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Ion Pairing in Transition-Metal Organometallic Chemistry

Alceo Macchioni*

Department of Chemistry, University of Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

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1. Introduction

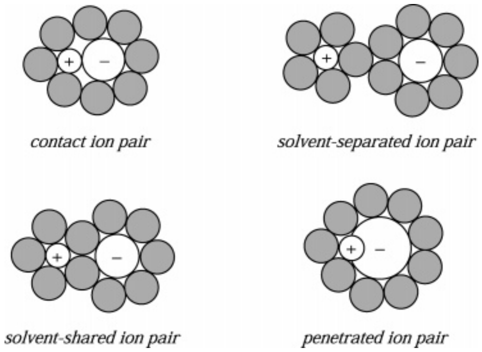
The ion-pair concept[1−4] was introduced in 1926 by Bjerrum[5] to account for the behavior of ionophores (species, such as alkali halides, that are ionic in the crystalline state and exist as ions in the fused state and in dilute solutions) in solvents with low relative permittivity.

Ion pairs are defined as pairs of oppositely charged ions, with a common solvation shell, held together prevalently by Coulombic forces with (a) lifetimes sufficiently longer than the correlation time of Brownian motion (kinetic stability) and (b) a binding energy higher than kT (thermodynamic stability). An ion pair in which no solvent molecule interposes between the two ions is called a contact (or intimate or tight) ion pair (Scheme 1).

In 1954 Winstein[6] and Fuoss[7] independently proposed the existence of another type of ion pairs in order to explain the kinetics of some solvolysis reactions and the conductance trends of tetrabutylammonium bromide in mixed solvents, respectively. This new type of ion pairs is called a solvent-separated (or loose) ion pair (Scheme 1). A further distinction was introduced to discriminate the situation in which only one solvent shell separates the two ions (solvent-shared ion pair) (Scheme 1) from that in which every ion has its own solvation shell (solvent-separated ion pair). The latter two types of ion pairs must also undergo the kinetic (a) and thermodynamic (b) constraints listed above in order to be considered distinct species. Both experimental and theoretical papers have confirmed[1,8,9] or contradicted[10,11] the existence of these new types of ion pairs. The presence of solvent-shared and solvent-

Alceo Macchioni was born in Città della Pieve, Italy, in 1963. He obtained his "Laurea" and Ph.D. degrees in Chemistry from the University of Perugia. After a two-year postdoctoral stay at the ETH of Zürich, Switzerland, he returned to Italy as a Researcher at the University of Perugia. In 2002 he was appointed Associate Professor in General and Inorganic Chemistry at the same University. In 2002 he received the "Raffaello Nasini" prize from the Inorganic Division of the Italian Chemical Society. His research interests include the investigation of intermolecular metallorganic adducts in solution to understand how weak interactions alter their reactivity and structure.

Scheme 1



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* To whom correspondence should be addressed. Phone: +39 075 5855579. Fax: +39 075 5855598. E-mail: alceo@unipg.it.

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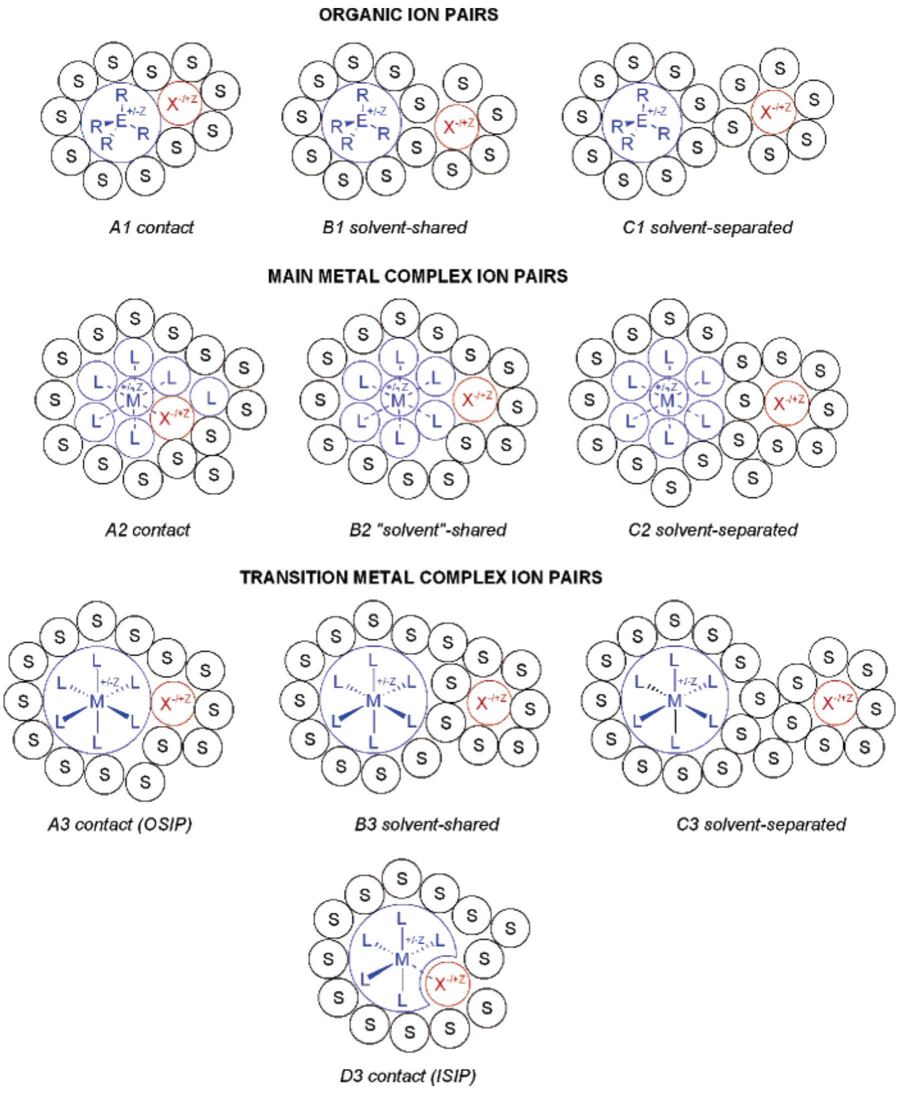
Scheme 2

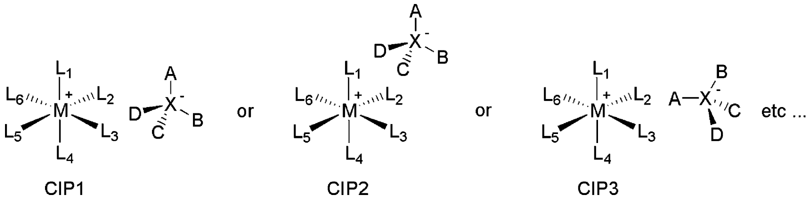


separated ion pairs has been proven at least in the case of solvated metallic ions.[12−15]

Finally, another type of ion pair was discovered by studying tetraalkylammonium tetrafluoroborates having a radius smaller than the sum of the van der Waals radii of the ions. It is called a penetrated ion pair (Scheme 1).[16]

Although the above-reported definitions of the different types of ion pairs can also be correctly applied to complex organometallic ion pairs,[17−19] some clarification is needed in order to avoid misunderstanding the nomenclature of main-group and transition-metal ion pairs. In complex organometallic ion pairs [ML$_n$]X the metal (M) binds n ligands (L). Usually the M−L bonds possess a predominant covalent contribution in transition metals, whereas in main-group metals they are prevalently of an ionic nature (particularly for alkali and alkaline-earth elements).[20,21] Perhaps this difference in bond type leads to the following variances in the definition of ion pairs for the two types of metals. In the case of transition metals, the moiety $ML_n^{\pm Z}$ is considered as a whole ionic moiety (analogously to NR_4^+ or BR_4^-, A1−C1 in Scheme 2, E = N or B) where the charge can be delocalized on L. Consequently, if the counterion(s) and the ligands of $ML_n^{\pm Z}$ are in contact, we have to speak about contact ion pairs (A3 in Scheme 2). When M is a main-group metal in the $ML_n^{\pm Z}$ moiety, the charge is localized on the metal and the neutral or ionic ligands surrounding the metal afford stabilization and protection of the $M^{\pm Z}$ center from the counterion(s) through nondirectional Coulombic interactions. This means that when the counterion(s) closely approach(es) L we still have solvent-shared ion pairs (B2 in Scheme 2) even if L and not solvent molecules (S) interpose between the two ions because of the analogy of the role played by L and S.[22−24] It can be noted that the two apparently similar situations shown in Scheme 2, B2 for main group metal ion pairs and A3 for transition-metal ion pairs, lead to different types of ion pairs owing to the different nature of the M−L bond. For main-group metal salts in solution, contact ion pairs are obtained when the counterion replaces one of the ligands of the first coordination sphere (A2 in Scheme 2). What happens if the same occurs for transition-metal ion pairs? We already have a contact ion pair in which the counterion is “relegated” in the second coordination sphere and, we now form another contact ion pair with the counterion in the first coordination sphere of the

Scheme 3



metal-containing moiety. Assuming that the anion−cation interactions are always of an electrostatic nature, we can define the two contact ion pairs as outer-sphere ion pairs (OSIPs) and inner-sphere ion pairs (ISIPs) (A3 and D3 in Scheme 2, respectively). Finally, another important point for transition-metal ion pairs is that the possibility of having solvent-shared (B3 in Scheme 2) or solvent-separated (C3 in Scheme 2) ion pairs becomes smaller. In fact, the positive charge on the metal is decreased due to the formation of M−L bonds that are more covalent than for main-group metals. In addition, if the same type of ion pair is considered, the distance between the counterion and the metal is increased for transition-metal ion pairs (compare B3 and C3 with B2 and C2, respectively, in Scheme 2). For these reasons, the present review will deal almost exclusively with contact ion pairs, including both ISIPs and OSIPs.

While the importance of ion pairing in organic chemistry has been recognized for a long time,[1,2,17] transition-metal complex ion pairs have only been extensively investigated in the last few decades.[18] In supramolecular chemistry ion pairing and hydrogen interactions naturally play a relevant role in developing anion or ion-pair receptors;[25−27] in addition, the control of interactions between anions and cationic building blocks is of primary importance in the syntheses of novel supramolecular architectures whose resulting structures often depend on the choice of the anion (anion-templated synthesis).[28] Another well-known feature of transition-metal complex ion pairs is represented by the outer-sphere charge-transfer transitions that often lead to interesting photochemical reactions.[29,30] All of these subjects have already been excellently reviewed and will not be treated here.[18,25−30] The possibility of obtaining detailed information about transition-metal complex ion pairs by NOE[31−33] and PGSE[32−34] NMR experiments has also been recently reviewed and will only be mentioned here when there is a connection between ion-pair structures and chemical reactivity.

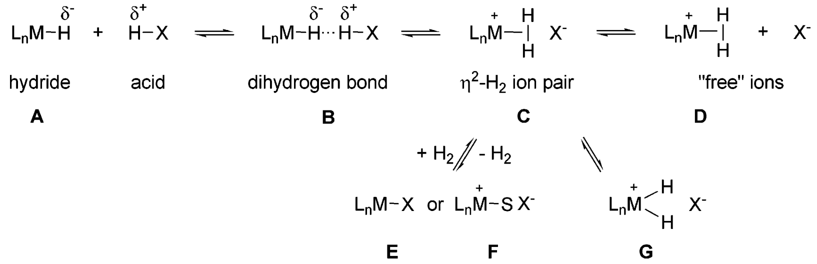
The present paper is focused on the effect of ion pairing in the structure and reactivity of transition-metal organometallic ion pairs, especially in cases in which the counterion, even when located in the first coordination sphere of the metal center, still maintains most of its original charge and, consequently, does not significantly share electron density with the metal. In some cases it is difficult to clearly distinguish between coordinated and uncoordinated counterions, and inevitably ion-pairing effects connected with partial coordination of the counterion will be found sporadically. Under these circumstances, some superposition between the subjects dealt with here and those excellently reviewed by Fagnou and Lautens,[35] in their review on the halide effects in transition-metal catalysis, will be present even if efforts have been made to minimize repetitions.

Ionic transition-metal organometallics are frequently used to promote organic reactions in solvents with low to moderate relative permittivity where, consequently, ion pairing plays an important role.[35,36] The counterions are engineered with the aim of reducing anion−cation interactions.[37−41] Since most of the ionic (pre)catalysts are cationic, the situation of reduced anion−cation interactions is usually reached by increasing the volume of the counteranion and dispersing the negative charge by introducing electron-withdrawing substituents.[42] As a consequence of the reduced anion−cation interactions, weak forces,[43] different from Coulombic ones, may play an important role in stabilizing the ion pairs and determining the relative locations and orientations of the two ions. Furthermore, in transition-metal organometallic ion pairs and, in particular, in the ionic fragment bearing the transition metal, due to the above-mentioned covalent nature of the M−L bonds and also to the marked elongation of the d orbitals and their consequent high polarizability, the charge is often highly dispersed onto different ligands. Several anion−cation relative orientations, having little difference in energy, are possible (Scheme 3).

One of the key points for transition-metal organometallic ion pairs becomes the role of substituents on the cation (L_1−L_6) and anion (A−D) in determining the relative anion−cation orientations, i.e., ion-pair structure, and the stoichiometric or catalytic reactivity.

The number of chemical reactions with transition-metal organometallic compounds that are affected by ion pairing is incredibly high and includes all the possible molecular geometries and electronic configurations of metal centers and types of ligands and counterions. To facilitate the reading of this review, the chemical reactions affected by ion pairing have been divided into two large classes, those concerned with stoichiometric reactions (section 2) and those with catalytic reactions (section 3). Within each class priority has been given to those reactions for which the effects of ion pairing are not only indirectly deducible or hypothizable by mechanistic considerations but also supported by experimental evidence. In addition, each subsection relative to the single reactions is thought to be self-consistent so that it can be read without any contextual difficulty. Finally, the order in which the reactions are presented for each class (stoichiometric and catalytic) reflects the amount of published material on the ion-pairing effect for the considered reaction that *often* reflects the current level of understanding.

Scheme 4



2. Ion-Pairing Effects in Stoichiometric Reactions

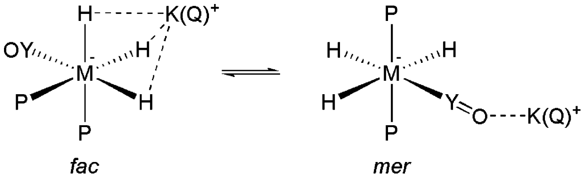
2.1. Formation and Heterolytic Splitting of Dihydrogen Metal Complexes

The reaction of transition-metal hydrides (**A**) with proton donors may produce adducts **B** in which the so-called dihydrogen bond is present,[44−49] i.e., the favorable interaction between a negatively polarized hydride and a positively polarized proton (Scheme 4).

From **B** proton donation may proceed forming the molecular hydrogen ion-paired complex (**C**) that may (1) evolve into "free" ions (**D**), (2) lose molecular hydrogen affording a complex in which the conjugate base of the starting acid (**E**) or a solvent molecule (**F**) is coordinated to the metal center, or (3) transform into a "classical" dihydride complex (**G**) (Scheme 4). All the chemical reactions reported in Scheme 4 may also occur in the reverse sense, namely, in the direction of the heterolytic splitting of dihydrogen metal complexes (from **D** or **C** to **B** and then **A**). As a result, the situation is rather complicated and involves species that usually differ little in thermodynamic stability and kinetic inertness; consequently, the phenomenon of ion pairing can be crucial in favoring one compound over the other. In addition, it has to be considered that while in Scheme 4 the dihydrogen bond is illustrated starting from a neutral transition-metal hydride, several cases are reported in the literature where cationic[50−54] and anionic[55−59] transition-metal hydrides serve as proton acceptors. As a consequence, ion pairing can be important not only at the level of "nonclassical" dihydride ion-paired complexes but also for the other species in Scheme 4.

