal about the origins of the enantioselectivity is given.

1. Introduction

Organometallic complexes containing stereogenic metal centers are ideally suited to obtain mechanistic information about the stereochemical course of reactions.[1−5] Most of these complexes posses half-sandwich geometries and contain chiral chelating ligands of C_1 symmetry.[6] Among

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Daniel Carmona (top, left) obtained his PhD degree in chemistry in 1980 at the University of Zaragoza under the supervision of Prof. Usón. After a postdoctoral stay at the E.T.H. of Zürich with Prof. Venanzi he returned to the University of Zaragoza joining Prof. Oro's group. Since 1988 he is a Research Scientist (Spanish Council for Scientific Research) at the Instituto de Ciencia de Materiales de Aragón. His current research interest is focused on the development of chiral transition metal catalysts, as well as in their application to asymmetric catalysis.

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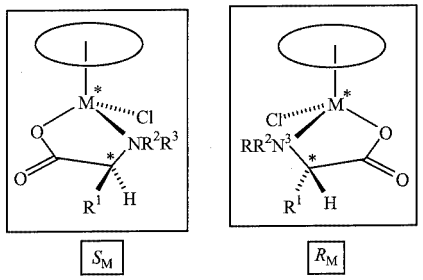
MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

them, transition-metal complexes with α-aminocarboxylates as ligands constitute an important class of compounds as they are closely related to both biochemistry and organometallic chemistry.[7]

In this context, Dersnah and Baird reported[8] in 1977 that the dimer $[\{(\eta^6\text{-}C_6H_6)RuCl\}_2(\mu\text{-}Cl)_2]$ reacted with glycinate or alaninate anions to form the pseudotetrahedral complexes $[(\eta^6\text{-}C_6H_6)Ru(Aa)Cl]$ (Aa = glycinate, L,D-alaninate), in which the ruthenium ion is chiral. After a strikingly dormant period, over the last decade several (η^6-arene)ruthenium[9–11] or -osmium[12] compounds, as well as (η^5-pentamethylcyclopentadienyl)rhodium,[9,13,14] -iridium[9,13–18] or -ruthenium[19,20] complexes with a variety of α-aminocarboxylate ligands have been reported.

On the other hand, half-sandwich compounds with chiral chelate ligands have been successfully employed as enantioselective catalysts. In particular, chiral (arene)ruthenium(II) complexes with α-aminocarboxylates,[21] L-prolinamide derivatives,[22] or *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine[23] as chiral ligands have achieved high levels of enantioselectivity in asymmetric transfer hydrogenations with 2-propanol as the hydrogen donor. The prolinamide complexes are also active catalysts for the asymmetric hydrogen transfer reduction of aromatic ketones in aqueous media.[24,25]

Our contribution to this field started with the publication in 1990 of a series of optically active pseudotetrahedral rhodium(III), iridium(III), and ruthenium(II) complexes with L-alaninato and L-prolinato ligands.[26] Since then, we have continued with the study of this type of compounds, including their application in enantioselective hydrogen transfer reactions. This Microreview presents our results in this area.



M = η^5-(C_5Me_5)M, (M = Rh, Ir); η^6-(*p*-MeC_6H_4iPr)M, (M = Ru, Os)

R^1	R^2	R^3	Abbrv.
Me	H	H	Ala
Et	H	H	Abu
*n*Pr	H	H	Ape
*i*Pr	H	H	Val
*n*Bu	H	H	Ahx
*s*Bu	H	H	Ile
*i*Bu	H	H	Leu
*t*Bu	H	H	Tle
Ph	H	H	Pgl
Bzl	H	H	Phe
Bzl	H	Me	MePhe
$(CH_2)_2$	H		Aze
$(CH_2)_3$	H		Pro
$(CH_2)_4$	H		Pip
$(CH_2)_3$	Me		MePro
$CH_2CHOHCH_2$	H		Hyp

Ala = Alaninate; Abu = 2-Aminobutyrate; Ape = 2-Aminopentanoate (norvalinate); Val = Valinate; Ahx = 2-Aminohexanoate (norleucinate); Ile = Isoleucinate; Leu = Leucinate; Tle = *tert*-leucinate; Pgl = Phenylglycinate; Phe = Phenylalaninate; MePhe = *N*-Methylphenylalaninate; Aze = 2-Azetidinecarboxylate; Pro = Prolinate; Pip = 2-Piperidinecarboxylate; MePro = *N*-Methylprolinate; Hyp = 4-Hydroxyprolinate

Scheme 1. L-α-Aminocarboxylato complexes

2. Chloro Complexes

The acetylacetonato complexes $[(\eta^n\text{-ring})M(acac)Cl]$ [$(\eta^n$-ring)M = (η^5-C_5Me_5)Rh, (η^5-C_5Me_5)Ir, (η^6-*p*-MeC_6H_4-*i*Pr)Ru; Hacac = acetylacetone], easily prepared from the corresponding dimer $[(\eta^n\text{-ring})MCl\}_2(\mu\text{-}Cl)_2]$ and Hacac,[27,28] reacted with stoichiometric amounts of free L-α-amino acids to give the neutral complexes $[(\eta^n\text{-ring})M(Aa)Cl]$ as a mixture of epimers at the metal center in an almost quantitative yield [Equation (1), Scheme 1].[29] The osmium analogues $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(Aa)Cl]$ were prepared starting from $[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)OsCl\}_2(\mu\text{-}Cl)_2]$, the amino acid and KOH [Equation (2)].[9,26,30–33]

$$[(\eta^n\text{-ring})M(acac)Cl] + HAa \rightarrow [(\eta^n\text{-ring})M(Aa)Cl] + Hacac \quad (1)$$

$$1/2\,[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)OsCl\}_2(\mu\text{-}Cl)_2] + HAa + KOH \rightarrow [(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(Aa)Cl] + KCl + H_2O \quad (2)$$

In solution, the diastereomeric composition of these compounds ranges from 0 to 100% *de*. In general, the lowest values correspond to aminocarboxylates such as Ala [*de* = 0 (Rh, Ir), 36% (Ru), 20% (Os)], Abu [*de* = 0 (Rh, Ir)], Val [*de* = 0 (Rh, Ir), 20% (Ru)] or Leu [*de* = 20% (Rh, Ir), 12% (Ru)], and the greatest to the conformationally more rigid cyclic amino acids [Pro = 90% (Rh, Ir), 80% (Ru), 86% (Os); MePro = 100% (Rh, Ir, Ru), 80% (Os)]. However, the complexes are configurationally labile at the metal center.[34] In this regard, the case of iridium prolinate [(η^5-C_5Me_5)Ir(Pro)Cl] is typical. A single crystal of the complex shows the presence of both epimers at the metal center in the unit cell in a 1:1 ratio (Figure 1). Nevertheless, for the same sample, a diastereomeric excess of 90% was measured by ^{1}H NMR spectroscopy in solution at room temperature, as stated above. The composition of the solid is maintained if the crystals are dissolved at −90 °C, but diastereomeric excesses of 30 and 90% were measured immediately after heating the sample to −35 °C and room temperature, respectively. The rhodium analogue [(η^5-C_5Me_5)Rh(Pro)Cl] behaves similarly. These facts indicate that (i) the epimerization process requires a low activation energy and proceeds at a high rate even at low temperatures and (ii) at room temperature, the measurements reflect thermodynamic compositions. A careful analysis of the crystal structures reveals that there is an intermolecular hydrogen-bond network. Thus, for example, in the iridium complex

(Figure 2), this network involves the NH group of the (R_{Ir}) isomer with the oxygen atoms of the carboxylate group of the (S_{Ir}) epimer [N(1b)···O(1a) = 3.196(11) Å, N(1b)H(1b)O(1a) = 140.9(9)°; N(1b)···O(2a) = 3.069(12) Å, N(1b)H(1b)O(2a) = 146.1(8)°], and the chloride ion of the (R_{Ir}) isomer with the NH group of the (S_{Ir}) epimer of the next unit cell [Cl(1b)···N(1a) = 2.510(8) Å, Cl(1b)H(1a)N(1a) = 145.2(7)°]. Most probably, the energy released from the formation of this network is the driving force for the observed epimerization on going from solution to the solid and, therefore, it would be precluded in *N*-substituted prolinates. In fact, we have only detected one diastereomer for the *N*-methylprolinates in both solid state and solution, and determined, from NOE measurements in solution and/or from X-ray diffraction analyses in the crystal, that it has an (*S*) configuration at the metal center for the four metals (Figure 3). On comparison of the circular dichroism (CD) spectrum of the *N*-methylprolinates with those of enriched mixtures of the remaining aminocarboxylates, we propose that the (*S*) configuration at the metal center is adopted for the major component of the mixtures, in all cases.