As far as cationic "classical" hydride complexes **A** and **G** are concerned, it has been observed[60,61] that ion pairing occurs with the anion that avoids being located close to the hydride even if in such a position it would closely approach the metal formally bearing the positive charge. The relative anion−cation orientation in ion pairs *cis,trans*-$[IrH_2(PRPh_2)_2(bipy)]X$ (where R = Ph or Me, $X^- = PF_6^-$, BF_4^-, $CF_3SO_3^-$, or BPh_4^-) was investigated through ^1H-NOESY and $^{19}F,^1H$-HOESY NMR spectroscopies, and it was found that the anion selectively interacts with external bipy and phosphine protons. DFT calculations also indicate that the positive charge is accumulated on these ligands.[60] Quantification of NOE interactions allowed the degree of specificity of anion−cation interactions to be determined that inversely correlates with anion dimensions: $BF_4^- > PF_6^- > CF_3SO_3^- > BPh_4^-$.[60] $^{19}F,^1H$-HOESY NMR studies were carried out by Pregosin and co-workers for complexes *cis*-$[IrH_2(P,N)(L,L)]PF_6$, and again, the anion specifically approaches the cationic moiety without interacting with the hydride ligands.[61] Even in the "amphoteric" hydride complex $[PdH(dppe)_2]X$ ($X^- = CF_3SO_3^-$, BF_4^-, or SbF_6^-), which is able to donate either H^- or H^+, the counteranion avoids being located close to the Pd−H moiety.[62] In one case IR investigations indicate that protonated metallocene $[(\eta^5\text{-}C_5Me_5)_2OsH]^+$ undergoes ionic hydrogen interactions with several anions ($CF_3CO_2^-$, $CF_3SO_3^-$, BF_4^-, or PF_6^-).[63]

Scheme 5



Moving a little to the right of Scheme 4 (**A**−**B** equilibrium) Morris and co-workers have shown that it is possible to take advantage of the synergistic effects of ion pairing and the intermolecular dihydrogen bond to assemble and design novel supramolecular structural types for anionic "classical" polyhydride complexes having the countercation trapped in crown ethers or cryptands.[55−59] In particular, they investigated $[K(Q)][MH_3(YO)(P^iPr_3)_2]$ (where M = Ru or Os and Y = C; M = Re and Y = N; Q = 18-crown-6, 1-aza-18-crown-6, or 2.2.2 crypt),[56] $[K(Q)][MH_5(P^iPr_3)_2]$ (where M = Ru or Os; Q = 18-crown-6, 1-aza-18-crown-6, or 1,10-diaza-18-crown-6),[55,57] $[K(Q)][ReH_6(PR_3)_2]$ (where R = Cy, ^{i}Pr, Ph, or Me; Q = 18-crown-6 or 1,10-diaza-18-crown-6),[58] and $[K(Q)][IrH_4(PR_3)_2]$ (where R = Cy, ^{i}Pr, or Ph; Q = 18-crown-6, 1-aza-18-crown-6, 1,10-diaza-18-crown-6, or 2.2.2 crypt).[59]

The crystal structure of complex [K(1-aza-18-crown-6)][*mer*-$OsH_3(CO)(P^iPr_3)_2$] appeared as a polymeric chain held together by CO···K^+ links and NH···HOs hydrogen bonds.[56] Very interestingly, solution NMR data indicated that both *mer*- and *fac*-isomers were present and that the equilibrium between them (Scheme 5) strongly depends on solvent and countercation.[56]

The equilibrium constants for the isomerization illustrated in Scheme 5 as a function of the metal, sequestering agent Q, and solvent are reported in Table 1. The crucial role of ion pairing in stabilizing the *fac*-isomer becomes evident by comparing the equilibrium constants (1) in toluene, which favors ion pairing, with those in THF and (2) relative to $[K(2.2.2\ crypt)]^+$, where K^+ is encapsulated and cannot interact with the anionic metal fragment, and $[K(18\text{-}crown\text{-}6)]^+$. The ion-paired [K(1-aza-18-crown-6)]-

Table 1. Isomers and Equilibrium Constants Observed in the ^{1}H NMR Spectra of Trihydrides $[K(Q)][MH_3(YO)(P^iPr_3)_2]$ (Q = 2.2.2 crypt, 18-crown-6, 1-aza-18-crown-6)[56]

complex	solvent	2.2.2 crypt	18-crown-6	1-aza-18-crown-6
$[RuH_3(CO)(P^iPr_3)_2]^-$	THF-d_8	mer	*mer*/*fac*, 8.8	*mer*/*fac*, 2.4
	toluene-d_8	mer	*mer*/*fac*, 0.29	*mer*/*fac*, 0.10
$[OsH_3(CO)(P^iPr_3)_2]^-$	THF-d_8	mer	*mer*/*fac*, 23.6	*mer*/*fac*, 6.1
	toluene-d_8	mer	*mer*/*fac*, 0.41	*mer*/*fac*, 0.17
$[ReH_3(NO)(P^iPr_3)_2]^-$	THF-d_8		mer	*mer*/*fac*, 23.0
	toluene-d_8		*mer*/*fac*, 6.2	*mer*/*fac*, 2.6

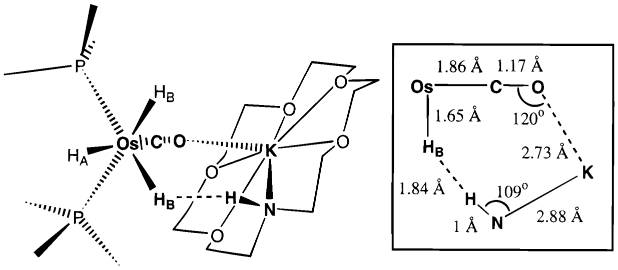


Figure 1. Selective K⋯O and H⋯H ion-pairing interactions of $[K(1\text{-aza-18-crown-6})][\textit{fac}\text{-}OsH_3(CO)(P^iPr_3)_2]$ in nonpolar solvents (ref 56).

$[MH_3(YO)(P^iPr_3)_2]$ is further stabilized by inter-ion-pair M−H⋯H−N interactions.

For the situation in which the *fac*-isomer is the most abundant, $[K(1\text{-aza-18-crown-6})][RuH_3(CO)(P^iPr_3)_2]$ in toluene-d_8, direct evidence of the N−H⋯H−Ru bond was obtained by the detection of an NOE between the two H nuclei: irradiation of the NH resonance resulted in the apparently preferential enhancement of the two equivalent hydrides trans to the phosphorus atoms.[56] A reasonable model for the *fac* trihydride paired with [K(1-aza-18-crown-6)] is shown in Figure 1; it was obtained taking into account NOE constraints and structural data in the solid state.

Assuming the anion−cation orientation illustrated in Scheme 5, the ion pair $[K(1\text{-aza-18-crown-6})][MH_3(CO)(P^iPr_3)_2]$ is stabilized by both K^+⋯O and N−H⋯H−M interactions.

The presence of proton−hydride bonding was also ascertained in the solid state (X-ray and IR investigations) and in solution (IR and ^{1}H, T_1, and NOE NMR experiments) for ion pairs $[K(Q)][MH_5(P^iPr_3)_2]$ (where M = Ru or Os; Q = 1-aza-18-crown-6, or 1,10-diaza-18-crown-6)[57] and $[K(Q)][ReH_6(PR_3)_2]$ (where R = Cy, ^{i}Pr, Ph, or Me; Q = 1,10-diaza-18-crown-6).[58] The strength of the protonic−hydridic bonds for the latter complexes was qualitatively examined by the change in the NH stretching frequency of the cation as a function of the ancillary phosphine ligands of the anions and was found to be in the order $PPh_3 \ll PMe_3 < P^iPr_3 < PCy_3$.[58] The more basic the anion, the stronger the dihydrogen bond.[64,65]

Ion pairs $[K(Q)][IrH_4(PR_3)_2]$ (where R = Cy, ^{i}Pr, or Ph; Q = 18-crown-6, 1-aza-18-crown-6, 1,10-diaza-18-crown-6, or 2.2.2 crypt) evidenced a remarkable sensitivity to the countercation and solvent for what concerns the trans and cis stereochemistry.[59] As an example, for $[IrH_4(P^iPr_3)_2]^-$ the [cis]/[trans] ratio in THF increased from 2:1 to 8:1 on changing the cation from $[K(18\text{-crown-6})]^+$ to $[K(1,10\text{-diaza-18-crown-6})]^+$. On changing the cation to K^+ the [cis]/[trans] ratio increases to 15:1, probably because the small and electrophilic K^+ cation can favorably interact with three facial hydride ligands of the cis isomer as observed in the solid-state structure (Figure 2, left). In addition, the largest [cis]/[trans] ratios are observed for $[K(1\text{-aza-18-crown-6})]^+$ and $[K(1,10\text{-diaza-18-crown-6})]^+$ salts in toluene and benzene for which no trans isomer is observed. The latter result can be reasonably explained invoking stronger ion pairing in toluene and benzene because of their lower dielectric constants compared to THF. The solid-state structure also depends on the countercation and, in particular, the competition between K^+⋯H−Ir and N−H⋯H−M interactions. While in $[K(18\text{-crown-6})][\textit{cis}\text{-}IrH_4(P^iPr_3)_2]$ and $[K(1\text{-aza-18-crown-6})][\textit{cis}\text{-}IrH_4(P^iPr_3)_2]$ the potassium bonds three hydrides on a face of the iridium octahedron (Figure 2, left), $[K(1,10\text{-diaza-18-crown-6})][\textit{trans}\text{-}IrH_4(P^iPr_3)_2]$ crystallizes in a chain structure held together by dihydrogen bonds (Figure 2, right).[59]

In addition to a change from trans to cis stereochemistry, the tetrahydride anion $[IrH_4(P^iPr_3)_2]^-$ displays a remarkable increase in basicity (ca. 100-fold) with a change from $[K(2.2.2\text{ crypt})]^+$ to $[K(18\text{-crown-6})]^+$ countercation.[59]

Experimental evidence for ion-pair intermediate **C** of Scheme 4, sometimes in a delicate equilibrium with adduct **B** in which dihydrogen bonding is active, has been reported in the protonation reaction of "classical" metal hydride with weak acids.[66−70] Interestingly, Chaudret and co-workers observed a dynamic equilibrium between $[\textit{trans}\text{-}Ru(dppm)_2(H)_2]$⋯H−OPh, where phenol is likely associated with a hydride ligand of the ruthenium moiety through a dihydrogen bond, and the dihydrogen ion pair $\textit{trans}\text{-}[RuH(dppm)_2(H_2)]OPh$.[68] Shubina and Limbach investigated the reaction of $CpRuH(CO)(PCy_3)$ with weak HA acids (such as CF_3CH_2OH, $(CF_3)_2CHOH$, $(CF_3)_3COH$, etc.) by variable-temperature IR and NMR spectroscopies.[69] Interestingly, in the IR spectra recorded at 200 K in CH_2Cl_2 they observed that the CO stretching assigned to a mixture equilibrium of $CpRuH(CO)(PCy_3)$ and $CpRu(CO)(PCy_3)H$⋯HA decreased in intensity and a new band at higher frequency appeared and grew in intensity. The latter was assigned to the ion pair $[CpRu(CO)(PCy_3)(\eta^2\text{-}H_2)]A$ by comparison with that of compound $[CpRu(CO)(PCy_3)(\eta^2\text{-}H_2)]BF_4$. Such a transformation was slow enough to be investigated from the kinetic point of view through low-temperature IR spectroscopy; it proved to be independent of the alcohol concentration and suggested a reaction mechanism of rapid preequilibrium: a hydrogen-bond formation diffusion-controlled process followed by the rate-determining-step relative to intracomplex conversion of $CpRu(CO)(PCy_3)H$⋯HA to $[CpRu(CO)(PCy_3)(\eta^2\text{-}H_2)]A$.[69] The latter ion pair was supposed

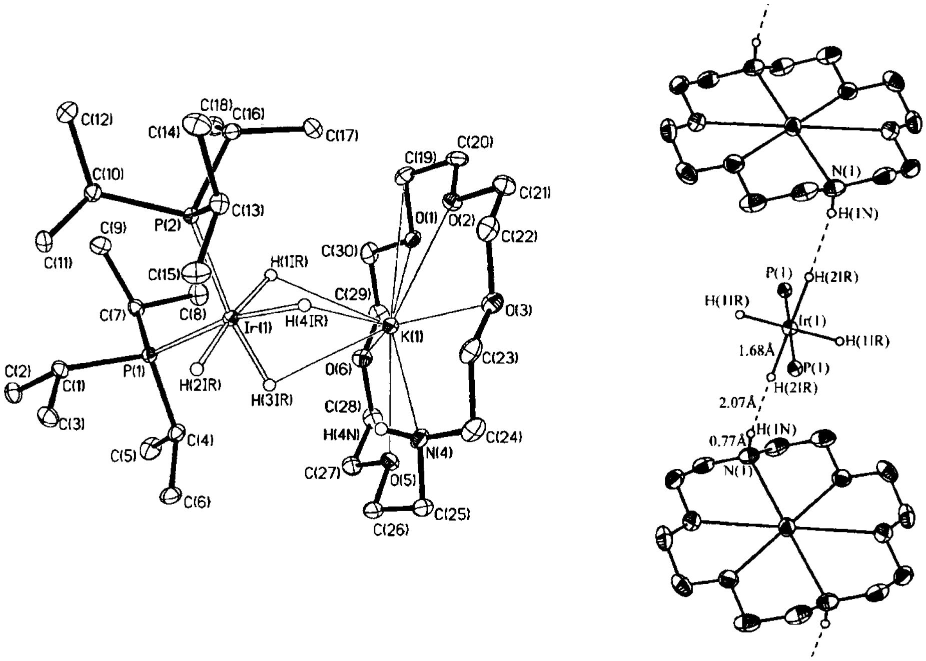


Figure 2. (Left) X-ray structure of [K(1-aza-18-crown-6)][*cis*-$IrH_4(P^iPr_3)_2$]. (Right) Chain structure of [K(1,10-diaza-18-crown-6)][*trans*-$IrH_4(P^iPr_3)_2$]. P^iPr_3 carbon and hydrogen atoms and nonessential crown hydrogen atoms have been omitted for clarity (from ref 59).

to be stabilized by a hydrogen bond between the counterion and the dihydrogen complex due to the sensitivity of the CO stretching band to the basicity of the conjugate base of the acid HA.

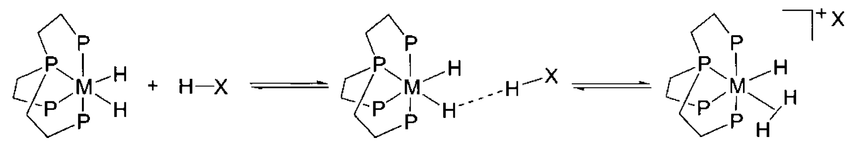
In a more recent study of the same system Lledós and Shubina[71] were able to measure the activation parameters for proton transfer from the dihydrogen-bonded complex to the (η^2-H_2)-complex ion pair (HA = $(CF_3)_3COH$) in *n*-hexane by means of low-temperature IR investigations: $\Delta H^{\#} = 11.0(5)$ kcal/mol and $\Delta S^{\#} = -19(3)$ eu. Both IR measurements and DFT calculations indicated that the major difference when moving from dichloromethane to hexane as the solvent is the decrease in the stability of the dihydrogen–anion ion pair. Calculations also showed the increase of the energy barrier in the charge-separation process when hexane is considered instead of dichloromethane.[71] In addition, the important role of homoconjugated pairs[72] $[RO\cdots H\cdots OR]^-$ was evidenced by means of the inclusion of an additional ROH molecule in the DFT calculations.

Direct NMR evidence about the importance of solvent and the presence of homoconjugated pairs was previously and elegantly reported by Chaudret and Limbach concerning the protonation of $Cp^*RuH_3(PCy_3)$ by fluorinated alcohols.[73,74] The authors compared the appearance of the ^1H NMR spectra at 200 K of $Cp^*RuH_3(PCy_3)$ and various amounts of alcohols in toluene-d_8 and $CDClF_2/CDF_3$ (2:1) (Freons). In addition to a modulation of quantum mechanical exchange couplings,[73,75−77] in the case of $CDClF_2/CDF_3$ (2:1) the formation of $[Cp^*Ru(PCy_3)H_4][A\cdots H\cdots A]$ ion pair was observed. The hydride chemical shift of the latter ion pair was found to be independent of the type of alcohol used, indicating that no hydrogen bonding is present between the anion and cation.[74] The fact that $Cp^*RuH_3(PCy_3)$ was protonated in Freons but not in toluene was explained by considering that at 200 K Freons has a much higher relative permittivity (ca. 20) than that of toluene (ca. 2.5) and favors the ionic form. Interestingly, at room temperature, where Freons has a substantially lower relative permittivity, protonation does not occur.[74]

The kinetics and mechanism of $Cp^*Fe(dppe)H$ protonation was investigated in depth by Poli and Shubina through variable-temperature IR, UV−vis (stopped-flow technique), and NMR spectroscopies.[78] All the results indicated an equilibrium process between adduct **B** of Scheme 4 (already bearing an alcohol molecule), in which the dihydrogen bond is active, and an intermediate $[Cp^*Fe(dppe)(\eta^2\text{-}H_2)]^+$ (**C** in Scheme 4). The equilibrium is shifted toward the latter complex to a greater extent for more acid alcohols and for higher alcohol/$Cp^*Fe(dppe)H$ ratios. Importantly, the observed equilibrium rate constant is linearly dependent on the alcohol concentration, in agreement with involvement of two alcohol molecules and formation of a homoconjugate pair $[RO\cdots H\cdots OR]^-$. The stabilizing effect of a homoconjugate pair on protonation products has recently been suggested for "nonclassical" dihydrogen bonding between early-transition-metal hydrides and alcohols.[79]

The thermodynamic parameters for the protonation of "classical" hydrides (**A**) leading to adducts **B**, in which dihydrogen bonding is present, and successively to "nonclassical" hydride ion pairs **C** (Scheme 4) have been determined for group 8 metals[80−82] and Re.[83] Interestingly, while the proton-accepting ability of the hydride ligands of complexes $[MH_2(PP_3)]$ (PP_3 = $P(CH_2CH_2PPh_2)_3$) shown in Scheme 6 increases in going down the iron triad (Fe−H < Ru−H < Os−H),[81] the propensity to form ion pairs varied aperiodically in the order Fe−H ≪ Os−H < Ru−H.[82] An analogous result was obtained by Morris and co-workers during their investigations on the

Scheme 6[a]



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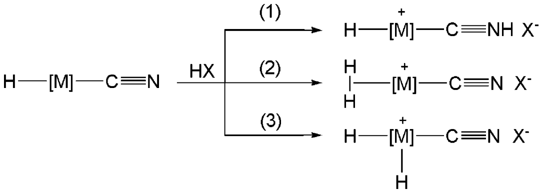
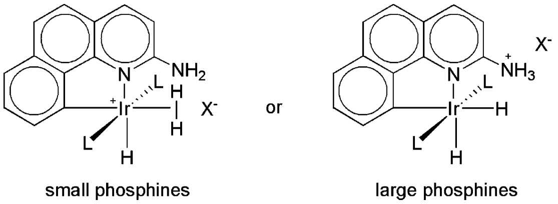
Scheme 7



Scheme 8



acidity of complexes *trans*-[MH(η^2-H_2)(P,P)$_2$]BF_4.[65,84] The aperiodic order of acidity (Ru > Os > Fe) was explained in terms of the strength of the M−(η^2-H_2) bond.

The protonation reaction of “classical” metal hydrides with strong acids has been used as one of the main synthetic methods for preparing dihydrogen complexes (**C** in Scheme 4).[85,86] Ion pairing was found to be important in contributing to direct the protonation reaction toward the desired site when more than one site is present in the complexes. Morris and Rigo investigated the protonation reaction of *trans*-[MH(CN)L_2] (M = Fe, Ru, and Os; L = dppm, dppe, dppp, and depe).[51−53] In principle, the protonation can take place at three different sites as indicated in Scheme 7: (1) at the cyanide, affording a hydrogen isocyanide ligand; (2) at the “classical” hydride bond, producing a dihydrogen complex; and (3) at the metal center, leading to a “classical” dihydride complex.

In agreement with other studies,[72,78] protonation never occurred at the metal[87] (pathway 3). In the case of the dppe, dppp, and dppm ligands, the tautomers [M(η^2-H_2)(CN)L_2]X (2) and [MH(CNH)L_2]X (1) are in a delicate balance that can be tipped one way or the other by changes in solvent and the hydrogen-bonding characteristics of the anion. The latter anion is supposed to shuttle the proton from the dihydrogen on one side of the molecule to the cyanide on the other side. The addition of a base or use of basic solvents (acetone or THF) favors pathway 1 over 2 from both a thermodynamic and kinetic point of view. In some cases addition of HOTf caused the rapid conversion of [MH(CNH)L_2]OTf (1) to [M(η^2-H_2)(CN)L_2][TfO···H···OTf] (2). In addition, complexes [M(η^2-H_2)(CN)L_2]X (2) with $X^- = BF_4^-$ were more stable than analogous OTf^- complexes with respect to the loss of H_2. The isocyanide complexes [MH(CNH)L_2]X (1) were not detected when L = depe. All these observations can be rationalized taking into account the strength of hydrogen bonding in the ion pairs in solution. The CNH ligand has a tendency to form strong hydrogen bonds,[52,88] especially to the triflate anion, which favors complexes [MH(CNH)L_2]X (1) unless the metal hydride becomes very basic, as in the case of depe complexes. The authors assumed that basic solvents might destabilize the putative M−(η^2-H_2)$^+$···X^- interaction[50,89] over M(CN−H)$^+$···X^- hydrogen bond. Finally, it is notable that, in some cases,[53,90,91] cationic dihydrogen complexes can be prepared though displacement of an anionic ligand (even Cl^-)[90] by H_2.

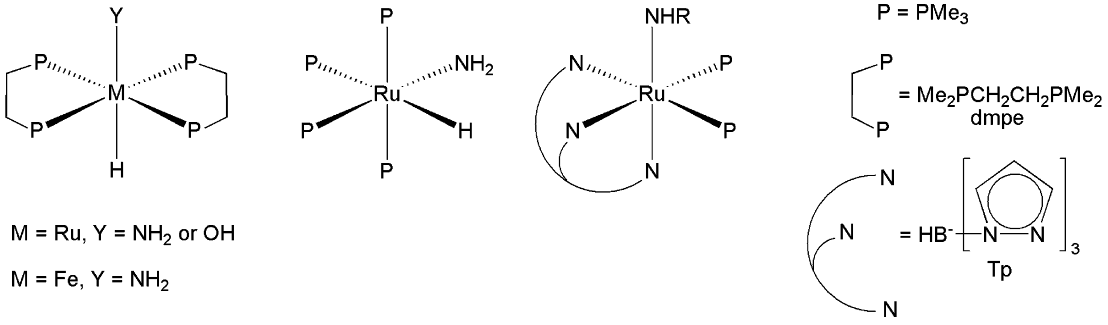
The kinetics of formation of the dihydrogen complex *cis*-[FeH(H_2){P($CH_2CH_2PPh_2$)$_3$}]$^+$ by reaction of *cis*-[FeH_2{P($CH_2CH_2PPh_2$)$_3$}] with strong acids (HX) has been electrochemically investigated in THF by Basallote and co-workers under conditions in which the starting dihydride is oxidized and the dihydrogen complex is not.[92] The limited effect of the acid clearly indicated that *cis*-[FeH_2{P($CH_2CH_2PPh_2$)$_3$}] reacts mainly with H^+···X^- ion pairs, while the observation of an inverse kinetic isotopic effect led them to hypothesize a late transition state with a structure close to that of the dihydrogen complex.

As for the reverse reactions from **D** or **C** to **A** probably through **B** (Scheme 4), it has been proposed that ion pairing plays a key role in the heterolytic H_2 activation occurring in a dihydrogen Ir(III) complex bearing a pendant 2-amino group (Scheme 8).[93]

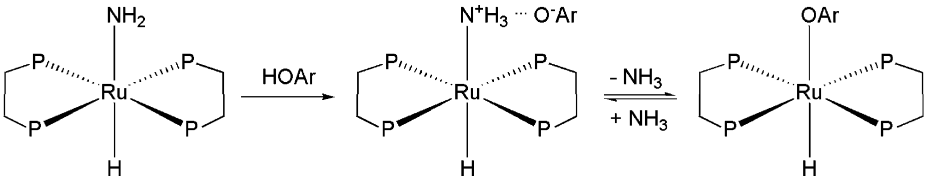
While theoretical studies in which no anion is included predict that the H_2 complex is more stable for all phosphines (L in Scheme 8), it has been only observed for the relatively small phosphine PMe_2Ph. When L are larger (PPh_3 or PCy_3), heterolysis occurs and the dihydride complex is formed independently of the electronic properties of L. On the basis of the potentials calculated for the two cationic isomers, it was suggested that the counteranion should be paired much closer to the metal in [IrH(H_2)(bq-NH_2)L_2]$^+$, while in [IrH_2(bq-NH_3)L_2]$^+$ it should stay much farther away from the metal and probably close to the NH_3^+ moiety (as observed in the ^{19}F,^1H-HOESY NMR spectra of related samples). Because bulky phosphines do not allow close ion pairing, they favor the dihydride complex [IrH_2(bq-NH_3)L_2]$^+$.

Clear indications about the relevance of ion pairing in the kinetic properties of the dihydrogen complexes have recently been reported by Basallote and Lledós.[94] They investigated the reaction of *trans*-[FeH(H_2)(dppe)$_2$]X with NEt_3 that affords *cis*-[FeH_2(dppe)$_2$] and $HNEt_3X$. They found that the reaction was accelerated by the presence of NBu_4BF_4 or NBu_4PF_6, while $NaBPh_4$ caused a significant decrease in the reaction rate. Calculations including the anion (BF_4^-) indicated that it favors separation of the reaction products through formation of a stable [$HNMe_3$]BF_4 ion pair. The deceleration effect exerted

Scheme 9



Scheme 10



by BPh_4^- was explained considering that the latter hinders the approach of the base to the *trans*-[FeH(H_2)(dppe)$_2$]BPh_4 ion pair due to its bulkiness.

Hidai and co-workers, during their very important studies on the possible bimetallic transformation of N_2 into NH_3 in mild conditions, found a significant counteranion effect.[95,96] In particular, they investigated protonation of coordinated N_2 of complex *cis*-[W(N_2)$_2$(dppe)$_2$] by the dihydrogen complex *trans*-[RuCl(η^2-H_2)(dppp)$_2$]X (X^- = PF_6^-, BF_4^-, OTf^-, or BPh_4^-) carried out at 55 °C in a methylene chloride/benzene mixture. The amount of NH_3 produced was much lower when X^- = BPh_4^-, probably due to degradation of the dihydrogen complex via nucleophilic attack of the BPh_4^- anion on the η^2-H_2 ligand, which afforded *trans*-[RuCl(H)(dppp)$_2$], BPh_3, and benzene.[97−99]

2.2. Deprotonation of Weak Acids by M−Y Groups (Y = NR_2, NH_2, OR, or OH)

The M−Y bond of late-transition-metal amido and alkoxo complexes and their parent M−NH_2 and M−OH complexes is thought to be highly polarized and surprisingly strong.[100,101] The M−Y complexes exhibit nucleophilic reactivity, forming strong hydrogen bonds to proton donors or deprotonating relatively weak acids.[102−106] Bergman and co-workers showed that the parent amido complex *trans*-[(dmpe)$_2$Ru(H)(NH_2)] illustrated in Scheme 9 is able to abstract a hydrogen atom from a weak C−H bond and that such an oxidation process likely occurs through a two-electron rather than one-electron process.[103] In fact, in cases of deprotonation of sterically encumbered weak acids (fluorene or triphenylmethane), stable ion pairs containing a cationic ammonia ruthenium complex are generated. The solid-state structure of ion pair *trans*-[(dmpe)$_2$Ru(H)(NH_3)]($C_{13}H_9$) was solved through single-crystal X-ray investigation and is shown in Figure 3.

It is interesting to note that the fluorenide anion is located on the side of the coordinated ammonia; the latter directs its protons toward the π-aromatic electron density of the central part of the fluorenide anion. This orientation is probably maintained in THF solution since the ammonia protons appear to be highly shielded and fall at δ = −0.6 ppm in the ^{1}H NMR spectrum.

Smaller weak acids (such as phenylacetylene, cyclobutanone, alcohols, and amines) are also deprotonated, generating similar ion pairs that usually evolve leading to substitution of ammonia by the counteranion with formation of a neutral complex. Gunnoe and co-workers[106] also found that reaction of complexes [TpRu(PMe_3)$_2$NHR] (R = H, ^{t}Bu, or Ph, Scheme 9) with phenylacetylene affords ion pairs [TpRu(PMe_3)$_2$$NH_2$R]CCPh but only in cases of highly basic amido ligands (R = H or ^{t}Bu).

A peculiar situation was found when *trans*-[(dmpe)$_2$Ru(H)(NH_2)] was reacted with phenol in that an equilibrium mixture of the phenolate ion pair, the ruthenium phenolate complex, and ammonia was obtained (Scheme 10). The ion pair exists as a

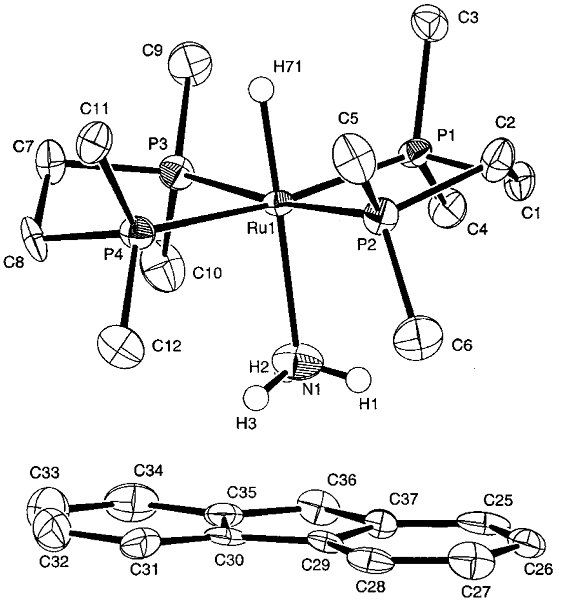


Figure 3. X-ray structure of ion-pair *trans*-[(dmpe)$_2$Ru(H)(NH_3)]($C_{13}H_9$) (ref 103).

Scheme 11

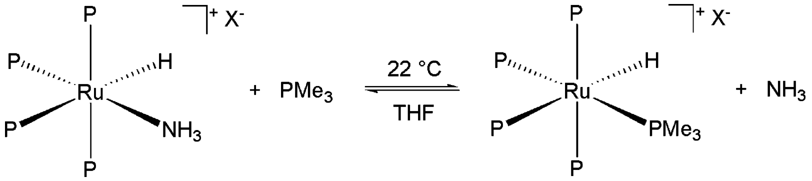


Table 2. Equilibrium Constants for the Displacement of NH_3 by PMe_3 for the Reaction Shown in Scheme 11 (from ref 105)

anion	K_{eq}
F^-	[a]
$OTol^-$	0.45(5)
OTf^-	1.0(1)
$C_{13}H_9^-$	1.4(1)
BF_4^-	4.5(1)
BPh_4^-	16(1)
$BARF^-$	19(1)

[a] No product.

hydrogen-bonded dimer in the solid state and seems to afford a dimeric or even a more complicated aggregate in solution.[103]

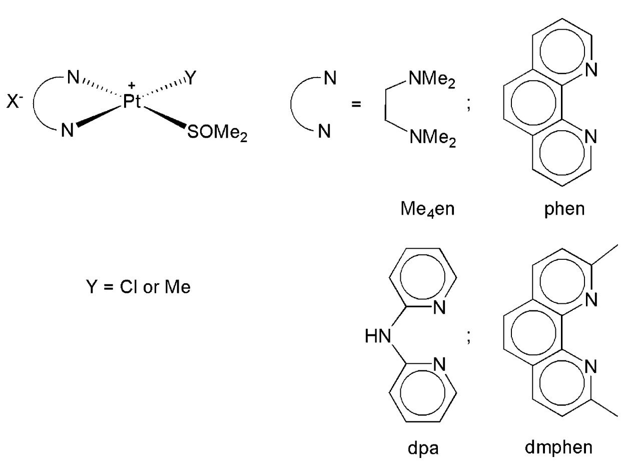
The basicity of the amido complex *trans*-$[(dmpe)_2Ru(H)(NH_2)]$ is really remarkable as demonstrated by the fact that it promotes H/D exchange between protons of its NH_2 group and weak acids such as ammonia-d_3, toluene-d_8, and propene-d_3. The authors suggest that these reactions also proceed via formation of "$Ru-NH_2D^+\cdots D_2Z^-$" ion pairs or through a concerted transition state "$Ru-NH_2^{\delta+}\cdots D_3Z^{\delta-}$".[103]

Similar results were obtained for the Fe(II) complex *trans*-$[(dmpe)_2Fe(H)(NH_2)]$,[104] which is found to be less basic than the analogous Ru(II) complex, probably due to the greater electron richness of ruthenium compared to iron. The complex *cis*-$[(PMe_3)_4Ru(H)(NH_2)]$ also showed reduced basicity with respect to *trans*-$[(dmpe)_2Ru(H)(NH_2)]$. This can be attributed to its cis geometry and the resulting stabilization of the NH_2 lone pair through interaction with the weakly accepting P−C σ^* orbitals of the trans PMe_3 ligand.[105] The basicity of *cis*-$[(PMe_3)_4Ru(H)(NH_2)]$ is enough to deprotonate fluorene and, reversibly, 1,3-cyclohexadiene and toluene, forming stable or transient ion pairs. In the case of the reaction of *cis*-$[(PMe_3)_4Ru(H)(NH_2)]$ with cresole, the formed ion pair *cis*-$[(PMe_3)_4Ru(H)(NH_3)]OTol$ reacts reversibly with PMe_3, affording $[(PMe_3)_5Ru(H)]OTol$ and NH_3 (Scheme 11).

This equilibrium reaction was investigated as a function of the counterion (X^-) in order to understand the role of anion hydrogen bonding in *cis*-$[(PMe_3)_4Ru(H)(NH_3)]X$. It was found that the ammonia complex is more favored by anions with localized charges and have little steric hindrance (Table 2).

Although Table 2 reports data that are useful for comparing anions in terms of their hydrogen-bonding acceptor ability, it can be noticed that the order found ($F^- \gg OTol^- > OTf^- > C_{13}H_9^- > BF_4^- > BPh_4^- > BARF^-$) correlates rather well with the extent to which the poorly coordinating anions donate electron density to metal centers.

Scheme 12



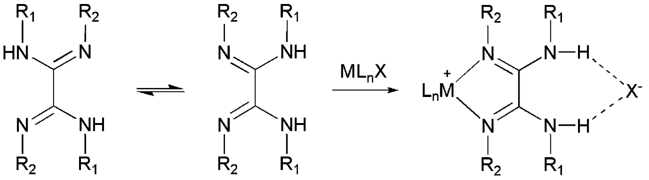
2.3. Substitution Reactions

Several kinetic studies on substitution reactions[107] in transition-metal complexes have led to the hypothesis of pathways involving ion pairs.[108,109] Romeo and co-workers obtained clear evidence that ion pairs intervene in substitution reactions involving square-planar complexes.[110−113] The investigated compounds are shown in Scheme 12.

They observed that the substitution rate of $SOMe_2$ with X^- strongly depended on the solvent and found that it was higher in the least polar solvents used, namely, methylene chloride or chloroform. All the experimental evidence was consistent with an interchange reaction within the preformed aggregates (presumably ion pairs). Interestingly, in the case of compound $[PtCl(SOMe_2)(Me_4en)]BPh_4$ it was possible to locate the anion in solution close to the methylene groups due to the shielding effect exerted by the anion phenyl moieties on such protons that causes a low-frequency shift of their ^1H NMR resonances.[110] Both the ^1H resonance shifts and conductivity measurements were used to determine the dissociation constants of ion pairs (ca. 10^4 M at 298 K), and the two methods were in good agreement.

Similar results were obtained for the displacement of dimethyl sulfoxide from $[PtMe(SOMe_2)(phen)]PF_6$ by a series of uncharged and charged nucleophiles.[111] For the reaction of the latter in dichloromethane, the reaction occurs as an interchange within a contact ion pair with reduced discrimination in reactivity between the various entering Y^- nucleophiles with respect to aqueous solutions. Substitution of the phen with the bis(2-pyridyl)amine (dpa) ligand afforded interactions of increased intensity with the counteranion specifically located close to the N−H bridging moiety in both the solid and solution states.[112] Interestingly, the interaction energy between the anion (PF_6^-) and N−H in $[PtMe(SOMe_2)(dpa)]PF_6$

Scheme 13

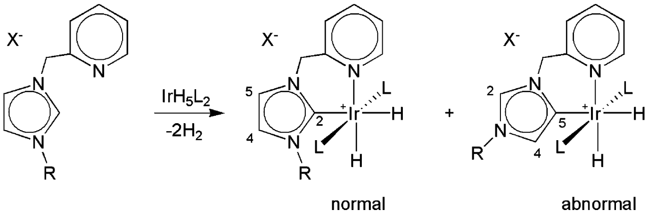


was high enough to allow a stopped-flow measure of the PF_6^- for Cl^- exchange rate at the NH site (96 M^{-1} s^{-1} at 298 K). The substitution of DMSO was affected little by $X^- \cdots H-N$ ion pairing and even by NH complete deprotonation. As in the case of the phen ligand-bearing compound, there was little nucleophile discrimination in chloroform.