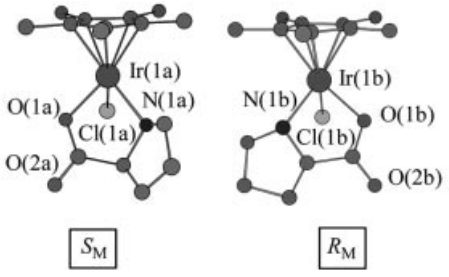


Figure 1. Molecular structure of [(η^5-C_5Me_5)Ir(Pro)Cl]

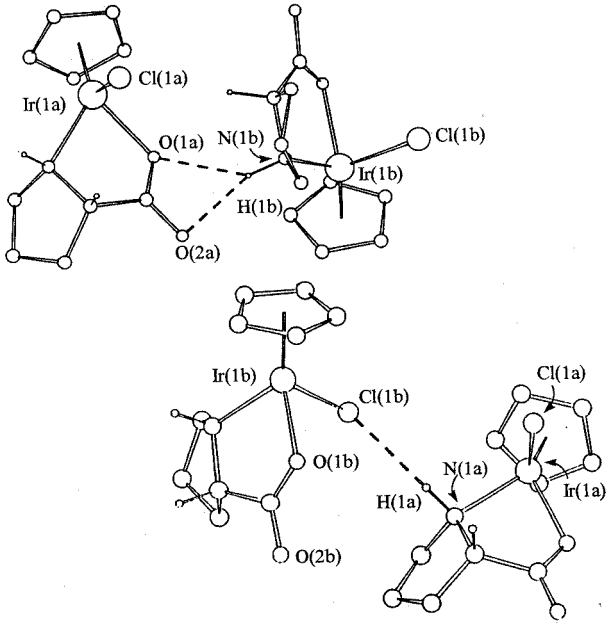


Figure 2. Hydrogen-bond network present in the iridium prolinate [η^5-C_5Me_5)Ir(Pro)Cl]

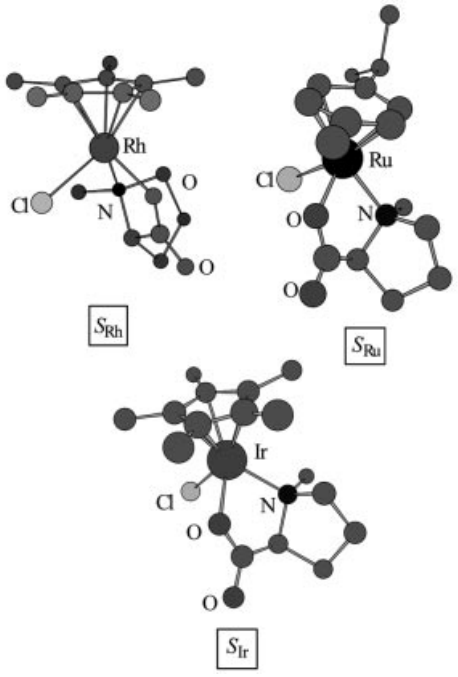


Figure 3. Molecular structures of *N*-methylprolinates

3. Alkynyl Compounds

The aforementioned aminocarboxylate compounds [(η^n-ring)M(Aa)Cl] reacted with terminal alkynes HC≡CR (R = CMe_3, $SiMe_3$, Ph, CO_2Me) in basic media (KOH or NEt_3), affording the corresponding alkynyl compounds [(η^n-ring)M(Aa)(C≡CR)] (Scheme 2).[35,36] In the preparation of the rhodium derivatives, it is necessary that KOH be used as the base. For the rhodium and iridium prolinate complexes, as well as for the ruthenium alaninate [{(η^6-*p*-MeC_6H_4*i*Pr)Ru(Ala)(C≡CPh)] two epimers at the metal center were detected. These complexes slowly epimerize in chloroform, acetone or methanol, the equilibrium composition is dependent on the metal, aminocarboxylate and alkynyl ligand. In particular, the equilibrium constant for the process (R_{Ir},S_C,S_N)-[(η^5-C_5Me_5)Ir(Pro)(C≡$CCMe_3$)] ⇆ (S_{Ir},S_C,S_N)-[(η^5-C_5Me_5)Ir(Pro)(C≡$CCMe_3$)] is 2.70 ± 0.41, in methanol at 20 °C. However, for the other alkynyl complexes only one epimer at the metal center was detected, their CD and NMR spectra remained essentially unchanged over several days.

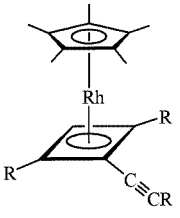
Although the reaction between aminocarboxylate compounds [(η^n-ring)M(Aa)Cl] and terminal alkynes in basic media usually affords alkynyl compounds of the formula [(η^n-ring)M(Aa)(C≡CR)], the reaction of the (alaninato)-rhodium chloride [(η^5-C_5Me_5)Rh(Ala)Cl] with the monosubstituted alkynes HC≡CR (R = Ph, *p*-tolyl) takes a completely different route. From the reaction medium the alkynylcyclobutadiene complexes [(η^5-C_5Me_5)Rh(η^4-C_4HR_2C≡CR)] (R = Ph, *p*-tolyl) can be isolated (Scheme 3).[37] Their formation implies a novel type of rhodium-mediated trimerization reaction. The most common trimerization process that alkynes undergo is cycloaddition,

$$[(\eta^n\text{-ring})M(Aa)Cl] + HC{\equiv}CR + Base \rightarrow [(\eta^n\text{-ring})M(Aa)(C{\equiv}CR)] \quad (3)$$

$(\eta^n$-ring)M	aa	R
$(\eta^5$-$C_5Me_5)Rh$	Pro	CMe_3
$(\eta^5$-$C_5Me_5)Rh$	Pro	$SiMe_3$
$(\eta^5$-$C_5Me_5)Ir$	Pro	CMe_3
$(\eta^5$-$C_5Me_5)Ir$	Pro	$SiMe_3$
$(\eta^5$-$C_5Me_5)Ir$	MePro	CMe_3
$(\eta^5$-$C_5Me_5)Ir$	MePro	$SiMe_3$
$(\eta^6$-*p*-MeC_6H_4iPr)Ru	Ala	Ph
$(\eta^6$-*p*-MeC_6H_4iPr)Ru	Ala	CO_2Me
$(\eta^6$-*p*-MeC_6H_4iPr)Ru	Pro	Ph
$(\eta^6$-*p*-MeC_6H_4iPr)Ru	Pro	CO_2Me

Scheme 2. Alkynyl aminocarboxylate complexes of Rh, Ir, and Ru

rendering arenes; however, as far as we know, cyclobutadiene-containing transition metal complexes have never been the result of an alkyne trimerization process.[38,39] Figure 4 displays the molecular structure of the phenyl complex. The structure of the cyclobutadiene ligand indicates that both oligomerization and cyclization steps have to be involved in its formation. In agreement with previously reported alkyne oligomerization processes, the pathway shown in Scheme 4 is suggested. The reaction could start with the protonation of the α-alaninato ligand by one alkyne molecule. Subsequently, a second alkyne molecule could substitute the chloride anion. At this point, the reductive tail-to-tail coupling of the two alkynyl ligands at the rhodium center could take place, rendering intermediate **B**. This reductive coupling is a key step since it has been proposed that in the absence of the amino acid ligand, $[(\eta^5\text{-}C_5Me_5)Rh(C_2Ph)_2(NCMe)]$ inserts acetylenes into the rhodium−acetylide bond in a series of stepwise *cis* insertions, which ultimately yields the rhodium complexes depicted in Scheme 5.[40] The substitution of the alanine by an alkyne molecule in **B**, followed by the oxidative coupling of the two alkyne ligands in **C**, may occur to give the unsaturated metallacyclopentadiene **D**. Finally, compound **D** could, through a reductive elimination, give the cyclobutadiene product.