The tendency of ion pairing and the acidity of the N−H moiety has also been evidenced by Beauchamp and co-workers in their studies on complexes *cis*-$[ReX_2L_2(biimH_2)]X$ (where $biimH_2$ = 2, 2-biimidazole; L = PPh_3[114] or PMe_3;[115] X^- = Cl^-, Br^-, I^-). Clear indications of ion pairing were observed in the X-ray solid-state structure of *cis*-$[ReX_2(PMe_3)_2(biimH_2)]X$ (X^- = Cl^- or Br^-), where $NH \cdots X^-$ hydrogen bonding was detected. Interestingly, neutral monodeprotonated complexes *cis*-$[ReX_2(PMe_3)_2(biimH)]$ (X^- = Cl^- or I^-) afforded associated pairs through complementary N−H hydrogen bonds.[115] In solution, indications of ion pairing were derived from IR, UV−vis, and ^1H NMR spectroscopies. In addition, electrochemical measurements further supported the presence of ion pairs in that they showed that the oxidation potential of X^- in complexes *cis*-$[ReX_2L_2(biimH_2)]X$ substantially increased (up to 349 mV for Cl^-) with respect to that of NBu_4X due to ion pairing.[115] The acidity of N−H protons in CH_2Cl_2 was estimated by previous deprotonation with MeO^- and successive competition with carboxylic acids followed through UV−vis spectroscopy. Contrary to what was expected, it was found that replacing PPh_3 by the better donor PMe_3 made the N−H groups more acidic. This indicated that ion pairing could play an important role in determining the acidity scale. Walther and co-workers also showed that complexes bearing the bifunctional 1,2-diimine/1,2-diamine-type ligands afford contact ion pairs via the two N−H moieties that do not participate in ligand coordination (Scheme 13).[116,117]

Coming back to the substitution reaction, in investigating a broad series of compounds $[PtMe(SOMe_2)(N,N)]X$, Romeo observed the highest reaction rate with the dmphen ligand (Scheme 12).[118] The latter ligand is known to cause a severe distortion of the square-planar coordination environment because of the steric hindrance of the methyl substituents that are directed in the proximity of the metal center. As a consequence, a two N-arm exchange is facilitated. Such an exchange was investigated in depth for complex $[PtMe(PPh_3)(dmphen)]X$,[113] and it was found to depend strongly on the nature of the counterion. In analogy with other studies,[119] the lower the coordinating ability of the counterion, the higher the reaction rate of the exchange reaction. The authors concluded that for strongly coordinating anions, such as Cl^- and NO_2^-, the N,N-exchange is promoted by an anion associative mechanism, while for weakly coordinating anions, a dissociative mechanism assisted by the anion could be operative.

Scheme 14



2.4. Other Reactions

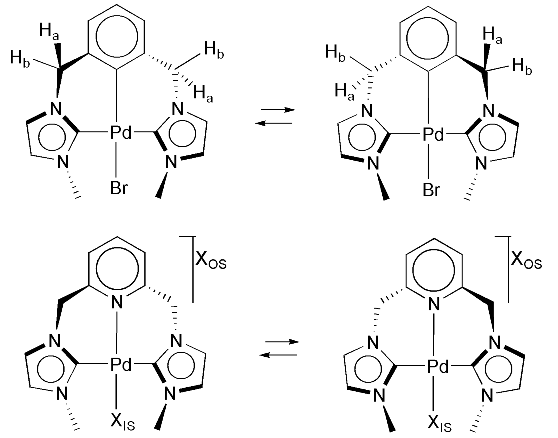
The counterion plays a crucial role in deciding the *coordination mode of an N-heterocyclic carbene to the metal center*. Crabtree and Faller recently showed that besides the normal C-2 coordination mode, N-heterocyclic carbene ligands can bind to the metal center in an "abnormal" C-5 coordination mode (Scheme 14).[120,121]

For example, the metalation reaction reported in Scheme 14 afforded a 45:55 ratio of C-2- and C-5-bound carbenes when X^- = BF_4^- and R = Me.[122] QM/MM ONIOM calculations on the cationic anion-free models indicated that the abnormal carbene was 10.1 kcal mol^{-1} higher in energy than the normal one. When the anion (BF_4^-) was included in the calculations, the difference in energy between the normal and abnormal carbenes was reduced to 1.6 kcal mol^{-1}. In addition, the choice of the anion was found to bias the experimental kinetic product of the reaction to give either normal or abnormal binding.[122] The former was by far the major product with strongly coordinating anions (as Br^-), while with weakly coordinating anions (as SbF_6^-), the latter was formed. Theoretical calculations and ^{19}F,^1H-HOESY NMR experiments[123] indicate that ion pairing occurs at the H-5 and CH_2 protons in the normal carbene and at the H-2 and CH_2 protons in the abnormal carbene. The acidity of the CH-2 moiety of imidazolium salts[124] and, in general, of a CH moiety between two nitrogen atoms is well known and may give rise to selective ion pairing.[125−129] The reason for the ion-pairing effect on the normal/abnormal product ratio is not yet understood, but it seems to be connected with the influence of the anion on the relative energies of the transition state vs the ground state of the ion pair.

Ion pairing has also been found to subtly affect the *conformational interconversion of some Pd pincer complexes* (Scheme 15, IS and OS indicate inner and outer sphere, respectively).[130] The free activation energy for the atropisomerization shown in Scheme 15 was substantially higher for the neutral complex ($\Delta G^{\#}_{298}$ = 71.4 kJ mol^{-1}) than for the cationic one ($\Delta G^{\#}_{298}$ = 53.2 kJ mol^{-1}).[131] In addition, it was remarkably dependent on the counteranion for the latter.[130]

A combined DFT/experimental work indicated that for neutral or cationic compounds with weakly nucleophilic counterions the fluxional process proceeds in two steps with one methyl at a time crossing the square-planar molecular plane. In cationic complexes with more nucleophilic counterions it has been sug-

Scheme 15[a]



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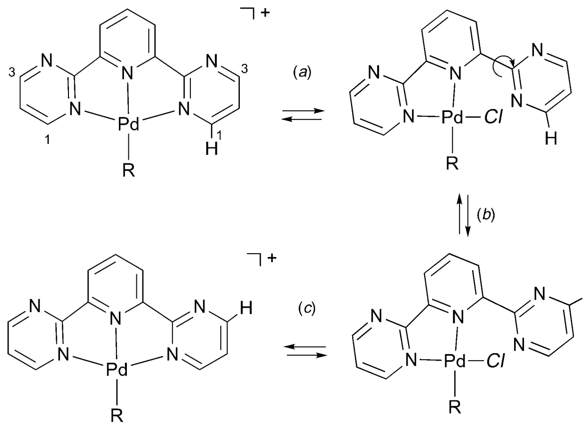
Scheme 16[a]



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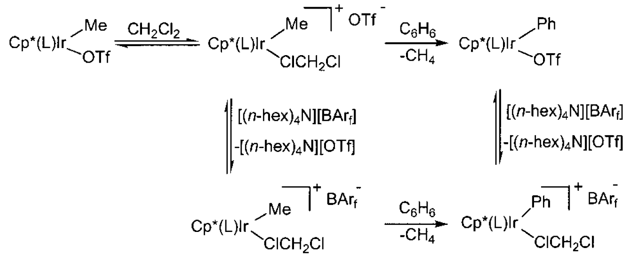
gested that the anion reversibly displaces the central N-arm in a rate-limiting step to form a neutral intermediate that undergoes rapid conformer interconversion.

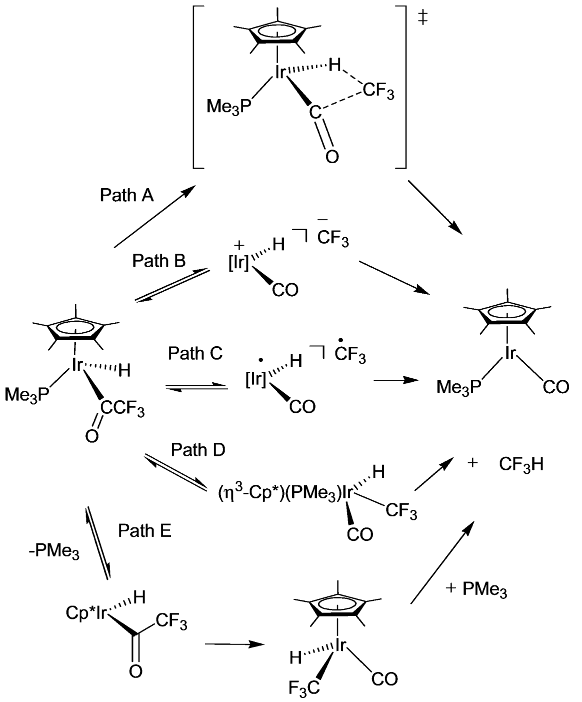
A similar counterion effect was previously observed by Vrieze and co-workers[132] for the dynamic behavior shown in Scheme 16 that exchanges the coordinated and uncoordinated pyrimidinyl nitrogen atoms (R = Me or COMe).

A mechanism explaining the exchange of protons H1 and H3 has been proposed and involves (a) dissociation of one of the coordinated pyrimidinyl nitrogen atoms, which may be initiated by the coordination of chloride, (b) rotation about the pyrimidinyl C−C bond, and (c) reformation of the Pd−N bond (Scheme 16). In agreement with the proposed mechanism, the exchange process was slower for compounds having OTf$^-$ or BARF$^-$ as counteranions.

Scheme 17



Scheme 18



Bergman and co-workers found that the *arene C−H bond activation by cationic Ir(III) complexes* involves ion pairs.[133] The reaction rate of Cp*(L)IrMe(OTf) (L = PMe_3 or $P(OMe)_3$) with arenes, which affords methane and arene coordination to the metal center, is strongly accelerated (up to 3 orders of magnitude when L = PMe_3) by the addition of (n-Hex)$_4$NBARF. The added BARF$^-$ anion presumably exchanges with the OTf$^-$ anion in the initially formed ion pair, giving the more reactive cation/borate ion pair (Scheme 17).

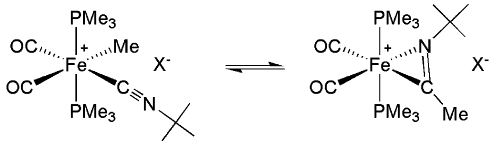
Consistent with such a mechanism, when (n-Hex)$_4$NBARF is added to a mixture of the preformed phosphine CH_2Cl_2/borate complexes and benzene, it does not affect the reaction rate that is already rapid. Further support for the mechanism shown in Scheme 17 comes from the observation that the reaction rate for the complex with PMe_3 is higher than that with $P(OMe)_3$. This is in agreement with the need for an initial ionization equilibrium that must be reasonably favored by a higher electron density on the metal.

Interestingly, results from the same laboratory indicate that metal cation/carbanion pairs are important intermediates in the *reductive elimination reaction of some iridium acyl hydrides*.[134,135] The considered reaction and likely mechanisms are reported in Scheme 18.

Detailed kinetic investigations (solvent effect, kinetic isotope effect, etc.) strongly suggest that the ionic intermediate, such as that illustrated in path B, could be involved.

Ion pairing can also affect the reaction rate of *insertion reactions*. It is well known that CO insertion in anionic complexes can be strongly accelerated by Lewis acids[136−140] that predispose it to accept the alkyl migration by interacting with the lone pair of the CO oxygen atom.[141] Insertion reactions that occur

Scheme 19



in cationic complexes has also been found to be affected by ion pairing, although to a lesser extent. Clear indications of the counteranion effect were obtained for carbon monoxide[142,143] and isocyanide[144−147] insertion reactions. The latter reaction was investigated in depth by Cardaci and co-workers for *cis*,-*trans*-[Fe(CO)$_2$(PMe$_3$)$_2$Me(CN-*t*-Bu)]X ($X^- = Cl^-$, Br^-, I^-, NO_3^-, ClO_4^-, BF_4^-, or BPh_4^-).[144,146] Such a complex in dichloromethane undergoes the isomerization reaction shown in Scheme 19 when $X^- = Cl^-$, Br^-, I^-, NO_3^-, or ClO_4^-.

The reaction rate is strongly affected by the counterion and follows the order $Cl^- \approx Br^- > I^- > NO_3^- \gg ClO_4^-$. For $X^- = BF_4^-$ or BPh_4^-, the isomerization shown in Scheme 19 does not occur. In this case more coordinating anions facilitate the reaction presumably because they stabilize the η^1-iminoacyl intermediate *cis*,*trans*-[Fe(CO)$_2$(PMe$_3$)$_2$(η^1-C(Me)=N-*t*-Bu)]X.

Deelman and co-workers demonstrated that ion pairing may strongly alter the *reactivity of [PdCl(NCN)] (NCN = 2,6-C$_6$H$_3$(CH$_2$NMe$_2$)$_2$) with either sodium or silver salts of weakly coordinating anions*.[148] Only when the small anion BF_4^- was employed, mononuclear complex [Pd(NCN)(H$_2$O)]BF$_4$ partially formed due to the establishment of F$_3$B−F···H$_2$O−Pd strong anion−cation electrostatic interactions. When the possibility for such strong stabilizing interactions is lacking, as in the case of B(4-SiMe$_3$−(C$_6$H$_4$))$_4^-$ or B(4-SiMe$_2$(CH$_2$CH$_2$C$_6$F$_{13}$)−(C$_6$H$_4$))$_4^-$ weakly coordinating anions, formation of Cl-bridged dinuclear palladium species was preferred.

Finally, Lledós, Ros, and co-workers studied the *stability trends of κ^2 and κ^3 forms of [Rh(N$_3^{Me}$)L$_2$]BF$_4$* (N$_3^{Me}$ = bis(1-pyrazolylmethyl)ethylamine and L$_2$ = cyclooctadiene or carbonyl ligands) in both the solid state and solution.[149] The κ^3-coordination mode was observed in the solid state, while both isomers coexisted in solution. By performing theoretical calculations they realized the importance of the counterion in determining the hapticity of the N$_3^{Me}$-multidentate ligand. In particular, in the X-ray crystal structure of [Rh(κ^3-N$_3^{Me}$)(COD)]BF$_4$ each cation has three anions at a Rh···B distance between 8 and 6 Å. Starting with these three positions they optimized independently the three ion pairs for both κ^3 (Figure 4, top) and κ^2 isomers (Figure 4, bottom). The positions of anions A and B were notably modified by changing the hapticity of the ligand (Figure 4). More importantly, the energy differences between the two isomers due to different anion−cation interactions were in the same range as the κ^3 vs κ^2 energy difference found in the cation.

Without the counterion the κ^2 structure was found to be more stable, but when the counterion was placed in the A region the stability ordering reversed. The counterion in the B region increased the stability of the κ^2 structure, whereas that in the C region slightly stabilized the κ^3 isomer.

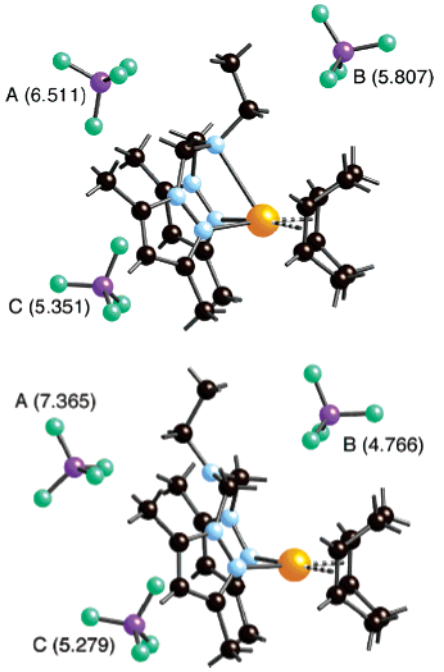


Figure 4. Positions of the BF_4^- counterion in the optimized structures of [Rh(κ^3-N$_3^{Me}$)(COD)]$^+$···BF_4^- (top) and [Rh(κ^2-N$_3^{Me}$)(COD)]$^+$···BF_4^- (bottom) ion pairs (ref 149). In parentheses, the optimized Rh···B distances (Å) are shown.

3. Ion-Pairing Effects in Catalytic Reactions

3.1. Olefin Polymerizations

The single-site version[150−158] of the classical Ziegler[159]-Natta[160] catalytic polymerization of olefins is the reaction for which the ion-pairing phenomenon has been studied in the greatest detail.[42,161,162] The two-component catalytic system consists of a main-group organometallic compound (cocatalysts or activator) and a transition-metal (organometallic) compound (catalyst precursors) that react generating an ion pair ($L_nM^+R\cdots X^-$) that is considered to be the main resting state of the polymerization process. By taking into account that (1) the cationic moiety of the ion pair bearing the transition metal has to be highly electrophilic and (2) the polymerizations are usually carried out in solvent with low relative permittivity (ϵ_r), it becomes immediately clear why ion pairing has a remarkable effect on the catalytic system. Solvents such as benzene and toluene, with ϵ_r around 2, are very frequently used in the polymerization of olefins catalyzed by both metallocene or half-metallocene and post-metallocene[155,158] early transition metals. It is now recognized that the counterion X^- strongly affects the catalyst stability and activity, the stereoregularity, the average molecular weights, and the branching of polymers in olefin polymerizations. An enormous number of experimental indications (vide infra) testify to such an influence, and an increasing amount of theoretical investigations[24,163−174] directly include the counterion. Because most of the studies on the effect of ion pairing have been concerned with early-transition-metal compounds, they will be taken

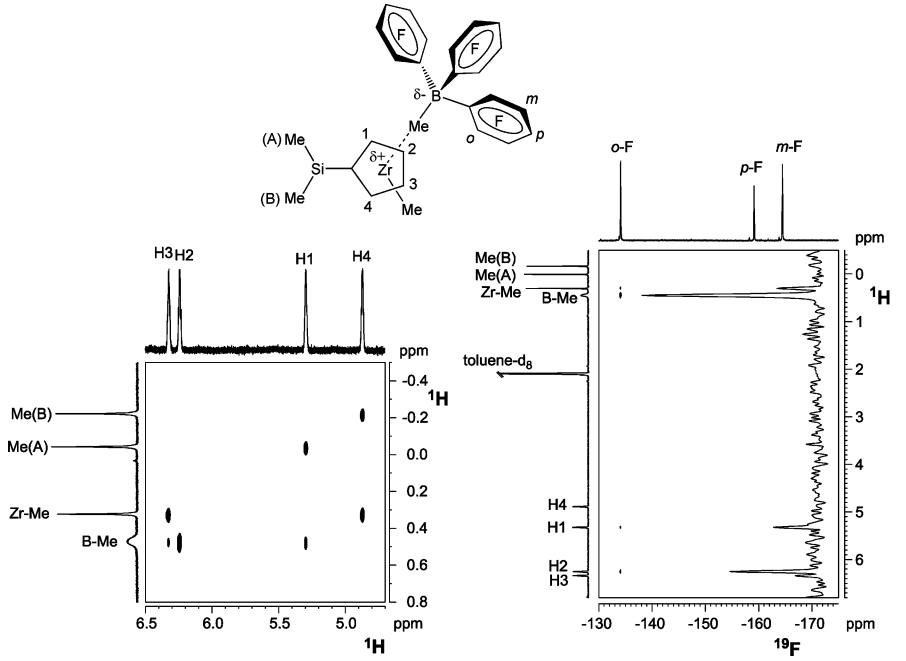


Figure 5. Sections of the ^{1}H-NOESY (left, 399.94 MHz, mixing time = 150 ms, benzene-d_6, 298 K) and ^{19}F,^{1}H-HOESY (right, 376.4 MHz, mixing time = 800 ms, toluene-d_8, 298 K) NMR spectra showing the interionic interactions between protons of the cationic moiety $(Me_2SiCp_2)ZrMe^+$ and protons or fluorine nuclei of $MeB(C_6F_5)_3^-$ anion (ref 196).

into account in this section. The effect of ion pairing[175] in late-transition-metal-catalyzed olefin polymerizations[176] seems to be limited, probably because the polymerizations are usually carried out in methylene chloride ($\epsilon_r = 8.93$ at 25 °C) where weakly coordinating anions do not afford a significant presence of contact ion pairs. The catalyst–cocatalyst structure–activity relationships were excellently reviewed by Chen and Marks in 2000.[42] In the present section emphasis will be placed on recent advances that were not included in that review.

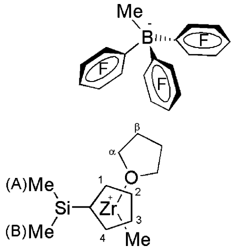
3.1.1. Anion–Cation Interactions

The ion pair $L_nM^+R\cdots X^-$ is a contact ion pair in which the metal is unsaturated and, consequently, the anion X^- occupies one of the coordination sites. According to the definitions reported in the Introduction, $L_nM^+R\cdots X^-$ has to be considered an ISIP. Due to the relevant unsaturation of the metal it could be argued that the interaction between L_nM^+R and X^- could have a partial coordinative nature, and it would be more correct to consider $L_nM^+R\cdots X^-$ as an acid–base Lewis adduct or a zwitterion.[177] Although the subject is still a matter of debate, it seems that the electrostatic interactions are largely predominant and it is presumably correct to speak about ISIPs.[164,165] Several single-crystal X-ray structures have been determined for $L_nM^+R\cdots X^-$ ion pairs;[42,178-185] from these the charge-separated character of these complexes appears evident even for "more coordinating" anions. For compounds bearing the moieties Zr^+-$Me^+\cdots MeB(C_6F_5)_3^-$, the anion orients the methyl group toward the zirconium center and the Zr–Me terminal distance is always much shorter than the $Zr^+\cdots MeB(C_6F_5)_3^-$ bridging distance with a Δr that ranges between 0.3 and 0.4 Å depending on the influence of ancillary ligands on the cation–anion separation. Some coordinative nature is still present under the guise of α-agostic interactions between the methyl group bonded to boron and the zirconium.[42] A similar situation was recently found by Weller and co-workers in $[Cp_2ZrMe]^+\cdots[Me\text{-}1\text{-}closo\text{-}CB_{11}HMe_{10}]^-$ with a slightly closer contact between the methylated anion and the metal center ($\Delta r = 0.25_5$ Å).[186] In compounds where the more coordinating PBA^- counteranion is present ($PBA^- = FAl(2\text{-}C_6F_5C_6F_4)_3^-$) there are clear indications of the presence of a coordinative "Zr⋯F–Al" bond derived from the solid-state structures.[187] In contrast, again solid-state structures indicate that an anion–cation interaction is mainly electrostatic for weakly coordinating anions such as $B(C_6F_5)_4^-$, $MePBB^-$ ($PBB = B(2\text{-}C_6F_5C_6F_4)_3$), and $HB(C_6F_5)_3^-$.[42] It is interesting that the latter anion does not afford a "Zr⋯H–B" bridge in analogy with $MeB(C_6F_5)_3^-$ and PBA^-.[188] These structural features, observed in the solid state, have been confirmed in solution by means of NMR spectroscopic investigations[189-194] based on the changes in ^{1}H and ^{19}F chemical shifts as a consequence of the strength of the anion–cation (coordinative) interactions that are related to an interplay of steric and electronic constraints at both the cation and anion.[195] More recently, a further direct confirmation of the analogy between the solid state and solution structures of $L_nM^+R\cdots X^-$ ion pairs has been derived from the observation of interionic NOE contacts in the ^{1}H-NOESY and ^{19}F,^{1}H-HOESY NMR solution spectra for a broad series of metallocenium ion pairs.[196] As an example, in Figure 5 the ^{1}H-NOESY and ^{19}F,^{1}H-HOESY spectra of the compound $[(Me_2SiCp_2)ZrMe]$-$[MeB(C_6F_5)_3]$ are reported.

As can be seen from Figure 5, the intensity of the interactions between the o-F fluorine nuclei on the anion and the Cp protons in the ^{1}H,^{19}F-HOESY spectrum follows the order H2 > H1 > H3, and no cross-peaks are detectable for the H4 proton. This indicates that the preferred contact point for the anion is proximate to H2. As a confirmation, a strong homonuclear cross-peak between the μ-Me group and the H2 proton is present in the ^{1}H-NOESY spectrum (Figure 5). The quantification of NOEs in the initial rate approximation[197] for $[Cp_2ZrMe][MeB(C_6F_5)_3]$ allowed the average internuclear distances to be estimated, and they were in very good agreement with those determined in the solid state.[198]

The olefin coordination that occurs with displacement of the counterion X^- from $L_nM^+R\cdots X^-$ leads to formation of $[L_nMR(olefin)]X$, where the counterion stays in the second coordination sphere of the metal. $[L_nMR(olefin)]X$ complexes are supposed to be key intermediates in olefin polymerization and have to be considered OSIPs. Such olefin complexes have been never observed in catalytic systems, presumably because of their low thermodynamic stability due to weak olefin coordination in the absence of metal−olefin back-donation and because of their high reactivity leading to alkyl migration into the coordinated olefin. As a consequence, no structural data are present for $[L_nMR(olefin)]X$ complexes, while several models have been synthesized and structurally and/or spectroscopically characterized. In olefin-containing models the necessary thermodynamic stabilization and/or chemical inertness is reached by chelation, i.e., using L-olefin,[199] R-olefin,[200] or π-allyl[201] ligands. Other model compounds have been investigated by Jordan by substituting the alkyl group with the alkoxide one.[202] Rougher models have been synthesized by substituting the olefin with much more nucleophilic L ligands[150,203−205] such as THF,[196,206,207] phosphines,[191,208,209] nitriles,[210] pyridine derivatives,[211] and heterocyclic carbenes.[212] While the latter models had substantially different electronic and steric features with respect to the olefin intermediates, they played a crucial role in demonstrating that the olefin insertion occurs in cationic L_nM^+R species rather than in a bimetallic species.[151] Several solid-state structures have been solved for $[L_nMRL']X$ OSIPs from which the anion−cation relative orientation in the solid state can be deduced. It must be said that different from $L_nM^+R\cdots X^-$ ISIPs, for which strong anion−cation interactions induced to predict, as later found, an identical ionic orientation in the solid state and in solution, $[L_nMRL']X$ OSIPs may give origin to ionic adducts in solution in which the relative anion−cation orientation is different from that in the solid state. This has now been well-documented[31,119] and is reasonable considering that the energy differences between the possible anion−cation orientations can be comparable to that involved in packing in the solid state and in solvation. The relative anion−cation orientation has been elucidated in solution only for compounds $[(Me_2SiCp_2)Zr(Me)L']X$ ($L' =$ THF, $X^- = MeB(C_6F_5)_3^-$ or $B(C_6F_5)_4^-$; $L' = PPh_3$, $X^- = MeB(C_6F_5)_3^-$), $[(Me_2Si(Me_4Cp)(t\text{-}BuN)Zr(Me)L'][B(C_6F_5)_4]$ ($L' =$ benzene or toluene), and $[(Cp_2ZrMe)_2(\mu\text{-}Me)][MePBB]$ through the direct observation of interionic NOEs in the ^{1}H-NOESY and ^{19}F,^{1}H-HOESY NMR spectra.[196] The qualitative and quantitative analysis of interionic NOEs for $[(Me_2SiCp_2)Zr(Me)THF]X$ ($X^- = MeB(C_6F_5)_3^-$ or $B(C_6F_5)_4^-$) OSIPs concluded that the anion is preferentially located on the THF side of the cation, shifted slightly toward the Me(A) group and farther away from the Zr−Me group (Scheme 20). In addition, the absence of interactions between the B−Me group ($X^- = MeB(C_6F_5)_3^-$) and the α and β THF and Me(A) protons seems to indicate a favored anion orientation in which the B−Me moiety points away from the metal center (Scheme 20).

Scheme 20

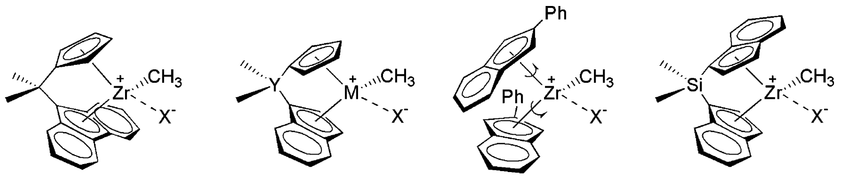


The solid structure of $[(Me_2SiCp_2)Zr(Me)THF][B(C_6F_5)_4]$ has been determined,[196] and none of the three nearest-neighbor anions of a given cation are positioned such that they would produce the observed NOE interactions in solution. Instead, there is an excellent agreement between computationally optimized interionic structures for analogous metallocenium olefin adducts, namely, $[Cp_2ZrMe(C_2H_4)][MeB(C_6F_5)_3]$,[166] and their rough models structurally studied in solution. The Zr−B distance estimated from NOE measurements for $[(Me_2SiCp_2)Zr(Me)THF][MeB(C_6F_5)_3]$ falls in the range 7.2−7.3 Å; the corresponding DFT-derived Zr−B distance calculated for the compound $[Cp_2ZrMe(C_2H_4)][MeB(C_6F_5)_3]$ is 6.7 Å,[166] while the corresponding ab-initio-derived distance is 7.4 Å in the related complex $[H_2Si(C_5H_4)(t\text{-}BuN)Ti(Me)(C_2H_4)][MeB(C_6F_5)_3]$.[164]

3.1.2. Activity

In terms of the catalyst activity, as a function of the counteranion, it has been found that the weaker the coordinating power of the anion, the higher the reactivity for a given cation.[213−219] A dramatic example of the influence of the counteranion on the catalytic activity has been found by Marks and coworkers[220] for ethylene polymerization catalyzed by [CGCMMe]X (CGC = $Me_2Si(\eta^5\text{-}Me_4C_5)(^{t}BuN)$) compounds. When $X^- = MeB(C_6F_5)_3^-$, the catalysts are inactive for M = Zr or marginally active for M = Ti, while when $X^- = MePBB^-$, the catalysts are highly active with rate enhancements of 10^5 and 70 for Zr and Ti, respectively. Strongly coordinating anions compete with olefins to occupy the coordination site cis to the polymeryl group, and consequently, the activity of the catalysts is reduced. As further confirmation, if the polymerizations are carried out in more polar solvents the catalyst activity increases. Although the macroscopic effect of the counterion on the activity is clear, there is still some controversy about the intimate mechanism of the counterion action, especially because of some contradictory results concerning the effect of an excess amount of activator on the polymerization. Schrock found that the addition of an excess amount of $[Ph_3C^+][B(C_6F_5)_4^-]$ cocatalyst significantly suppressed the living polym-

Scheme 21



(I) (II) (III) (IV)

erization of 1-hexene catalyzed by [(^{t}BuNON)ZrMe][B(C_6F_5)$_4$],[221] while in other cases an excess amount of cocatalyst had no influence.[222,223] In this respect, the critical point to clarify is if the initial contact ion pair with an anion in the first coordination sphere converts into a contact ion pair with the anion in the second coordination sphere, leaving a coordination site "free" with a successive reaction with olefin, or if a purely associative transition state has to be considered. Although elegant mechanistic studies have recently been carried out mainly by Landis and co-workers,[222,224−226] more investigations are necessary to discriminate the two possibilities. Also, in cases of dimethyl complexes that undergo double methyl abstraction by M(C_6F_5)$_3$ (M = B or Al) Lewis acids, contradictory results have been obtained. In fact, while the doubly activated species [(t-Bu$_3$PN)$_2$Ti][MeB(C_6F_5)$_3$]$_2$ exhibited negligible polymerization activity compared to the monoactivated one [(t-Bu$_3$PN)$_2$TiMe][MeB(C_6F_5)$_3$],[227] [CGCTi][MeAl(C_6F_5)$_3$]$_2$ and *rac*-[Me$_2$Si(Ind)$_2$Zr][MeAl(C_6F_5)$_3$]$_2$ were found to be far more efficient catalysts than the corresponding monocationic catalysts.[228]

Interestingly, for a given counterion the polymerization activity of [L$_n$MR]X does not necessarily correlate with the intrinsic electrophilicity as L is varied.[229,230] When L becomes more electron donating and/or sterically encumbered, the stability of the ion pairs is reduced and the cationic moiety is more accessible for the olefin even though it is less elecrophilic.[229]

3.1.3. Stereochemistry

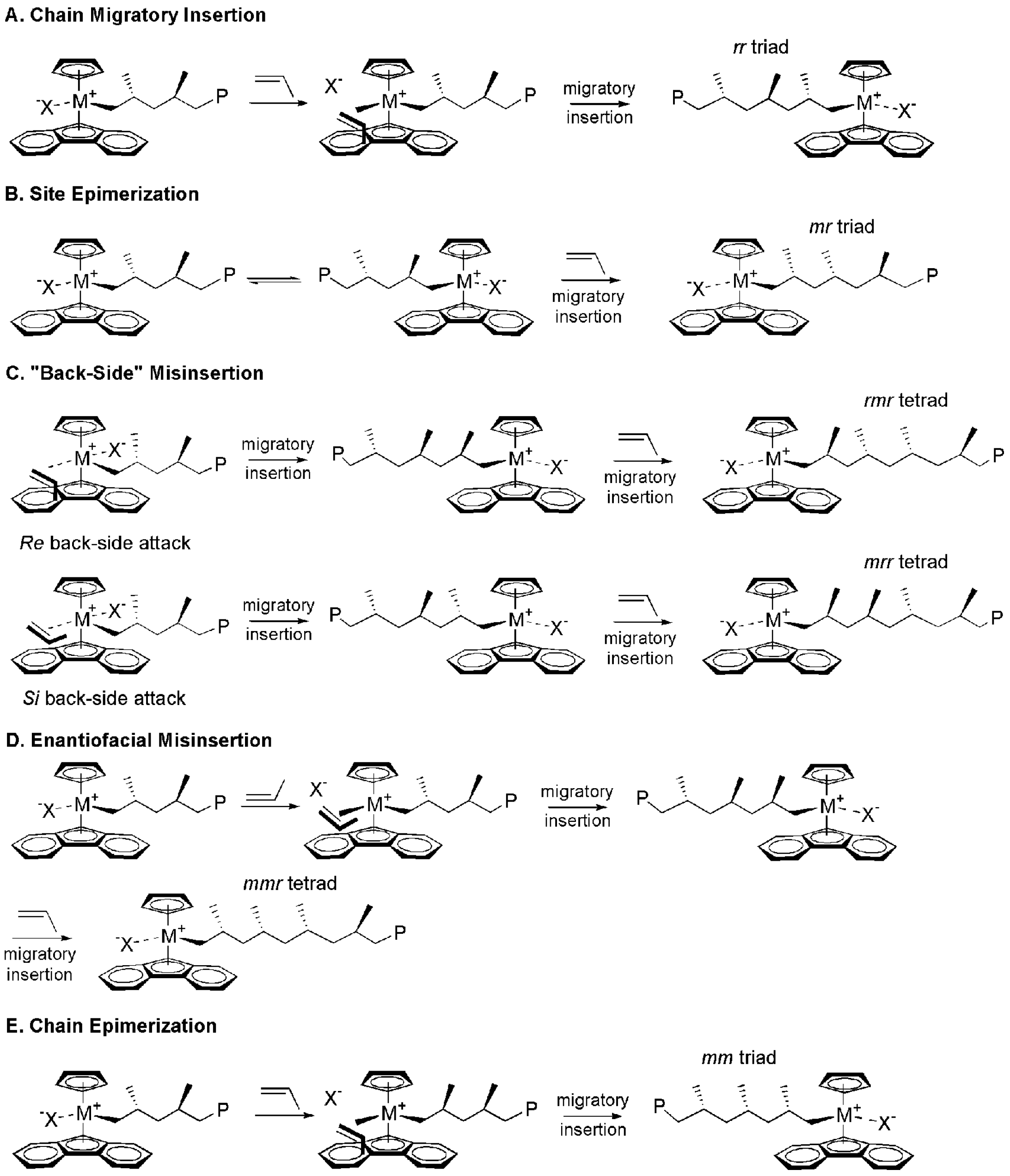
The effect of the counteranion on the stereoregularity of propylene polymerization has been investigated in depth for *ansa*-C_s-[231−234] (I), *ansa*-C_1-[235,236] symmetric (II), unbridged 2-phenylindenyl[237,238] (III) and, to a lesser extent, *ansa*-C_2-symmetric metallocene precatalysts[187,239−241] (IV) (Scheme 21).[242] The role of the counterion with respect to the stereoregularity of the polymers is much less intuitive than that to the activity. For this reason, in the following discussion, the three cases (I−III), for which more experimental studies have been carried out, are analyzed at a certain level of detail, gradually increasing the complexity of the system, i.e., decreasing the catalyst symmetry, passing from I to II, and eliminating the bridge between the substituted Cp ligands and, consequently, allowing for different conformational isomers (III).