R = Ph, *p*-Tolyl

Scheme 3. Alkynylcyclobutadiene complexes

4. Cationic Trimers

The α-aminocarboxylate chloride complexes $[(\eta^n\text{-ring})M(Aa)Cl]$ (M= Ir, Rh, Ru, Os) were found to behave as ionic conductors in polar solvents such as methanol or

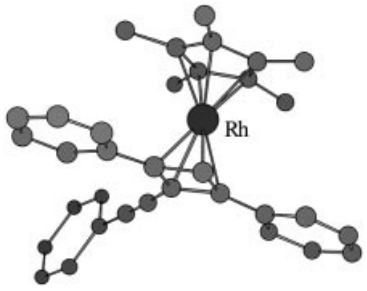
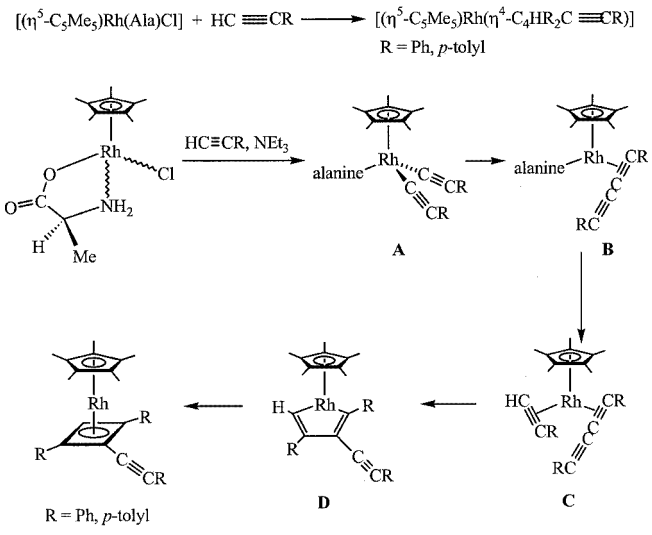
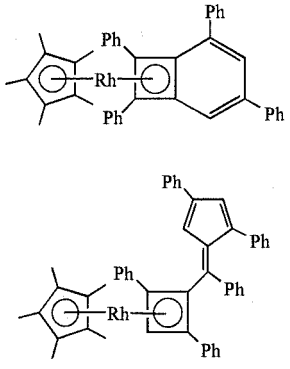


Figure 4. X-ray molecular structure of $[(\eta^5\text{-}C_5Me_5)Rh(\eta^4\text{-}C_4HPh_2C{\equiv}CPh)]$



Scheme 4. Suggested pathway for the formation of the (cyclobutadiene)rhodium complexes



Scheme 5. Related (cyclobutadiene)rhodium complexes

water. Molar conductances greater than 60 $\Omega^{-1}cm^2mol^{-1}$ were achieved in the latter solvent. This behavior was explained by assuming a reversible ionization of the chloride ligand.[26,41] However, conductance measurements in water gave values for the slope of the Onsager equation that clearly pointed to a molecular complexity greater than that of univalent electrolytes.[41] To obtain further insights into the actual nature of this ionic species, the reactions of a variety of the aforementioned chloro complexes with $AgBF_4$ were carried out. The reactions resulted in the preparation of a family of chiral-at-metal trimers of the general formula

$[\{(\eta^n\text{-ring})M(Aa)\}_3](BF_4)_3$ (Scheme 6). Two members of this family, namely $[\{(\eta^5\text{-}C_5Me_5)Rh(Phe)\}_3](BF_4)_3$ and $[\{(\eta^5\text{-}C_5Me_5)Ir(Pro)\}_3](CF_3SO_3)_3$, have been previously reported by Beck et al.[42−45] Figure 5 shows the X-ray molecular structures of four members of this series. The aminocarboxylate ligand acts as a tridentate bridging group. The nitrogen atom and one of the carboxylic oxygen atoms of each amino acid are bonded to a metal center in a chelated fashion forming a five-membered metallacycle; the remaining oxygen atom coordinates to a second, different metal center and confers an additional intermetallic bridging nature to the amino acid anion ligand. The coordination environment confers a chiral nature to each metal center and, interestingly, only the two diastereomers with the same absolute configuration for the three metal centers, i.e. the ($R_MR_MR_M$) or the ($S_MS_MS_M$) isomers, were detected. Thus, the cyclization process occurs *with chiral self-recognition* among the mononuclear fragments. Solution studies revealed that in highly polar solvents isomerization of the trimers readily takes place. The rates of diastereomerization are strongly metal-dependent, increasing in the sequence Ru ≈ Os << Ir < Rh. Furthermore, while in solvents of low polarity, such as dichloromethane or acetone, the ($R_MR_MR_M$) isomer is thermodynamically preferred, in water the ($S_MS_MS_M$) isomer is thermodynamically favored. A theoretical analysis carried out at a supramolecular level for the trimer $[\{(\eta^5\text{-}C_5Me_5)Ir(Ala)\}_3](BF_4)_3$ led us to suggest a plausible explanation for the different stabilities encountered: the low number and the relatively restrained localization of the polar groups (amino hydrogen atoms) on the molecular surface of the ($R_{Ir}R_{Ir}R_{Ir}$) diastereomer (Figure 6) could sterically constrain the accessibility of solvent molecules to this area, thus reducing the number of polar trimer−solvent intermolecular interactions formed.[41] On the other hand, for the ($S_{Ir}S_{Ir}S_{Ir}$) diastereomer, the change in the metal configuration is associated to a change in the

$$[(\eta^n\text{-ring})M(Aa)Cl] + AgBF_4 \rightarrow$$
$$1/3\ [\{(\eta^n\text{-ring})M(Aa)\}_3](BF_4)_3 + AgCl \qquad (4)$$

Aa =	(η^n-ring)M =
Ala	[Rh], [Ir], [Ru], [Os]
Abu	[Rh]
Val	[Rh], [Ir], [Ru]
Tle	[Rh], [Ir], [Ru]
Phe	[Rh], [Ir], [Ru], [Os]
MePhe	[Ru], [Os]
L-Pro	[Rh], [Ir], [Ru], [Os]
D-Pro	[Rh], [Ir], [Ru]
Aze	[Ru], [Os]
Pip	[Ru], [Os]
MePro	[Rh], [Ir]
Hyp	[Rh], [Ir], [Ru]

Scheme 6. Cationic aminocarboxylate trimers

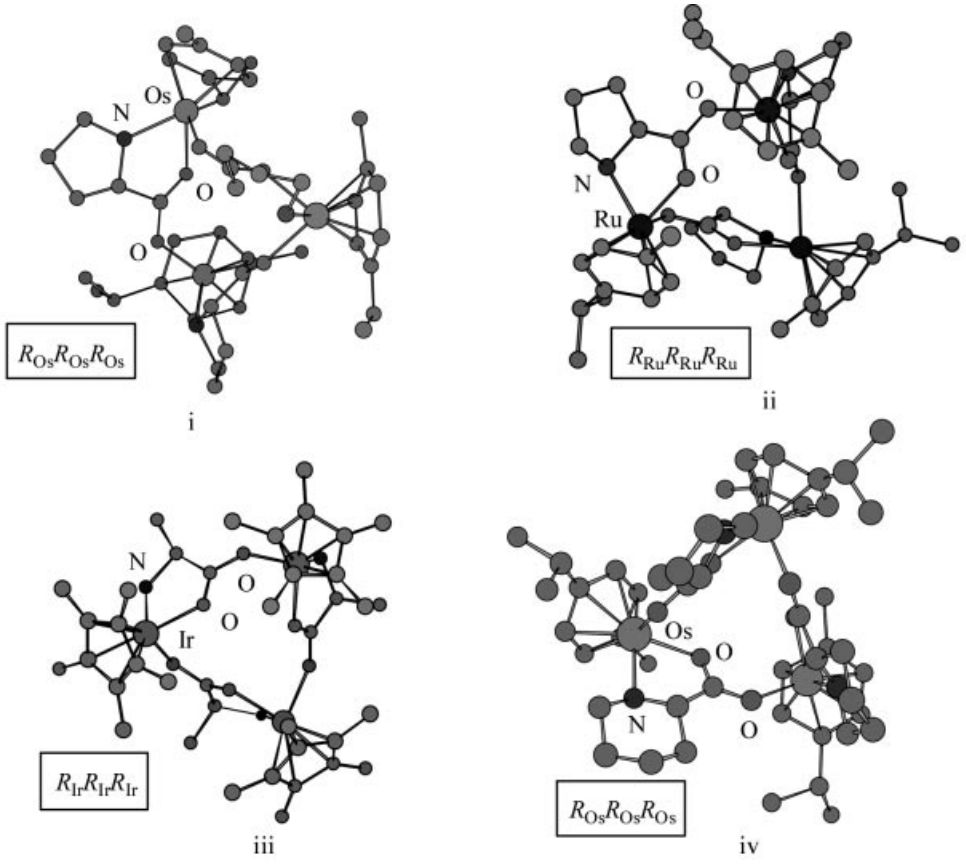


Figure 5. Molecular representations of the trinuclear cations of i) $[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(Pro)\}_3]^{3+}$, ii) $[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(Pro)\}_3]^{3+}$, iii) $[\{(\eta^5\text{-}C_5Me_5)Ir(Ala)\}_3]^{3+}$, and iv) $[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(Pip)\}_3]^{3+}$

localization of amino hydrogen atoms on the surface of the molecule. They are dispersed on the molecular surface allowing interaction with solvent molecules when dissolved, with no apparent steric constrain. This major accessibility of the polar groups in the ($S_MS_MS_M$) diastereomers compared with that of the ($R_MR_MR_M$) isomers seems to be responsible for the greater stability of the ($S_MS_MS_M$) diastereomers in solution as the polarity of the solvent molecules is increased.

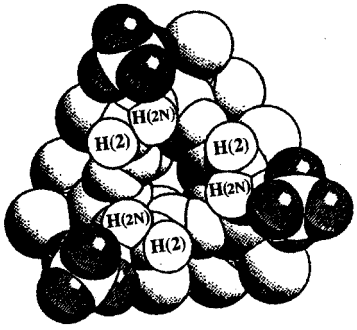


Figure 6. Space-filling model of the ($R_{Ir}R_{Ir}R_{Ir}$)-[{(η^5-C_5Me_5)Ir(Ala)}$_3$](BF_4)$_3$ compound showing the location of one of the amino hydrogen atoms [H(2N)] which is hydrogen-bonded to the BF_4 groups (shaded spheres: carbon atoms; open spheres: hydrogen atoms; black spheres: fluorine atoms of the BF_4 anions)

The equilibrium constant for Equation (5) was determined in methanol, for the range 270−318 K, by integration of corresponding ^{1}H NMR signals of the equilibrated solutions. The equilibrium obeys a simple van't Hoff dependence on the temperature, with $\Delta H^\circ = 23.4 \pm 0.5$ kJ mol^{-1} and $\Delta S^\circ = 80.6 \pm 1.7$ JK^{-1} mol^{-1}.

$$(R_{Rh}R_{Rh}R_{Rh})\text{-}[\{(\eta^5\text{-}C_5Me_5)Rh(Tle)\}_3](BF_4)_3 \leftrightarrows (S_{Rh}S_{Rh}S_{Rh})\text{-}[\{(\eta^5\text{-}C_5Me_5)Rh(Tle)\}_3](BF_4)_3 \quad (5)$$

5. Cationic Phosphane Complexes

Attempts to prepare [(η^n-ring)M(Aa)L]$^+$ compounds by treating [{(η^n-ring)M(Aa)}$_3$]$^{3+}$ trimers with ligands L, such as carbon monoxide, olefins or alkynes, proved to be unsuccessful. However, reaction with tertiary phosphanes readily produces the corresponding cationic monometallic compounds [(η^n-ring)M(Aa)(PR_3)]$^+$ [Equation (6), Scheme 7].[9,26,30,31]

$$1/3\,[\{(\eta^n\text{-ring})M(Aa)\}_3](BF_4)_3 + PR_3 \rightarrow [(\eta^n\text{-ring})M(Aa)(PR_3)]BF_4 \quad (6)$$

The phosphane complexes have been prepared as mixtures of (S_M) and (R_M) epimers. The assignment of the absolute configuration of the metal center was accomplished by a combination of X-ray diffraction (Figure 7), CD and

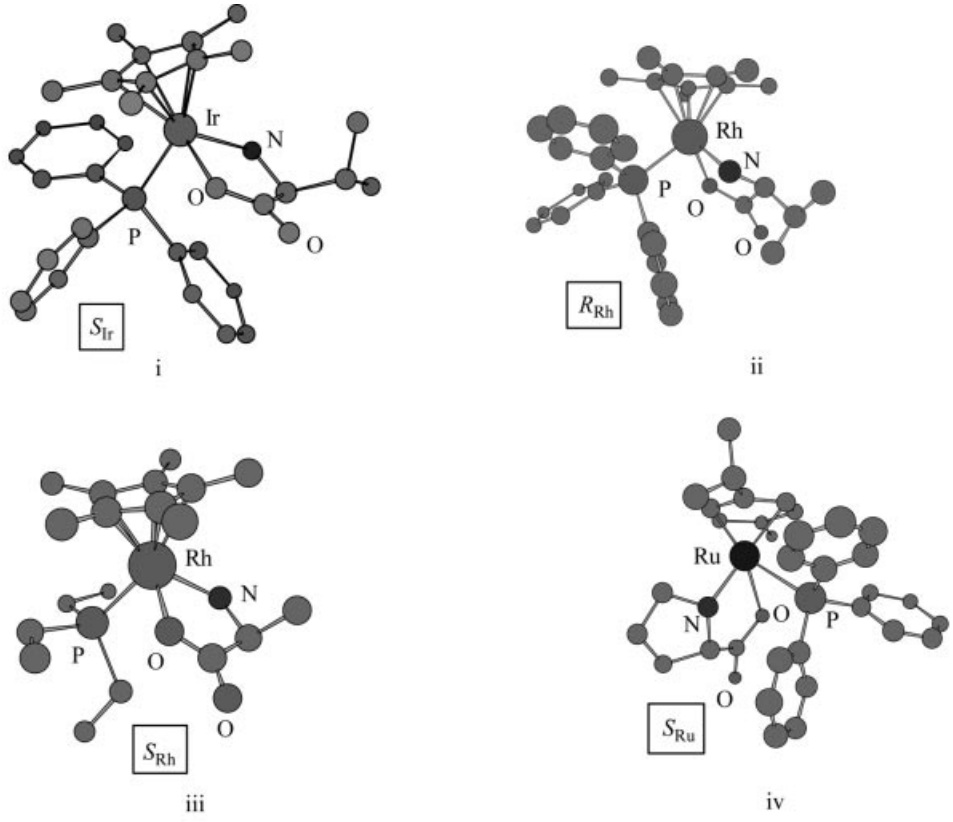


Figure 7. Molecular structures of the cationic phosphane complexes i) [(η^5-C_5Me_5)Ir(Val)(PPh_3)]$^+$, ii) [(η^5-C_5Me_5)Rh(Val)(PPh_3)]$^+$, iii) [(η^5-C_5Me_5)Rh(Ala)(PEt_3)]$^+$, and iv) [(η^6-*p*-MeC_6H_4*i*Pr)Ru(Pro)(PPh_3)]$^+$

NMR spectroscopic measurements. The isolated compounds were always enriched in the (S_M) isomer, which is the kinetically preferred epimer. In alcoholic solutions the (S_M) isomers epimerize at the metal center, the (R_M) isomers are thermodynamically preferred. The kinetic formation of the (S_M) isomers can be accounted for by assuming the preferential attack of the PR_3 ligand through the *Re*-face (hydrogen-shielded), rather than the *Si*-face (R^1- and R^2-shielded),[46] of a planar intermediate derived from the cleavage of the metal−oxygen bridging bonds of the trimers (Scheme 8). Support for this proposal stems from the measured diasteroselectivities. Thus, the kinetic diastereoselectivity in the (triphenylphosphane)rhodium series [(η^5-C_5Me_5)Rh(Aa)(PPh_3)](BF_4), Aa = Ala (R^1, Me), Abu (R^1, Et), Val (R^1, *i*Pr), and Tle (R^1, *t*Bu)] is 46, 50, 70, and 78% *de*, respectively, reflecting the increase in the size of the R^1 group.

The epimerization rate strongly depends on the metal and on the phosphane. Again, it increases in the sequence Ru < Ir < Rh. Table 1 presents the values of the rate constant for a series of (*tert*-leucinato)rhodium complexes with different tertiary phosphanes. The epimerization rate increases as the phosphane basicity decreases. Thus, arylphosphanes with electron-withdrawing substituents have the largest rate constants.