C_s-Symmetric [Me$_2$C(Cp)(Flu)ZrMe]X Catalysts. It is well known that the C_s-symmetric complex [Me$_2$C(Cp)(Flu)ZrMe]X (Flu = fluorenyl, I in Scheme 21) catalyzes the syndiotactic polymerization of propylene and that the syndiotacticity strongly depends on the nature of the counteranion.[231−234] The accepted pathway for syndiospecific propylene polymerization[243] (Scheme 22A) consists of (1) coordination of propylene with the enantioface that places the methyl group anti to the growing chain (P) that is directed into an open sector (consequently, it imposes a chiral orientation to the growing chain) followed by (2) migratory 1,2-insertion of the polymer chain with generation of chiral carbon with an opposite configuration with respect to the preceding one (Scheme 22A). If this process were repeated without stereodefects, perfect syndiotactic polypropylene would be produced with a perfect alternation of configurations at the carbon atoms of chain P. In Scheme 22A the case of three C-stereocenters is shown that generates the triad *rr,* where *r* stands for racemic. Several processes have been proposed as the source of stereodefects, and some of them are reported in Scheme 22. The most important in syndiotactic polymerization of propylene is thought to be the site epimerization (Scheme 22B) in which the "chain swinging" occurs by itself and is not due to chain migratory insertion into the precoordinated olefin, which generates *m* stereodefects. Other possible processes that generate stereodefects are "backside" misinsertions[232] in which the olefin coordinates at the metal center from the opposite direction with respect to the counteranion (the two possibilities *re* and *si* are shown in Scheme 22C), enantiofacial misinsertion, where the methyl group of the propylene is oriented syn to the growing chain (Scheme 22D), and chain epimerization,[244,245] which can occur through β-hydrogen elimination (only one of the possible pathways is shown in Scheme 22E).[231,233]

In principle, the occurrence of these processes can be quantified using ^{13}C NMR spectroscopy to analyze their signatures in terms of triads, tetrads, pentads, etc., in the produced polymers.[246,247] The counteranion can manifest its role on the syndiotacticity of polypropylene in every single process, and consequently, the resulting global effect can be nonintuitive. Numerous propylene polymerizations catalyzed by [Me$_2$C(Cp)(Flu)ZrMe]X have been investigated in which the anion effect has been systematically studied by changing the temperature, monomer concentration, and solvent.[231−233] In almost all circumstances the syndiotacticity follows the order PBA$^-$ > MeMAO$^-$ > B(C_6F_5)$_4^-$ ≈ MePBB$^-$ > MeB(C_6F_5)$_3^-$. Clearly this order does not parallel with the noncoordinating tendency of the anion that NMR studies on ion-pair reorganization barriers and anion displacement equilibria have indicated: MePBB$^-$ > B(C_6F_5)$_4^-$ > MeB(C_6F_5)$_3^-$ > PBA$^-$.[42,187−189,214]

The accurate analysis of the polymer microstructure carried out by Busico et al.[232] led to the evalu-

Scheme 22



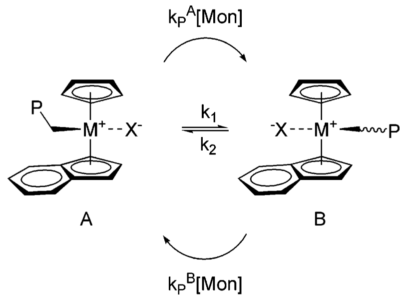
ation of k_{epi}/k_{ins} (k_{epi} = rate constant of site epimerization, k_{ins} = rate constant of propene insertion) of the upper limit of fractional abundance of *r* dyads in the absence of epimerization ([$r°$]) and the fraction of *r* dyads formed in the hypothesis of ideal chain migratory insertion ($[r]_{enantio}$). They found that (i) the value of k_{epi}/k_{ins} does not track with the coordinating ability of the anion and (ii) for a given system the values of [$r°$] and $[r]_{enantio}$ are not necessarily coincident. Such observations led authors to suggest the above-mentioned "backside" misinsertion (Scheme 22C) in which olefin approaches the catalyst from the opposite side of the counterion as a possible competitive source of stereodefects for sticky anions. Because this pathway implies double chain migration, it can generate *m* stereodefects even in the absence of epimerization.

Interestingly, in a recent investigation Marks and co-workers estimated the absolute rate constants for all the processes reported in Scheme 22 as a function of the counterion.[233] The data are reported in Table 3. Excluding the $MeMAO^-$ anion from the discussion because of the necessity for a large excess of aluminoxanes in reactions and a lack of detailed information on its structure, data in Table 3 clearly show an inverse correlation between the coordinating tendency of the anion and the entities of k_p, k_{se}, k_{bsa}, and k_{em}. The higher the coordinating tendency of the anion, the lower the *k* values of these processes. In addition, the most coordinating PBA^- anion minimizes all types of stereodefects. These considerations partially reconcile the observed effects of the counteranion on the syndiotacticity with the intuitive consideration that there must be a correlation with the coordinating nature of the counteranion. For example, $MeB(C_6F_5)_3^-$ is certainly more coordinating than $B(C_6F_5)_4^-$, but when used as cocatalyst, polypropylene, less syndiotactic than that obtained with

Table 3. Estimated Absolute Rate Constants for Propagation (k_p), Site Epimerization (k_{se}), "backside" Misinsertion (k_{bsa}), Enantiofacial Misinsertion (k_{em}), and Chain Epimerization (k_{ce}) for Polymerizations Mediated by $[Me_2C(Cp)(Flu)ZrMe]X$ under 1.0–5.0 atm Propylene at 60 °C (from ref 233)

anion	k_p (M^{-1} s^{-1})	k_{se} (s^{-1})	k_{bsa} (M^{-1} s^{-1})	k_{em} (M^{-1} s^{-1})	k_{ce} (s^{-1})
PBA^-	33.7(16)	0.474(47)	0.486(65)	0.807(74)	0.03(44)
$MeB(C_6F_5)_3^-$	41.8(8)	1.85(26)	3.61(38)	1.09(11)	0.239(75)
$B(C_6F_5)_4^-$	297(4)	11.1(11)	9.5(16)	7.75(62)	0.69(42)
$MePBB^-$	321(12)	10.9(19)	10.9(14)	9.36(65)	0.29(37)
$MeMAO^-$	402(44)	9.8(13)	5.9(13)	8.2(12)	1.04(55)

Scheme 23



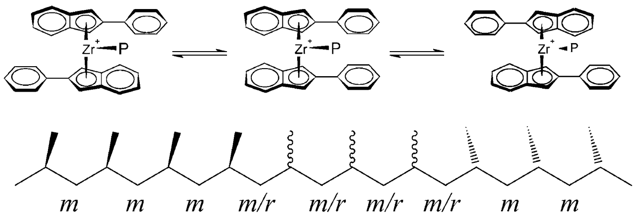
$B(C_6F_5)_4^-$, is produced. From the above data it appears evident that $MeB(C_6F_5)_3^-$ reduces both k_p and k_{se}. What is important is the differential effect on the latter rate constants: the observation of a higher presence of *m* stereodefects indicates that, in polymerization conditions, k_p is more affected than k_{se} when the counteranion $B(C_6F_5)_4^-$ is changed with $MeB(C_6F_5)_3^-$. In other words, a smaller number of errors are generated with $MeB(C_6F_5)_3^-$ but they have a greater effect on the polymer stereoregularity because a much smaller amount of polymer is obtained with respect to $B(C_6F_5)_4^-$.

C_1-Symmetric $[Me_2Y(Cp)(Ind)MMe]X$ Catalysts. Generally speaking, the peculiar feature of C_1-symmetric metallocenes is that the two coordination sites are diastereotopic. As a consequence, depending on the substituent on the cyclopentadienyl ligand, the stereochemistry of polypropylene synthesized using C_1-symmetric metallocene catalysts can vary from hemiisotactic (having an alternation of methynes with the same configuration and with a random configuration) to highly isotactic.[243]

Collins et al. recently investigated the counterion effects on propylene polymerization catalyzed by C_1-symmetric $[Me_2Y(Cp)(Ind)MMe]X$ catalysts[236] (Y = C or Si, M = Zr or Hf, Ind = indenyl, II in Scheme 21). They analyzed the experimental results with the help of a kinetic approach for modeling stereosequence distribution in polypropylene produced using two states bridged or fluxional metallocene catalysts developed by the same authors.[248] They found that for C_1-symmetric catalysts the microstructure of the polypropylene was sensitive to the nature of the counterion when M = Hf and Y = C. In such a case the counterion only affects the parameter δ that is defined as k_P^B/k_2 (Scheme 23), i.e., the relative rate constants of insertion to inversion.

The counterion does not seem to affect the single specificity of state A or B. In addition, the ordering of the counterion effect on δ ($MeB(C_6F_5)_3^- < B(C_6F_5)_4^- < PBA^- \approx MeMAO^-$) does not correlate with the coordinating ability ($B(C_6F_5)_4^- < MeB(C_6F_5)_3^- \ll PBA^-$) or with trends in polymerization activity ($B(C_6F_5)_4^- \gg MeB(C_6F_5)_3^- > PBA^-$). The observed behavior is difficult to explain because both inversion and insertion involve dissociation and/or displacement of the counterion. Evidently there must be a differential sensitivity of these two processes to the nature of the counterion as observed for C_s-symmetric precatalysts.

Scheme 24

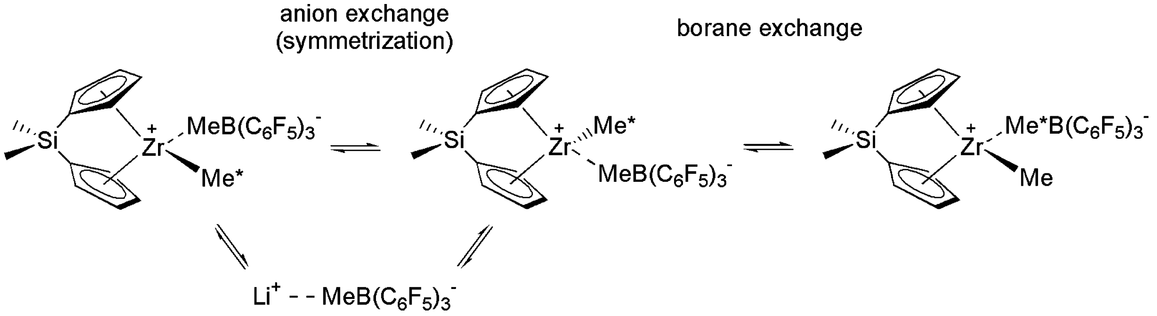


Unbridged 2-Phenylindenyl Catalysts. Unbridged 2-phenyl-1-indenyl zirconocene precatalysts (III in Scheme 21)[249] polymerize propene, producing polypropylene, which contains isotactic and atactic sequences. To explain this it has been hypothesized that the catalytic species "oscillates" between isospecific *rac* rotamers of opposite stereoselectivity and an aspecific *meso* rotamer at a rate that is slower than monomer insertion (Scheme 24).

The influence of the cocatalyst on the stereoselectivity of propylene polymerization catalyzed by unbridged 2-phenylindenylmetallocene catalysts has been investigated by Waymouth.[237] The polymerizations were carried out in the presence of aluminum scavengers. Even taking into account the effects of such aluminum scavengers, it was found that the nature of the cocatalysts significantly influences the stereospecificity and productivity of 2-phenylindenylmetallocenes. For $MeB(C_6F_5)_3^-$ the latter was found to be dramatically lower than those for MAOs or $B(C_6F_5)_4^-$. The authors suggest that the strongly coordinating anion $MeB(C_6F_5)_3^-$ inhibits the rate of olefin insertion to the point where it becomes competitive with the conformation isomerism (Scheme 24). In such a case an atactic polypropylene would result.

By accurately analyzing the microstructure of the polymers by means of high-field ^{13}C NMR techniques Busico and co-workers[238] deduced that the less stable *meso*-like conformation of oscillating $[(2\text{-Ar-indenyl})_2ZrP]^+$ catalysts (Scheme 24) can be disregarded and that the active species is always the *rac*-like conformation. When the two enantiomorphous *rac*-like conformations are in fast interconversion, the probability of oscillation depends mainly on the bulkiness of the Ar substituents on the indenyl groups, monomer concentration, and temperature. If the probability of oscillation is lower than the probability of

Scheme 25



monomer insertion, an isotactic−stereoblock chain propagation will be obtained. In the case of similar probabilities, chain propagation will be nonstereoselective. The authors hypothesized that the oscillation can be frozen by association of the active cation with the counterion whose role is analogous to that of the covalent bridge in *ansa*-metallocenes.

C_2-Symmetric *rac*-[$Me_2Si(Ind)_2ZrMe$]X Catalysts. *ansa*-C_2-Symmetric metallocene precatalysts are extremely important because, depending on the biscyclopentadienyl ligand structure, they can produce highly isotactic polypropylene.[243]

For the isospecific propylene polymerizations catalyzed by *rac*-[$Me_2Si(Ind)_2ZrMe$]X (IV in Scheme 21), the effect of the counterion on the polymerization of propene was investigated, and it was found that the activity increases passing from $X^- = MeB(C_6F_5)_3^-$ to $B(C_6F_5)_4^-$ to $MePBB^-$, while the isotacticity remains essentially the same.[187,239−241] The latter finding is not surprising because most of the sources of stereodefects are suppressed in rigid *rac*-C_2-symmetric metallocene catalysts with homotopic sites.[151,238b,243,246] Only the strong ion-paired PBA^- anion slightly enhanced the isotacticity of polypropylene compared to other anions, albeit with reduced polymerization activity.[187]

3.1.4. Aggregates Higher than Ion Pairs

As stated above, $L_nM^+R\cdots X^-$ metallocene ion pairs catalyze olefin polymerizations in low-polarity solvents such as benzene or toluene. It has been proposed that ion quadruples and even higher aggregates may be significantly present in solution and could play some role in the catalytic cycle.[250] Brintzinger used 2D-NOESY methods to determine the first-order rate constant for anion-exchange reactions of several zirconocene compounds having $MeB(C_6F_5)_3^-$ or $B(C_6F_5)_4^-$ as counteranion (Scheme 25).[251] Interestingly, he found an acceleration of the dynamic symmetrization (Scheme 25) of zirconocene ion pairs by adding $Li^+\cdots MeB(C_6F_5)_3^-$ and increasing the concentrations of zirconocene ion pairs. In addition, the rate constant for anion exchange between $Li^+\cdots MeB(C_6F_5)_3^-$ and "$Zr^+\cdots MeB(C_6F_5)_3^-$" is about 3 times greater than that of symmetrization, indicating the occurrence of an unproductive attack of $MeB(C_6F_5)_3^-$ at the Zr center. Importantly, the temperature dependence of exchange rates for different concentrations of zirconium salts indicated the exclusively entropic nature of these rate changes.

All these observations induced Brintzinger to conclude that anion exchange proceeds predominantly by way of ion quadruples or higher order ionic aggregates. Interestingly, Sita and co-workers[252] were able to isolate and structurally characterize in the solid state the bicationic zirconium amidate [((Cp*)(^{t}BuNC(Me)NEt)Zr)$_2$(μ-Me)$_2$][$B(C_6F_5)_4$]$_2$ complex in which the two cationic moieties are held together through two bridging Me groups undergoing α-agostic interactions (Figure 6). In addition, they demonstrated that mononuclear [(Cp*)(RNC(Me)NR′)ZrMe]$^+$ units undergo direct methyl-group exchange and methyl−polymeryl transfer.[253]

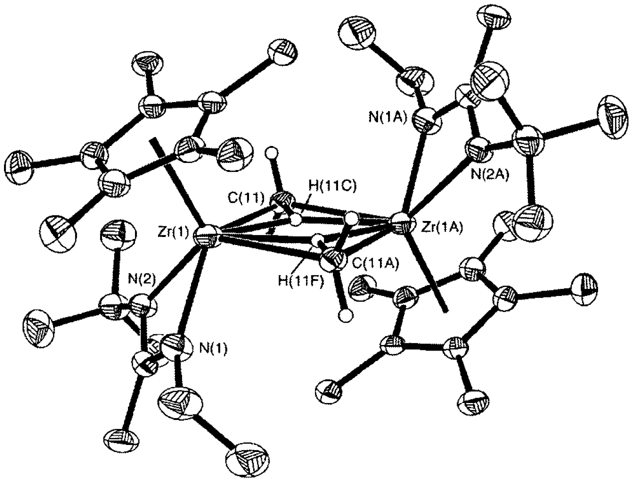
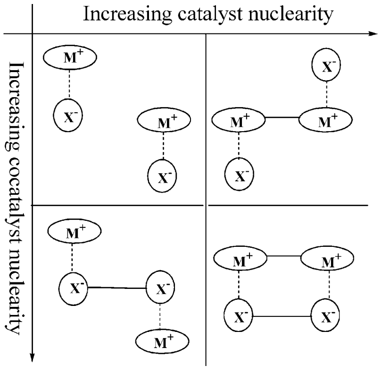


Figure 6. Molecular structure of [((Cp*)(^{t}BuNC(Me)NEt)Zr)$_2$(μ-Me)$_2$][$B(C_6F_5)_4$]$_2$ (30% thermal ellipsoids). The two anions and all but the bridging hydrogen atoms have been omitted for clarity (ref 253).

Some PGSE[254,255] (pulsed field gradient spin−echo) NMR[97,196,256] and cryoscopic[256] investigations were carried out in order to verify and quantify the existence of metallocenium aggregates higher than ion pairs in solution. It was found that for most of the ISIPs the percentage of higher aggregates is not appreciable in the concentration range 0.5−20 mM.[196,256,257] Some indications of the presence of ion quadruples for $(Cp)_2ZrMe^+\cdots X^-$ with $X^- = B(C_6F_5)_4^-$ were obtained from PGSE NMR measurements.[250] On the other hand, [L_nMRL']X OSIPs show a marked tendency to aggregate at concentrations greater than 0.5 mM.[196,257,258] As a general consideration, it seems that a reduced ion-pairing strength and a consequent increased dipole moment favors the formation of ion quadruples or higher aggregates. In this respect, estimations of the dipole moment of some silicon-bridged bisindenyl zirconocene catalysts as a function of the propylene chain length, carried out by Klesing and Bettonville, could assume particular importance

Scheme 26



because they indicated that there was a sudden increase of the overall dipole moment with the insertion of a second propylene monomer.[259] This could increase the tendency of metallocenes to form ion quadruples during polymerization reactions. Finally, although the presence of metallocenium ion quadruples is negligible even at concentrations far above those used in catalysis, few studies have been carried out to ascertain their possible relevance. To date, there are some results that negate[233] and others that favor[223] the importance of ion quadruples in catalysis. Further investigations are needed before a definitive conclusion can be reached.