6. Epimerization Processes

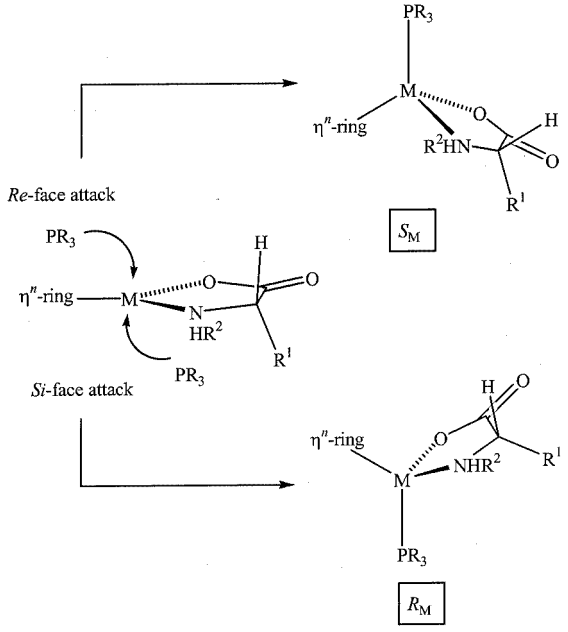
As stated above, most of the aminocarboxylate derivatives epimerized at the metal center. To gain a better insight into the epimerization mechanism some kinetic and scrambling experiments have been performed. Thus, for example: (i) Kinetic measurements for the epimerization of (R_{Ir},S_C,S_N)-[(η^5-C_5Me_5)Ir(Pro)(C≡CCMe$_3$)] in chloroform for the temperature range 293−318 K revealed that the epimerization obeys a first-order rate law, with derived rate constants ranging from (2.74 ± 0.02) × 10^{-5} s^{-1} ($t_{1/2}$ = 6 h, 293 K) to (61.7 ± 5.3) × 10^{-5} s^{-1} ($t_{1/2}$ = 0.25 h, 318 K); the activation parameters are $\Delta H^{\neq}$ = 91.4 ± 3.4 kJmol^{-1} and $\Delta S^{\neq}$ = −20.8 ± 10.8 JK^{-1}mol^{-1}. (ii) The rate of isomerization of the iridium compound [{(η^5-C_5Me_5)Ir(MePro)}$_3$](BF_4)$_3$ at 51°C in methanol, was adequate to be monitored by ^{1}H NMR spectroscopy; a first-order rate law was obtained with a rate constant *k* of 2.45 ± 0.01 × $10^{-5}$$s^{-1}$. (iii) Epimerization of the triphenylphosphane complex [(η^5-C_5Me_5)Rh(Tle)(PPh_3)]BF_4 in methanol also follows a first-order rate law, and from the dependence of its rate constant on the temperature in the 296−307 K interval, activation parameters of $\Delta H^{\neq}$= 88.7 ± 0.6 kJmol^{-1} and $\Delta S^{\neq}$ = −24.9 ± 1.7 JK^{-1}mol^{-1} have been obtained.[31]

On the other hand, an equimolar mixture of (R_{Ir},S_C,S_N)-[(η^5-C_5Me_5)Ir(Pro)(C≡CCMe$_3$)] and (S_{Ru},S_C)/(R_{Ru},S_C)-[(η^6-*p*-MeC_6H_4*i*Pr)Ru(Ala)(C≡CPh)] [(S_{Ru},S_C)/(R_{Ru},S_C) = 70:30 molar ratio] was allowed to epimerize in methanol at 22 °C (Scheme 9). The processes were monitored by ^{1}H NMR spectroscopy and this technique clearly showed that both compounds epimerize independently to the corresponding (S_{Ir},S_C,S_N) and (R_{Ru},S_C) derivatives. Thus, no intermolecular processes rendering compounds containing Ru(Pro), Ru(C≡CCMe$_3$), Ir(Ala) or Ir(C≡CPh) moieties have been observed.

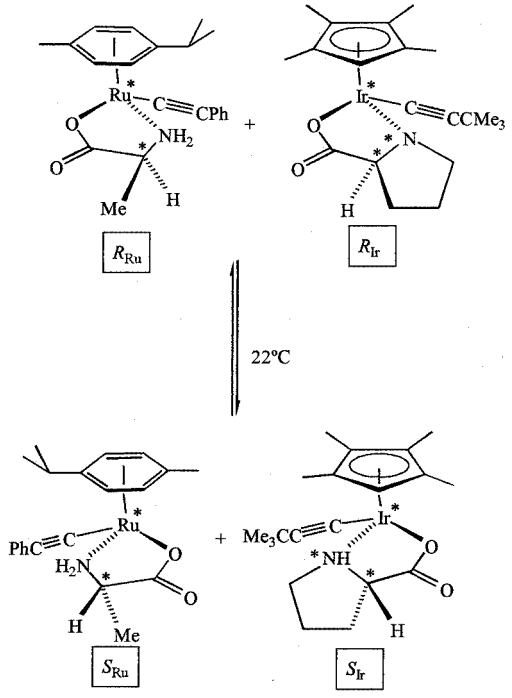
However, when equimolar amounts of the cationic complexes with an (*S*) configuration at the ruthenium center, [(η^6-*p*-MeC_6H_4*i*Pr)Ru(Val)(PPh_3)]BF_4 and [(η^6-*p*-MeC_6H_4-

α-Amino-carboxylate	Phosphane	(η″-ring)M
Ala	P(4-$MeOC_6H_4$)$_3$	[Rh], [Ir], [Ru]
	P(4-MeC_6H_4)$_3$	[Rh], [Ir], [Ru]
	PPh_3	[Rh], [Ir], [Ru]
	P(4-FC_6H_4)$_3$	[Rh], [Ir], [Ru]
	P(4-ClC_6H_4)$_3$	[Rh], [Ir], [Ru]
	P(3-MeC_6H_4)$_3$	[Rh], [Ir], [Ru]
	P(3-ClC_6H_4)$_3$	[Rh], [Ir]
	P(2-MeC_6H_4)$_3$	[Ir]
	PEt_3	[Rh], [Ir]
Abu	PPh_3	[Rh]
Val	P(4-$MeOC_6H_4$)$_3$	[Ru]
	P(4-MeC_6H_4)$_3$	[Ru]
	PPh_3	[Rh], [Ir], [Ru]
	P(4-FC_6H_4)$_3$	[Ru]
	P(4-ClC_6H_4)$_3$	[Ru]
	P(3-MeC_6H_4)$_3$	[Ru]
	P(3-ClC_6H_4)$_3$	[Ru]
Leu	P(4-$MeOC_6H_4$)$_3$	[Ru]
	P(4-MeC_6H_4)$_3$	[Ru]
	PPh_3	[Ru]
	P(4-FC_6H_4)$_3$	[Ru]
	P(4-ClC_6H_4)$_3$	[Ru]
Ile	PPh_3	[Ru]
Tle	P(4-$MeOC_6H_4$)$_3$	[Rh]
	P(4-MeC_6H_4)$_3$	[Rh]
	PPh_3	[Rh], [Ir]
	P(4-FC_6H_4)$_3$	[Rh]
	P(4-ClC_6H_4)$_3$	[Rh]
	P(3-MeC_6H_4)$_3$	[Rh]
	P(3-ClC_6H_4)$_3$	[Rh]
	$PMePh_2$	[Rh]
Phe	PPh_3	[Rh], [Ir], [Ru]
Pro	P(4-$MeOC_6H_4$)$_3$	[Rh], [Ir], [Ru]
	P(4-MeC_6H_4)$_3$	[Rh], [Ir], [Ru]
	PPh_3	[Rh], [Ir], [Ru]
	P(4-FC_6H_4)$_3$	[Rh], [Ir], [Ru]
	P(4-ClC_6H_4)$_3$	[Rh], [Ir], [Ru]
	P(3-MeC_6H_4)$_3$	[Rh], [Ir], [Ru]
	P(3-ClC_6H_4)$_3$	[Ir], [Ru]
	PEt_3	[Rh], [Ir]
Hyp	PPh_3	[Ru]

Scheme 7. Cationic (aminocarboxylato)(phosphane) complexes



Scheme 8. Proposed formation of the two epimers for the cationic phosphane complexes



Scheme 9. Epimerization of an equimolar mixture of (R_{Ir},S_C,S_N)-[(η^5-C_5Me_5)Ir(Pro)(C≡CCMe$_3$)] and (S_{Ru},S_C)/(R_{Ru},S_C)-[(η^6-*p*-Me-C_6H_4*i*Pr)Ru(Ala)(C≡CPh)] [(S_{Ru},S_C)/(R_{Ru},S_C) = 70:30 molar ratio]

Table 1. Rate constant k at 296 K in methanol for the (S_{Rh}) → (R_{Rh}) epimerization process

Compound	$k \times 10^5$ [s^{-1}]
[(η^5-C_5Me_5)Rh(Tle){P(4-MeOC$_6$H$_4$)$_3$}]BF_4	4.22 ± 0.09
[(η^5-C_5Me_5)Rh(Tle)(PMePh$_2$)]BF_4	5.63 ± 0.09
[(η^5-C_5Me_5)Rh(Tle){P(4-MeC$_6$H$_4$)$_3$}]BF_4	5.06 ± 0.06
[(η^5-C_5Me_5)Rh(Tle){P(3-MeC$_6$H$_4$)$_3$}]BF_4	6.00± 0.07
[(η^5-C_5Me_5)Rh(Tle)(PPh$_3$)]BF_4	13.6 ± 0.4
[(η^5-C_5Me_5)Rh(Tle){P(4-FC$_6$H$_4$)$_3$}]BF_4	66.1 ± 0.6
[(η^5-C_5Me_5)Rh(Tle){P(4-ClC$_6$H$_4$)$_3$}]BF_4	209.8 ± 6.6
[(η^5-C_5Me_5)Rh(Tle){P(3-ClC$_6$H$_4$)$_3$}]BF_4	262.8 ± 6.0

*i*Pr)Ru(Pro){P(4-MeOC$_6$H$_4$)$_3$}]BF_4, were allowed to epimerize, the formation of the (phosphane)metal scrambling products [(η^6-*p*-MeC$_6$H$_4$*i*Pr)Ru(Val){P(4-MeOC$_6$H$_4$)$_3$}]BF_4 and [(η^6-*p*-MeC$_6$H$_4$*i*Pr)Ru(Pro)(PPh$_3$)]BF_4 [(*R*)- and (*S*)-metal epimers] was also observed (Scheme 10). Therefore, epimerization occurs with the dissociation of the phosphane ligand.

In a related experiment, an equimolar mixture of the (*tert*-leucinato)rhodium and -iridium complexes [{(η^5-C_5Me_5)M(Tle)}$_3$]$(BF_4)_3$ was dissolved in CD_3OD at −77 °C and the reaction monitored by ^{1}H NMR spectroscopy. An initial ^{1}H NMR spectrum was immediately recorded at −84 °C and it revealed that only the two starting compounds were present in solution, but after 5 min at the same temperature, new signals emerged in the C_5Me_5 region. At room temperature the spectrum showed nine new resonances in this region (most probably due to a mixture of diastereomers of heterometallic trimers), and an FAB$^+$ mass spectrum of the solution revealed peaks at *m*/*z* values of 828, 1196, and 1285, which are assigned to [(η^5-C_5Me_5)$_2$RhIr(Tle)$_2$]$^+$, [(η^5-C_5Me_5)$_3$Rh$_2$Ir(Tle)$_3$]$^+$, and [(η^5-C_5Me_5)$_3$RhIr$_2$(Tle)$_3$]$^+$ fragments, respectively (Scheme 11). Thus, most likely diastereomerization implies the dissociation of the trimers into monomers.

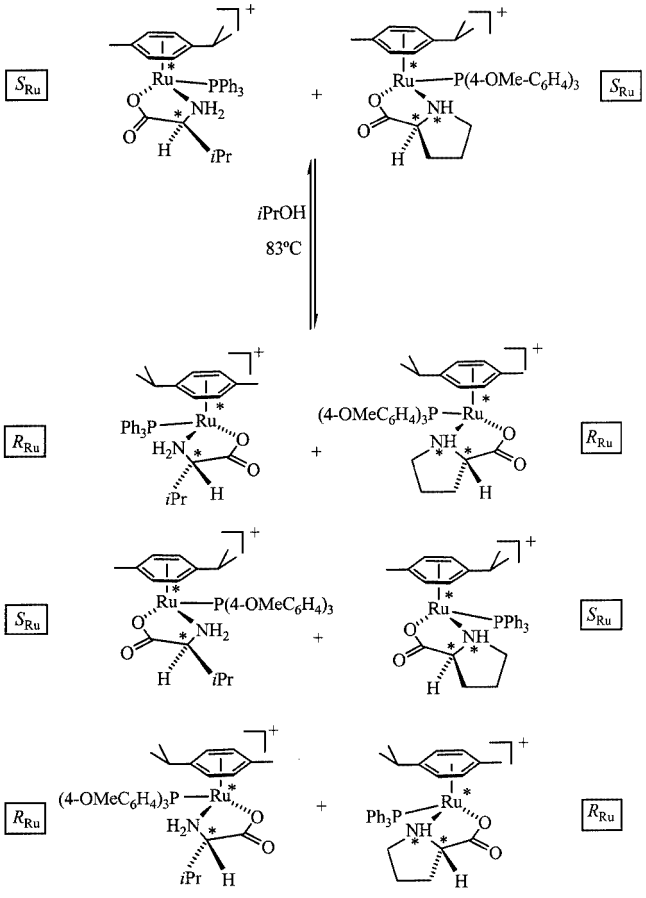
The data collected from all these experiments are compatible with a common epimerization pathway that is outlined in Scheme 12. Dissociation of the chloride ion in the aminocarboxylates [(η^n-ring)M(Aa)Cl], or of the phosphane ligand in the cationic complexes [(η^n-ring)M(Aa)(PR$_3$)]BF_4, and cleavage of the M−O or M−N bonds in the alkynyl compounds [(η^n-ring)M(Aa)(C≡CR)], or of the M−O(bridging) bond in the trimers [{(η^n-ring)M(Aa)}$_3$]$(BF_4)_3$ produce an unsaturated pyramidal species **A** which is in equilibrium with its metal center epimer **C** through a planar achiral intermediate **B**. Subsequent re-coordination of the separated moiety from the other side of the intermediate completes the process. This path accounts for all the experimental observations.

7. Asymmetric Hydrogen Transfer Reactions

Enantioselective transfer hydrogenation of prochiral ketones is a major catalytic procedure for the synthesis of chiral nonracemic secondary alcohols. The results obtained in this field have been reviewed[47] and considerable efforts have recently been paid to elucidate the operating mechanism(s).[48−57]

We have found that both the neutral (aminocarboxylato)(chloro) compounds [(η^n-ring)M(Aa)Cl] and the cationic

trimers $[\{(\eta^n\text{-ring})M(Aa)\}_3](BF_4)_3$ are active catalysts for the hydrogen transfer reaction from 2-propanol to acetophenone (Scheme 13).[41,58] 2-Propanol was used as a hydrogen donor and the solvent; reactions were carried out at refluxing temperature and sodium formate was used as the base. Both conversion and enantioselectivity were measured by gas chromatography. Table 2 presents the results achieved after treating acetophenone under the aforementioned conditions with some selected catalysts.



Scheme 10. Epimerization of an equimolar mixture of (S_{Ru},S_C)-$[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(Val)(PPh_3)](BF_4)$ and (S_{Ru},S_C,S_N)-$[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(Pro)\{P(4\text{-}MeOC_6H_4)_3\}](BF_4)$

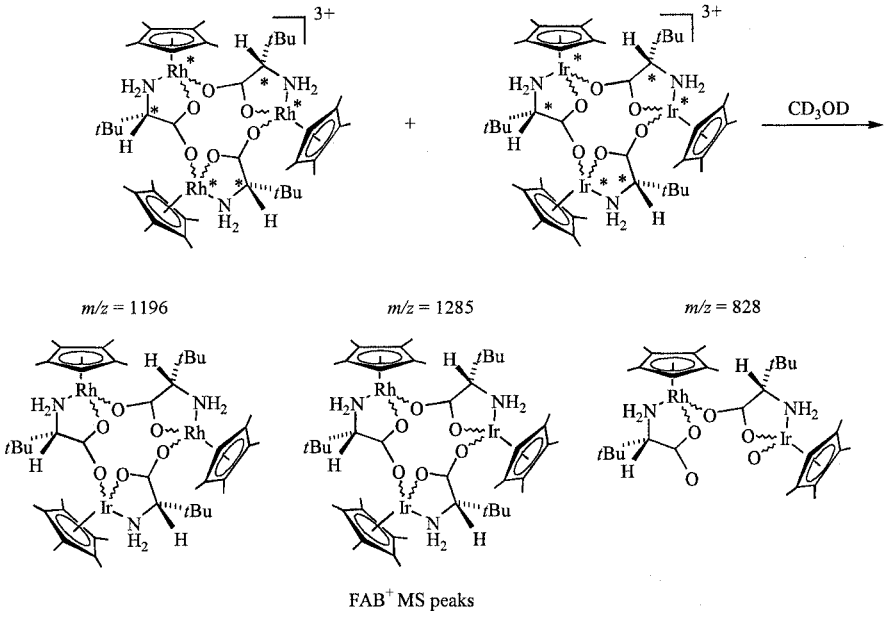
The results deserve some comments:

(i) The best conversions, as well as enantioselectivities were obtained with ruthenium or osmium catalysts. Compare, for example, Entries 1 and 2 (rhodium and iridium prolinate trimers as catalysts) with Entries 3 and 4 (ruthenium and osmium analogues as catalysts).