Recently, Marks showed that an increased nuclearity of catalysts and/or cocatalysts, by both covalently or electrostatically bonding mononuclear units (Scheme 26), significantly affects the polyethylene branching and α-olefin comonomer enchainment.[260−262]

The bisborate dianion cocatalysts $\mathbf{B_2}$ (Scheme 27) substantially increases the efficiency of heterobimetallic enchainment by bringing the methyl cations of $\mathbf{Ti_1}$ and $\mathbf{Zr_1}$ into proximity, thereby increasing selectivity for branched LLDPE formation.[261]

Furthermore, combining $\mathbf{Zr_2}$ with $\mathbf{B_2}$ leads to an enhancement of branching in ethylene polymerization and comonomer incorporation in ethylene/1-pentene copolymerization with respect to $\mathbf{Zr_1/B_1}$.[260] It is notable that compared with mononuclear analogues the catalytic system $\mathbf{Ti_2/BN_2}$ affords polyethylenes with high molecular weights and significantly enhanced α-olefin comonomer incorporation, even of traditionally unreactive isobutene.[262]

3.2. Diels−Alder Reactions[263]

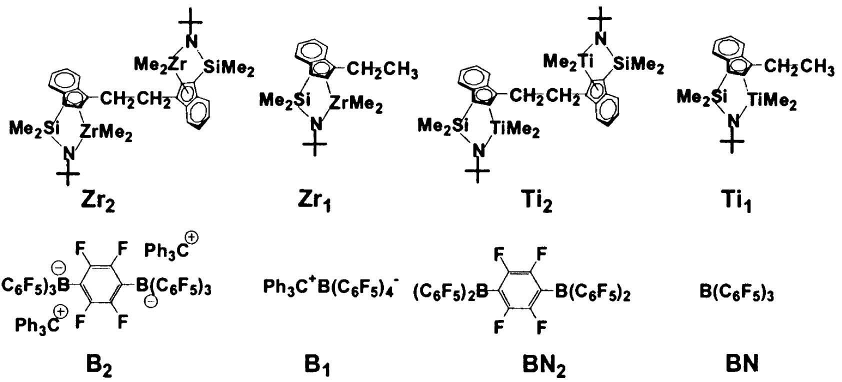
Several cationic chiral metal complexes have been found to be excellent catalysts for enantioselective Diels−Alder reactions.[264,265] In 1995 Evans first documented[266] that counterions strongly influence the reactivity of C_2-symmetric cationic copper(II) Lewis acids shown in Scheme 28.

The cycloaddition of methacrolein with cyclopentadiene, catalyzed by (t-Bu-pybox)Cu(X)$_2$, required 120 h for complete conversion when $X^- = OTf^-$, while it was complete in 8 h when $X^- = SbF_6^-$ (Figure 7). Evans also investigated the enantioselective Diels−Alder reaction of imide-derived dienophiles with dienes catalyzed by (t-Bu-box)Cu(X)$_2$ reported in Scheme 29, obtaining analogous results for the reaction rate that was about 20 times faster for SbF_6^- than OTf^-.[267]

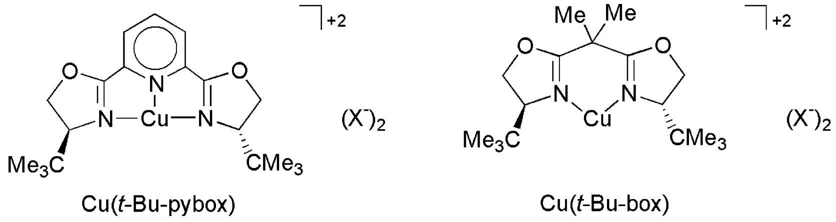
In addition, the cationic Cu(II) complexes with SbF_6^- afforded higher levels of asymmetric induction than the analogous triflate complex. Interestingly, the *endo*/*exo* ratio was found to be dependent on the counterion: the lower the coordinating tendency of the counterion, the less diastereoselective the Diels−Alder reaction.

In the case of R-box ligand-containing copper(II) catalysts, it seems certain that the reaction proceeds with the formation of the slightly distorted square-planar adduct reported in Scheme 29 with a two-point catalyst−dienophile binding. Characterization of such an intermediate in solution through NMR experiments was prevented by the d^9 paramagnetic

Scheme 27



Scheme 28



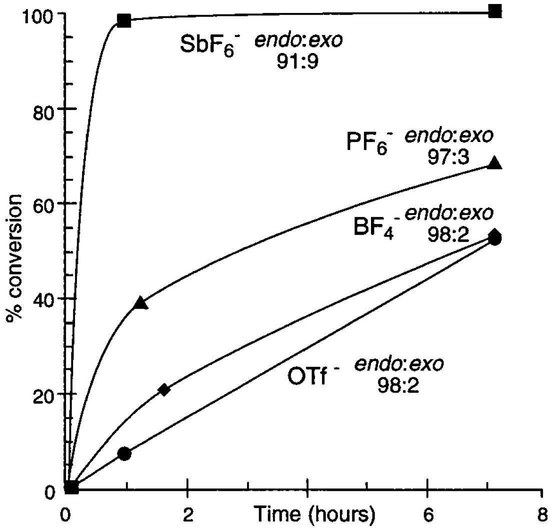
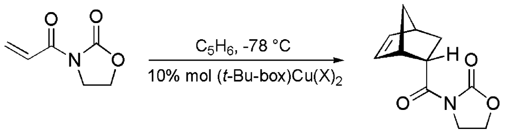
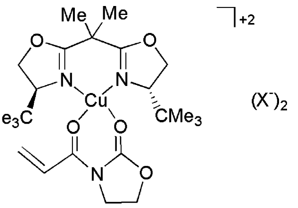


Figure 7. Conversion of reaction reported in Scheme 29 catalyzed by complexes (t-Bu-pybox)Cu(X)$_2$ at −78 °C as a function of time. The endo ee was >98% in all cases (ref 267).

Scheme 29



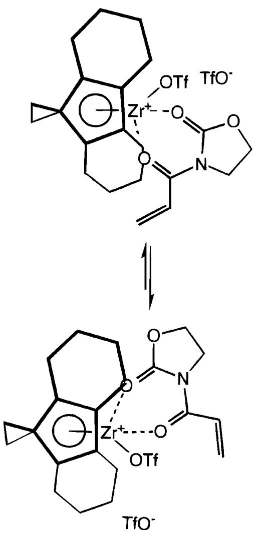
Scheme 30



Cu center. Spectroscopic investigations demonstrated that an unsymmetric square-pyramidal geometry exists in solution for a catalyst bearing C_2-symmetric bis(sulfoximines) ligand and the dienophile where one triflate anion occupies the fifth coordination site.[268] In the solid state several X-ray structures of [(t-Bu-box)CuL$_2$](X)$_2$ complexes (L = H$_2$O, halogen or L$_2$ = substrate or substrate-like compounds) were determined[269−273] that support a distorted square-planar intermediate for reactions catalyzed by these complexes. As far as the bis(aquo) complexes [(t-Bu-box)-Cu(H$_2$O)$_2$](X)$_2$ (X$^-$ = OTf$^-$ or SbF$_6^-$) are concerned,[269−271] in the case of the triflate counterion a distorted square-pyramidal geometry with one triflate counterion weakly bonded to the metal center in the apical position was found. In contrast, for the hexafluoroantimonate complex none of the counterions appeared to be coordinated to the metal center, which assumes a distorted square-planar geometry. Theoretical calculations for the catalyst−substrate two-point complex (Scheme 30) suggest a distorted square-planar geometry for the cations analogous to that found in the solid state.[267,273−275]

Two factors seem to be responsible for the counterion effect on the catalyst activity. The entering substrates must first displace the counterion from the two equatorial coordination sites. Second, the fifth coordination site on copper(II) is required for catalyst turnover through the associative displacement of the bound neutral oxygen ligands by additional dienophile.[267] Both factors are facilitated by the least coordinating anions, and this explains the correlation between the catalytic activity and the "noncoordinating" tendency of the counterions. The understanding of the counterion effect on the diastereoselectivity and on the asymmetric induction is less trivial and is still a matter of debate. The moderately lower enantioselectivity observed in some cases with OTf$^-$ instead of SbF$_6^-$ might be due to the intervention of a competing cycloaddition by a less highly organized one-point catalyst−dienophile complex. The possibility that the catalyst geometry could be affected by changing the counterion must also be taken into account. No explanation has been suggested for the counterion effect on the diastereoselectivity of the catalyst.

Scheme 31



Johannsen and Jørgensen found that hetero-Diels−Alder reactions catalyzed by (t-Bu-box)Cu(X)$_2$ Lewis acids can be accelerated by performing them in polar noncoordinating solvents such as nitromethane or 2-nitropropane.[276] In addition, they provided evidence for the solvent/counterion interplay and found that the combination of noncoordinating solvents with weakly coordinating anions maximizes the yield of the Diels−Alder reactions, in some cases at the expense of enantioselectivity.[277,278] The latter was found to be tremendously affected (even inverted) by the choice of the solvent for the hetero-Diels−Alder reaction of ethyl glyoxalate with 1,3-cyclohexadiene catalyzed by [((S,S)-Ph-box)Cu](OTf)$_2$.[273]

Analogous solvent acceleration was previously documented by Collins and co-workers for chiral metallocene triflate complexes.[279,280] They reported a dramatic enhancement in both reaction rate and asymmetric induction in passing from methylene chloride to nitromethane or 2-nitropropane for the Diels−Alder reaction shown in Scheme 29 catalyzed by [(S)-1,2-ethylenebis(η^5-tetrahydroindenyl)Zr](OTf)$_2$. The two complexes shown in Scheme 31 were present in solution in which the dienophile coordinates to the metal center with both carbonyl groups and adopts the *s-cis* geometry.

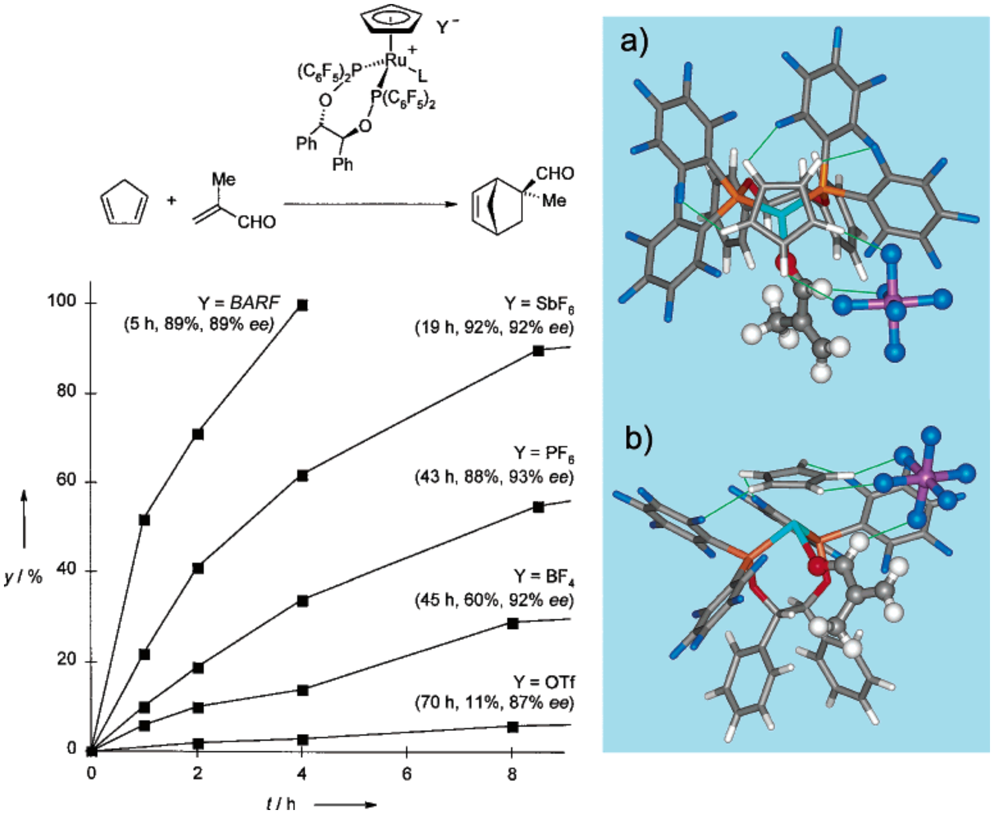


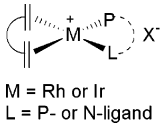
Figure 8. (Left) Plot of GC yield (*y*) as a function of reaction time (*t*) for the catalyzed reaction of methacrolein with cyclopentadiene catalyzed by the complex shown (in parentheses: total reaction time, yield of isolated product, and ee of the *exo*-cycloadduct). (Right) Top view (a) and front view (b) of one of the ion pairs present in the asymmetric unit. (Reprinted with permission from ref 287. Copyright 1999 Wiley-VCH.)

Detailed spectroscopic and kinetic studies[280] revealed that the minor isomer (top, Scheme 31) reacts most rapidly and selectively with cyclopentadiene. Changing the solvent from methylene chloride to nitromethane shifted the equilibrium toward the most reactive isomer, partially accounting for the dramatic enhancement in selectivity. Substituting OTf^- with the less coordinating $BARF^-$ counterion afforded promising dicationic catalysts.[281]

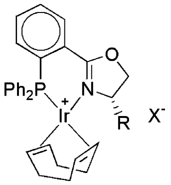
A counterion effect was also observed for Diels–Alder reactions catalyzed by square-planar palladium(II) and platinum(II) complexes bearing diphosphine ligands.[282–286] For the test reaction reported in Scheme 29 catalyzed by $[Pd(S\text{-BINAP})(PhCN)_2]X_2$ ($X = BF_4^-$ or PF_6^-)[282] or $M(R\text{-BINAP})X_2$ (M = Pd or Pt, $X = OTf^-$, PF_6^-, or SbF_6^-)[283] it was found that both the activity and enantioselectivity were enhanced by using the least coordinating counterions. By investigating the reaction between cyclopentadiene and acrolein catalyzed by $[(P{-}P)M(\mu\text{-}Cl)]_2X_2$ complexes (where M = Pd(II) or Pt(II), $X^- = OTf^-$, ClO_4^-, or BF_4^-) bearing chiral diphosphines, Strukul and co-workers observed an analogous counterion effect on the activity while an opposite effect was found with respect to the enantioselectivity, which was found to be higher with more coordinating anions.[284] Gagné and co-workers recently studied the binding of catalytically relevant Lewis bases (counterions, substrate (S), product (P), and water) to the Lewis acid $[(P, P)Pt]^{2+}$ from a thermodynamic and kinetic point of view.[285,286] For P,P = dppe or *R*-BINAP, the following scale for the relative binding strengths was found: $BF_4^- \ll OTf^- < S < P \ll H_2O$. The main kinetic result was that the rates of ligand substitution processes (rather than electrophilicity) emerged as the most important factors controlling the activity of $[(P,P)Pt]X_2$ Lewis acids as catalysts for Diels–Alder reaction.

Kündig and co-workers noticed a marked counterion effect on the catalytic activity of chiral Ru(II)[287] and Fe(II)[288] Lewis acids, which have a single coordination site at the disposal of the substrate, for the Diels–Alder reaction of methacrolein with cyclopentadiene (Figure 8). As can be seen from Figure 8, the catalytic activity of Ru(II) complexes tracks with the noncoordinating tendency of the counterion. Similar trends were observed for Fe(II) complexes for which the reaction rates were higher than those for Ru(II) ones; no further increase in activity was found on going from the SbF_6^- to $BARF^-$ counterion. The enantioselectivity remained unaffected by the counterion for both Ru(II) and Fe(II) catalysts. The authors succeeded in isolating the Ru(II) intermediate in which methacrolein is coordinated to the metal center and determined the solution and solid-state structure ($X^- = SbF_6^-$) through ^1H-NOESY NMR experiments and X-ray diffraction analysis, respectively. In both cases *s-trans*-coordinated methacrolein with the formyl proton pointing toward the Cp ring was observed (Figure 8). In the solid state cationic moieties are associated in pairs with SbF_6^- ions with Ru–Sb distances around 5.78 Å. Three H···F interionic contacts were observed: two with the cyclopentadienyl ring and one with the formyl atom of the

Scheme 32



Scheme 33



methacrolein moiety. The existence of contact ion pairs in CD_2Cl_2 solution for the Ru(II) catalysts having BF_4^- counterion was demonstrated by $^{19}F,^1H$-HOESY[288,289] and PGSE[289] NMR spectroscopies: interionic interactions between fluorine atoms of the counterion and Cp and formyl protons were detected, in agreement with the solid-state observations.

Detection of such interionic interactions in both the solid and solution states induced the authors to hypothesize that the effect of the anion on the reaction rate could be due to not only its competition with the aldehyde substrate for the Lewis acid coordination site of the catalyst, but also a decrease in the rate of product release due to cooperative binding of the anion to both the aldehyde product and the catalyst.

Finally, Jacobsen and Weller found counterion effects in Diels–Alder reaction catalyzed by chiral tri-[290] and tetradentate[291] Cr(III) and Ag(I)[292] phosphines complexes, respectively. In the latter case carborane monoanions $CB_{11}H_{12}^-$ and $CB_{11}H_6Br_6^-$ were found to afford much higher yields of the final product and faster reaction rates compared with BF_4^-, OTf^-, or ClO_4^-.[292] Livinghouse[293] observed counterion effects in the diastereoselective cyclization of trienes catalyzed by Rh(I) catalysts with respect to the reaction rate and selectivity.

3.3. Hydrogenation Reactions

Ion-pairing effects have been mainly observed for catalytic hydrogenations of olefins mediated by cationic square-planar Rh(I) or Ir(I) precatalysts bearing a cyclic diene and two P-monodentate ligands or a bidentate P,P or P,N ligand (Scheme 32).