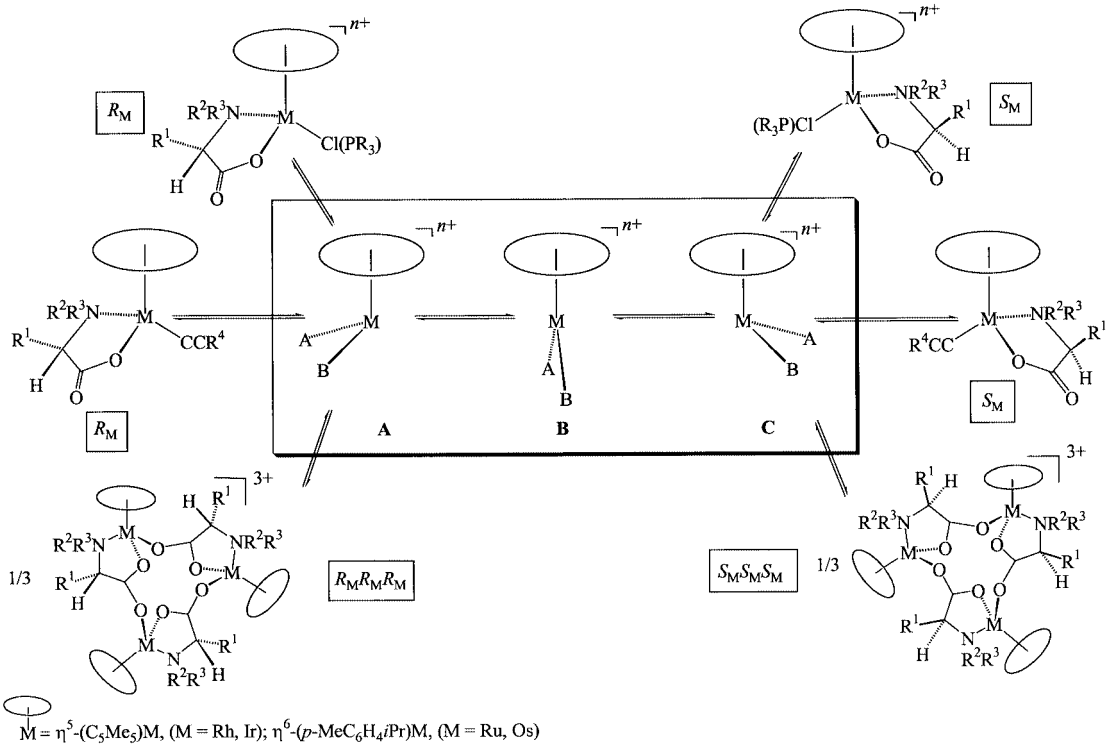
(ii) Catalysts based on cyclic aminocarboxylates produced the best enantioselectivities. Entries 1−4 correspond to cyclic aminocarboxylates, while entries 5−8 correspond to linear aminocarboxylates. Probably, the greater conformational rigidity of the cyclic aminocarboxylates with respect to the linear ones, accounts for the apparent changes in *ee*.

(iii) For a fixed metal and aminocarboxylate, mononuclear chloro complexes and cationic trimers afforded very similar conversions and enantioselectivities. Compare Entries 5 and 7 or Entries 2 and 10. Most probably both species catalyze through a common solvate intermediate $[(\eta^n\text{-ring})M(Aa)S]$, formed by cleavage of the M−O(bridging) bonds in the trimers and halogen abstraction in the chloride ions.

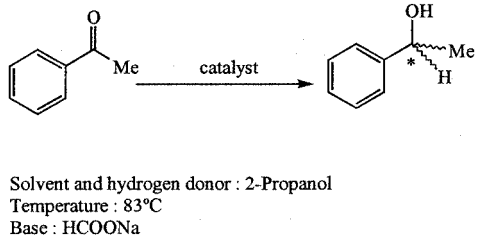
(iv) Catalysts without the NH functionality were almost inactive. Very poor conversions and enantioselectivities have been achieved with *N*,*N*-dimethylphenylalaninate (Entry 15) or *N*-methyl-substituted prolinate (Entries 16 and 17) catalysts. Very recently, Noyori and co-workers have proposed a new metal−ligand bifunctional mechanism that operates for ruthenium-based catalysts containing primary or secondary amines (Scheme 14). The catalyst **A** incorporates hydrogen from the hydrogen donor molecule to form an NH-containing hydride **B** which, in turn, simultaneously transfers the NH proton and RuH hydride to the unsatur-



Scheme 11. Epimerization of a mixture of the complexes $[\{(\eta^5\text{-}C_5Me_5)M(Tle)\}_3](BF_4)_3$ (M = Rh, Ir) in CD_3OD



Scheme 12. Proposed pathway for the epimerization processes



Scheme 13. Standard conditions for the hydrogen transfer reactions

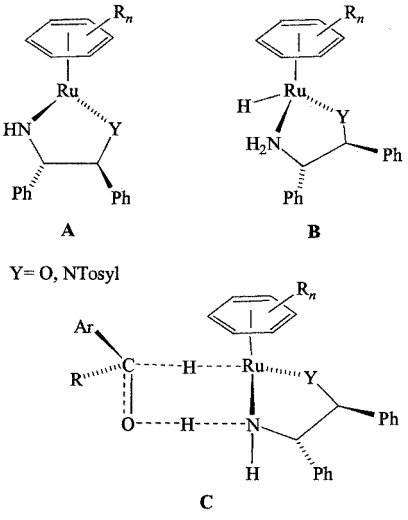
ated substrate through a six-membered cyclic intermediate **C**.[23,59] Probably, this mechanism is operating in the aminocarboxylate catalysts and, therefore, aminocarboxylates, not containing NH groups, are almost inactive.

(v) The (*R*)-alcohols were selectively obtained, except for the piperidine-2-carboxylates (Entries 12 and 14) and *N*-methylphenylalaninate derivatives (Entry 18) which preferentially rendered (*S*)-configured alcohols. When *N*-substituted α-aminocarboxylates coordinate to a metal center through the nitrogen atom, this atom becomes a chiral

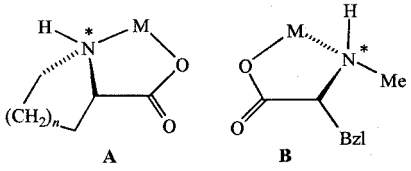
Table 2. Reduction of acetophenone by hydrogen transfer from 2-propanol

Entry	Catalyst	M/Base/Subst.	*t* [h]	Conv. (%)	TOF	*ee* (%)
1	$[\{(\eta^5\text{-}C_5Me_5)Rh(Pro)\}_3][BF_4]_3$	1:2:214	1	8.7	19	60
2	$[\{(\eta^5\text{-}C_5Me_5)Ir(Pro)\}_3][BF_4]_3$	1:2:214	1	15.6	33	64
3	$[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(Pro)\}_3][BF_4]_3$	1:1:100	1	97	97	75
4	$[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(Pro)\}_3][BF_4]_3$	3:4:200	1.25	70	37	72
5	$[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(Phe)\}_3][BF_4]_3$	1:2:214	1	86	184	22
6	$[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(Ala)\}_3][BF_4]_3$	3:4:200	1.5	74	33	14
7	$[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(Phe)Cl]$	1:2:214	1	87.5	187	23
8	$[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(Ala)Cl]$	3:6:200	1	87	58	8
9	$[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(Pro)Cl]$	3:6:200	1	86	57	66
10	$[(\eta^5\text{-}C_5Me_5)Ir(Pro)Cl]$	1:2:214	1	17	36	58
11	$[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(Aze)\}_3][BF_4]_3$	1:1:100	1	70	70	55
12	$[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(Pip)\}_3][BF_4]_3$	1:1:100	0.5	48	97	60 (*S*)
13	$[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(Aze)\}_3][BF_4]_3$	3:4:200	1.25	35	19	50
14	$[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(Pip)\}_3][BF_4]_3$	3:4:200	1.75	70	27	52 (*S*)
15	$[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(Me_2Phe)Cl]$	3:6:200	2	16	5	–
16	$[(\eta^5\text{-}C_5Me_5)Ir(MePro)Cl]$	1:2:214	1	1.8	4	–
17	$[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(MePro)Cl]$	3:6:200	1.5	3	1	–
18	$[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(MePhe)Cl]$	3:6:200	1	90	30	37 (*S*)

center. This is the case for the metal piperidine-2-carboxylates, prolinates or azetidine-2-carboxylates (Scheme 15A, n = 2, 1, or 0, respectively) or for the *N*-methylphenylalaninates (Scheme 15B).



Scheme 14. Metal−ligand bifunctional mechanism



Scheme 15. Chiral nitrogen centers generated by coordination of *N*-substituted aminocarboxylates

Several molecular structures of prolinato complexes determined by X-ray diffraction have been reported and, interestingly, the nitrogen atom always adopts the same configuration as the asymmetric aminocarboxylate carbon atom.[46] Similarly, only diastereomers with the same configuration at both carbon and nitrogen atoms have been detected in the crystal structures for azetidine-2-carboxylate complexes.[9,60]

In sharp contrast, the molecular structures of the L-piperidine-2-carboxylato-containing osmium compounds, [(η^6-*p*-MeC_6H_4*i*Pr)Os(Pip)Cl] and [(η^6-*p*-MeC_6H_4*i*Pr)Os(Pip)]$_3$[BF_4]$_3$, as well as those of the *N*-methyl-L-phenylalaninates, [(η^6-*p*-MeC_6H_4*i*Pr)M(MePhe)Cl] (M = Ru, Os), show that the nitrogen and the asymmetric carbon atoms of the aminocarboxylate adopt opposite configurations, (S_C,R_N) (Figure 8).[61,62]

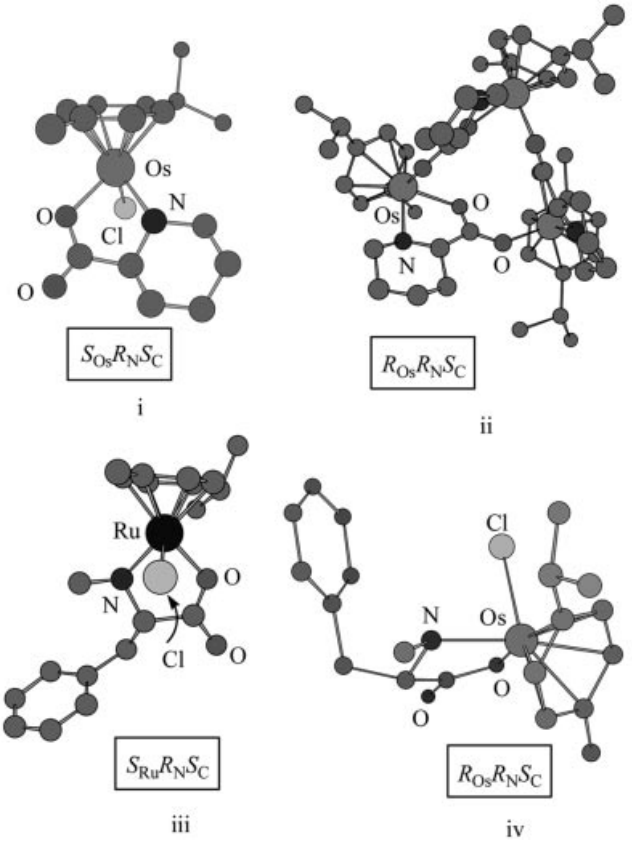
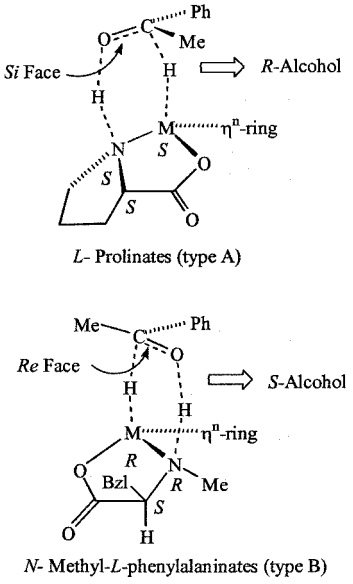


Figure 8. Molecular structures of the (L-piperidine-2-carboxylato)osmium compounds i) [(η^6-*p*-MeC_6H_4*i*Pr)Os(Pip)Cl] and ii) [(η^6-*p*-MeC_6H_4*i*Pr)Os(Pip)]$_3$[BF_4]$_3$, and those of the *N*-methyl-L-phenylalaninates [(η^6-*p*-MeC_6H_4*i*Pr)M(MePhe)]Cl with iii) M = Ru, iv) M = Os

At this point, we suspect that the enantioselection would be related to the different configuration adopted by the nitrogen atom when it coordinates. In fact, we can explain the observed *ee* assuming that the concerted mechanism proposed by Noyori and co-workers is being used.[23,59] Scheme 16 shows the proposed six-membered cyclic intermediate. L-Prolinates (type **A**) and *N*-methyl-L-phenylalaninates (type **B**) have been selected as representative examples of the two types of enantioselection. The cyclic intermediate can only be formed when the metal center and the nitrogen atom adopt the same configuration, i.e. for (S_M) epimers of the **A**-type (S_C,S_N), or for (R_M) epimers of the **B**-type (S_C,R_N). To account for the obtained results [(*R*)-alcohol for the former and (*S*)-alcohol for the latter] the acetophenone phenyl group has to eclipse the *p*-MeC_6H_4*i*Pr ring. In this disposition the carbonyl group interacts with catalysts of type **A** through its *Si* face, but via its *Re* face with those of type **B**, which is in good agreement with the stereochemical outcome. Most probably, recognition of carbonyl enantiofaces is possible through attractive CH−π interactions between the arene ligand and the aromatic acetophenone group, as Noyori et al. have recently proposed, based on theoretical calculations for related (arene)ruthenium systems.[56,57]



Scheme 16. The two possible types of six-membered cyclic intermediates

To obtain further evidence for this proposal we have attempted the reduction of the dialkyl ketone 4-phenyl-2-butanone. Using this substrate, we tried to disrupt the CH−π interactions and then, on the basis of steric grounds, to reverse the enantioselection for both types of catalysts. The results presented in Table 3 strongly support this hypothesis. The L-prolinates [(η^6-*p*-MeC_6H_4*i*Pr)M(Pro)Cl] (M = Ru, Os) afforded (*S*)-4-phenyl-2-butanol, whereas *N*-methyl-L-phenylalaninates produced (*R*)-4-phenyl-2-butanol, preferentially. Thus, the assumption of Noyori's mechanism for the hydrogen transfer reaction from 2-propanol to acetophenone or 4-phenyl-2-butanone, catalyzed by α-aminocarboxylate complexes, explains the *ee* obtained.

Table 3. Reduction of 4-phenyl-2-butanone by hydrogen transfer from 2-propanol

Entry	Catalyst	*t* [h]	TOF	*ee* (%)
1	[(η^6-*p*-MeC_6H_4*i*Pr)Ru(Pro)Cl]	1.5	42	32 (*S*)
2	[(η^6-*p*-MeC_6H_4*i*Pr)Ru(MePhe)Cl]	1	56	14 (*R*)
3	[(η^6-*p*-MeC_6H_4*i*Pr)Os(Pro)Cl]	3	45	30 (*S*)
4	[(η^6-*p*-MeC_6H_4*i*Pr)Os(MePhe)Cl]	6	36	5 (*R*)

8. Conclusions

In this Microreview, we have described half-sandwich aminocarboxylato compounds of rhodium, iridium, ruthenium or osmium with a chlorine atom, alkynyl groups or tertiary phosphanes as ancillary ligands. The neutral chloro compounds [(η^n-ring)M(Aa)Cl] reacted with $AgBF_4$, most probably yielding the corresponding mononuclear solvates [(η^n-ring)M(Aa)S]$^+$. Whichever metal was used and whatever the aminocarboxylate was, the solvates rearranged to trinuclear compounds through the coordination of the free oxygen atom of the carboxylate group. This trimerization takes place with chiral self-recognition; from the four possible diastereomers only the formation of trimers with equally configured metal centers, that is (*R*,*R*,*R*) or (*S*,*S*,*S*)trimers, was observed. Most of the new aminocarboxylate derivatives epimerized at the metal center following the epimerization pathway outlined in Scheme 12. Chloro compounds [(η^n-ring)M(Aa)Cl] and cationic trimers [{(η^n-ring)M(Aa)}$_3$]$(BF_4)_3$ are active catalysts for the hydrogen transfer reaction from 2-propanol to acetophenone. Finally, it is possible to rationalize that the recognition of the carbonyl enantiofaces of the ketone for the ruthenium catalysts occurs as a result of attractive CH−π interactions between the arene ligand and the aromatic acetophenone group, a mechanistic proposal recently suggested by Noyori et al.

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Received January 10, 2002
[I02014]