The progenitors of such catalysts were introduced by Osborn and Schrock[294,295] and Crabtree[296,297] when L = P and N ligand, respectively. A chiral version of Crabtree's catalyst $[Ir(COD)(Pcy)_3(py)]PF_6$ (COD = cyclooctadiene, cy = cyclohexyl; py = pyridine), bearing a bidentate phosphinodihydrooxazole ligand (Scheme 33), was used by Pfaltz for the asymmetric hydrogenation of unfunctionalized tri- and tetrasubstituted olefins.[298]

Replacing the PF_6^- anion with $BARF^-$ or other perfluoroborate anions had a dramatic effect on the conversion and catalytic loading of the catalyst.[299] In addition, the catalyst with $BARF^-$ proved to be much more robust and much less sensitive to moisture.[299,300] A kinetic comparison between the hydrogenation of (*E*)-1,2-diphenyl-1-propene with "$IrPF_6$" and "IrBARF" indicated high initial turnover frequencies (TOF) with a consequent likely diffusion-limited reaction for both compounds. While the reaction remained very fast and diffusion-limited up to ca. 100% conversion for the "IrBARF", a remarkable reduction of reaction rate was observed for "$IrPF_6$" after 10–15% conversion (Figure 9).[301]

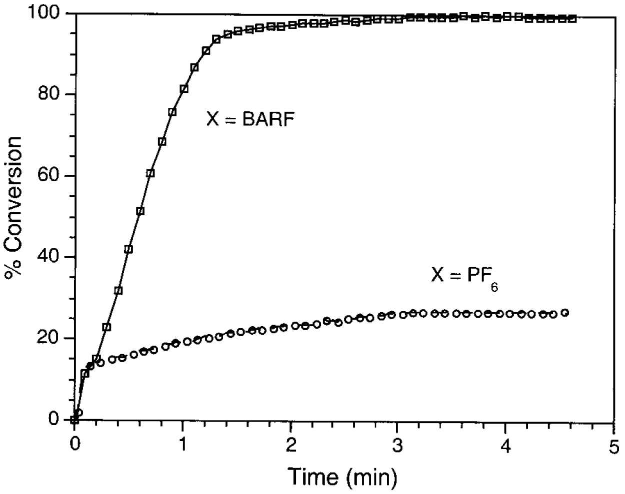
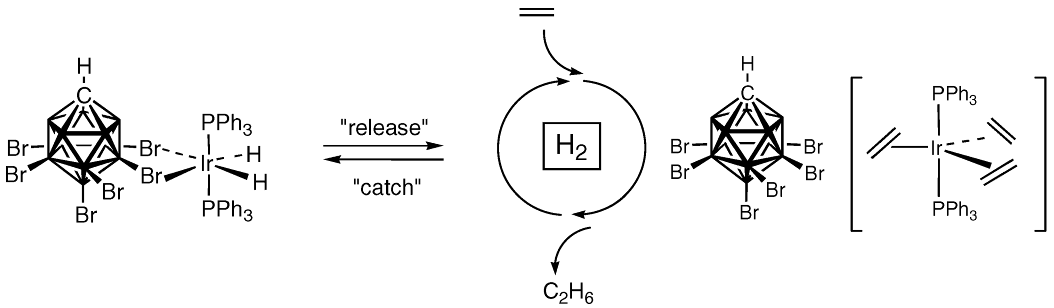


Figure 9. Comparative kinetic studies of the hydrogenation of (*E*)-1,2-diphenyl-1-propene with "$IrPF_6$" and "IrBARF" complexes. (Reprinted with permission from ref 301. Copyright 2000 Wiley-Liss, Inc., a subsidiary of John Wiley & Sons, Inc.)

A kinetic study on anion effects has been recently carried out for a broader range of counterions.[302] A strong decrease of the reaction rate was observed in the series $Al(OC(CF_3)_3)_4^- > BARF^- > B(C_6F_5)_4^- > PF_6^- \gg BF_4^- > OTf^-$. Catalysts with $Al(OC(CF_3)_3)_4^-$, $BARF^-$, and $B(C_6F_5)_4^-$ counterions were found to be not only more reactive but also more stable than other salts. The effects of alkene concentration and hydrogen pressure were comparatively investigated for the $BARF^-$ and PF_6^- salts. While an approximately first-order rate dependence on hydrogen pressure was determined for both salts, the rate dependence on the alkene concentration was strikingly different. For "IrBARF" the reaction rate depended little on alkene concentration, indicating that the alkene is not involved in the turnover-limiting step. On the contrary, a rate order of ≈ 1 was determined for "$IrPF_6$" at low alkene concentration. In the latter case the alkene it is involved in the turnover-limiting step. Presumably, PF_6^- decreases the reaction rate of the alkene with the catalyst through coordination to the metal center. As a consequence, deactivation leading to an unreactive trimeric hydroiridium complex competes with the productive hydrogenation pathway. It is known that the addition of hydrogen to iridium(I) precatalyst affords bi- and trimetallic Ir–hydride. These are catalytically inactive complexes probably due to the combination of 14-electron $[L_2Ir(H)_2]^+$ moieties.[303,304]

Weller and co-workers were able to isolate and structurally characterize the intermediate of the hydrogenation process $[L_2Ir(H)_2][$*closo*-$CB_{11}H_6Br_6]$.[305] Interestingly, *closo*-$CB_{11}H_6Br_6^-$ counterion, different from BF_4^- and $BARF^-$, affords enough stabilization

Scheme 34



to stop decomposition in the absence of olefin, but it can be easily displaced from the metal center by the olefin when needed. As confirmation, by adding ethylene to $[L_2Ir(H)_2]$[*closo*-$CB_{11}H_6Br_6$] $[L_2Ir(\eta^2\text{-}C_2H_4)_3]$[*closo*-$CB_{11}H_6Br_6$] was isolated and structurally characterized. The starting compound was reobtained by adding H_2 to the latter complex, and the cycle can be repeated a number of times without appreciable decomposition (Scheme 34).

The advantage of using such a carborane anion was previously demonstrated for the hydrogenation of olefins with $[(PPh_3)_2Rh(NBD)]X$ (NBD = norbornadiene) precatalysts. When X^- = *closo*-$CB_{11}H_6Br_6^-$, the precatalysts were significantly more active than when $X^- = BF_4^-$ or *closo*-$CB_{11}H_{12}^-$.[306]

So far we have only seen cases in which the counterion affects the conversion or TOF of catalytic hydrogenation reactions while the ee remains substantially unaffected. Buriak and Osborn showed that the asymmetric hydrogenation of imine[307] and olefins,[308] catalyzed by $[((-)bdpp)Rh(NBD)]ClO_4$ (bdpp = 2,4-bis(diphenylphosphino)pentane), is affected by the presence of anions in terms of not only reaction rate but also of asymmetric induction. In particular, by investigating the effect of surfactant sulfonate salts on hydrogenation reactions, they discovered that besides the TOF the enantioselectivity was also affected but that the factor responsible was the sulfonate anion and not the reverse micellar structure. The same effect was in fact obtained by replacing the sulfonate surfactant with simple sulfonate salts or halides (the influence of halides on the enantioselectivity of transition-metal catalysis was recently reviewed,[35] so it will not be further discussed here).

A special role is currently attributed to counterions in designing catalytic processes mediated by ionic transition-metal complexes carried out in supercritical fluids.[309] For instance, highly fluorinated counterions are usually selected for reactions performed in supercritical CO_2 ($scCO_2$) in order to enhance the solubility of metal-containing catalysts. It has been shown that hydrogenation reactions catalyzed by [(P,P)Rh(COD)]X complexes can be successfully carried out when X^- = BARF$^-$ or OTf$^-$.[310] Leitner and Pfaltz explored the possibility of asymmetrically catalyzing the hydrogenation of imines in $scCO_2$[311] and ILs (ionic liquids)/$scCO_2$[312] using the iridium(I) catalyst shown in Scheme 33 or a slightly modified version having the fluorinated $-CH_2CH_2C_6F_{13}$ groups in the 4-positions of the two phenyl rings bonded to the phosphorus atom.[311] They also contrasted the results obtained in $scCO_2$ with those in conventional media. Interestingly, a higher efficiency was observed in $scCO_2$ compared to conventional organic solvents. In the latter the anion markedly influenced the reaction rate but had only minor effects on asymmetric induction; on the other hand, in $scCO_2$ both the reaction rate and the enantioselectivity remarkably depended on the counterion. The best results were obtained with BARF$^-$.[311] As for the catalytic reactions carried out in ILs/$scCO_2$, remarkable effects were observed on the stereoselectivity of the hydrogenation reaction upon variation of the anion in the IL. The ee values varied from 30% with BF_4^- to 78% with BARF$^-$.

Finally, the effect of the counterion in the hydrogenation of 1-octene with [(dppb)Rh(COD)]X (dppb = 1,4-bis(diphenylphosphino)butane, X^- = BF_4^-, BPh_4^-, $B(C_6H_4(4\text{-}SiMe_3)_4)^-$, BARF$^-$, $B(C_6H_4\text{-}(4\text{-}Si(Me_2)CH_2CH_2C_6F_{13})_4)^-$, $B(C_6H_4(4\text{-}C_6F_{13})_4)^-$, or $B(C_6H_3(3,5\text{-}(C_6F_{13})_2)_4)^-$) was investigated in acetone. It was found that the TOF at 50% yield in octane increased as the fluorination of the counterion increased.[313] Less importance seems to be attributed to the steric properties of the counterion. Using $B(C_6H_3(3,5\text{-}(C_6F_{13})_2)_4^-$ counterion and fluorinated diphosphine ligand afforded significant affinity of the catalysts for perfluorinated solvents and catalyst recycling through fluorous biphasic separation.[313]

3.4. Carbonylation Reactions

Ion pairing has been found to substantially affect Reppe carbonylations,[314] oxo syntheses,[315,316] and CO/alkenes copolymerizations.[317−319] In such reactions the catalytic precursors are very often neutral palladium(II) complexes bearing at least two monodentate P and/or N or one bidentate P,P, P,N, or N,N ancillary ligands and one or two anionic ligands (Y). The addition of strong acids (HX) to the catalytic precursor causes the protonation of Y^- and the consequent elimination of HY with the formation of the $[Pd]^+X^-$ ion pair in which the cationic unsaturated moiety is stabilized by solvation and electrostatic or coordinative interactions with the counteranion X^-. The solvent/counterion interplay naturally contributes to determine the activity, regioselectivity, and enantioselectivity of the catalytic systems.

As far as Reppe reactions are concerned, the nature of the counterion can significantly affect both activity and selectivity.[314,320−322] The anion can direct the carbonylation of butadiene toward hydroesterification (with coordinating anions) or oligomerization and

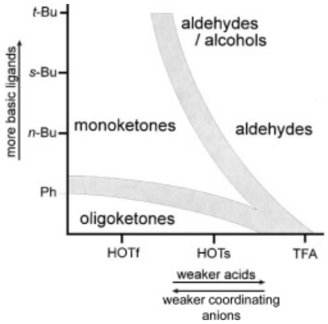


Figure 10. Schematic representation of chemoselectivity as a function of ligand $[R_2P(CH_2)_3PR_2]$ and acid properties. (Reprinted with permission from ref 315. Copyright 2000 Elsevier.)

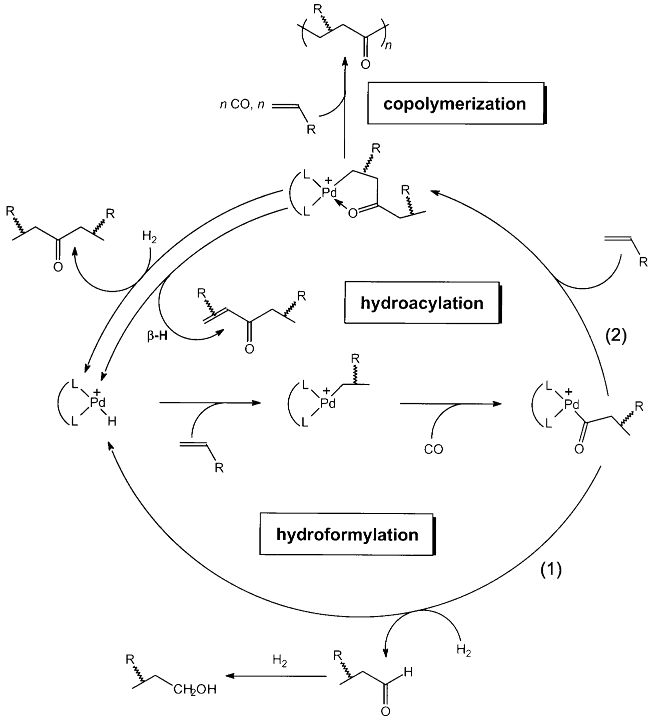
telomerization (with weakly coordinating anions).[323] In the hydroesterification of styrene contrasting results have been reported: in some cases the activity of palladium(II) catalysts was favored by weakly coordinating anions[324,325] and in other cases by strongly coordinating ones.[326] For the hydroxycarbonylation of styrene[327,328] and styrene derivatives[327] it was found that the branched products are preferentially formed with coordinating anions while linear products are obtained with weakly coordinating anions. Using diphoshine ligands a dependence of the regioselectivity on the counterion was observed, although to a lesser degree. A beneficial effect of OTs^- anion was observed in the biphasic hydroxycarbonylation of alkenes.[329,330] As an example, van Leeuwen and co-workers[330] used palladium(II) compounds bearing water-soluble diphosphine with a xanthene-type backbone as catalysts to show that anions that are weaker coordinating than OTs^- gave rise to the formation of metallic palladium. More strongly coordinating anions stabilized the cationic center but slowed the reaction.

Oxo synthesis involves reactions of olefins with mixtures of carbon monoxide and hydrogen to give aldehyde, alcohol, and/or ketone products. Drent and Budzelaar showed that using palladium(II) catalysts of the general formula L_2PdX_2, with a suitable choice of ligand (L) and counterion (X^-), the hydrocarbonylation of olefins (propene and 1-octene) could be tuned to proceed selectively toward either aldehydes (alcohols) or ketones.[315,316] The course of hydrocarbonylation seems to be determined by the electronic properties of both neutral and anionic ligands. As illustrated in Figure 10, highly electrophilic complexes, bearing phosphine ligands with lower basicity and weakly coordinating anions, are efficient copolymerization or hydroacylation catalysts. In contrast, more basic ligands and more coordinating anions lead to the formation of aldehydes/alcohols (hydroformylation).

An important role is also clearly played by the solvent. For example, OTs^- anion behaves as a weakly coordinating anion in polar solvents (methanol) and a coordinating anion in nonpolar solvents (diglyme).

The proposed mechanism for aldehyde- and ketone-forming reactions is illustrated in Scheme 35. The actual active species in both reactions is considered to be the cationic hydride complex L_2PdH^+ formed by heterolytic splitting of H_2 at the electrophilic palladium center of the precursor L_2PdX_2. L_2PdH^+ undergoes coordination and migratory insertion of olefin and, successively, CO to yield the acyl complex $L_2PdC(O)R^+$. It is at this stage that hydroformylation (1) and hydroacylation (2) reactions are thought to diverge. In 1 hydrogenolysis of the Pd−acyl bond takes place to give aldehyde product and regenerate the L_2PdH^+. In 2 a second olefin molecule coordinates to the Pd−acyl and migratory insertion affords an internally coordinated Pd−alkyl complex. The latter can undergo hydrogenolysis to form a saturated ketone and regenerate L_2PdH^+. Alternatively, it can β-eliminate to give the hydride and an unsaturated ketone. These terminating reactions compete with further insertion steps to give oligo- or polyketones (Scheme 35).

Scheme 35. Proposed Mechanism of Palladium-Catalyzed Hydroformylation, Hydroacylation, and Olefin/CO Copolymerization[a]



[a] OTf^- and OTs^- are typical counterions of the cationic Pd species. Reprinted with permission from ref 315. Copyright 2000 Elsevier.

Since the catalytic cycles for hydroformylation and hydroacylation diverge at the Pd−acyl stage, it seems that a more electrophilic metal center favors olefin insertion (formation of ketones) over hydrogenolysis (formation of aldehydes). A possible explanation could be found in the stabilization of the internally coordinated Pd−alkyl complex that could be partially felt in the transition state. The insertion barrier should be lower than that for a normal olefin insertion. A more electrophilic metal should therefore favor olefin insertion over hydrogenolysis.

Concerning the role of counterion in directing the reaction toward the hydroformylation or hydroacylation (because it is thought that it involves heterolytic dissociation of H_2 at a single Pd center) it has been proposed that the anion may assist the heterolytic dissociation of H_2 by binding H^+.[316] Weakly coordinating anions such as OTf^- are not basic enough to fulfill this role and do not stay close to the Pd center.

The regioselectivity in hydroformylation is also affected by the anion. A higher preference for linear product is observed with more coordinating anions. According to the above-hypothesized mechanism this could indicate that the anion-assisted hydrogenolysis reaction discriminates between Pd−*n*-acyl and Pd−*i*-acyl species, favoring the former.

Also, for Pt(II)-catalyzed hydroformylation of styrene it was observed that weakly coordinating anions led to a reduced activity and an increased amount of branched aldehyde (2-phenylpropanal).[331]

Regarding CO/olefin copolymerizations, a counterion effect has been found to mainly affect the activity of the catalytic system.[317−319] As stated above and illustrated in Scheme 35, weakly coordinating anions are necessary to obtain active catalytic systems. It should be noted that because CO/olefin copolymerization reactions are carried out in more polar solvents (often in methanol), anions such as OTf^- are considered weakly coordinating anions. In the case of olefin polymerizations catalyzed by metallocenium complexes, they are usually carried out in toluene or benzene, where OTf^- would be such a strongly coordinating anion that it would completely inhibit the catalytic process.

When the CO/olefin copolymerization reactions are carried out in methylene chloride, the counteranion effect becomes more marked. The CO/styrene copolymerization in methylene chloride, catalyzed by $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(bipy)]X$ (where bipy = 2,2′-bipyridine), was found to be strongly affected by the nature of the counterion X^-.[119] The weaker the coordinating anion, the higher the catalytic activity: $BARF^- > SbF_6^- > PF_6^- > BF_4^- > CF_3SO_3^- \gg BPh_4^-$. ^1H-NOESY and $^{19}F,^1H$-HOESY NMR investigations showed that the strength of interionic interactions in methylene chloride-d_2 inversely tracks with the catalytic performances; this indicates that the presence of fewer contact ion pairs leads to a benefit in terms of catalytic activity. Inspection of the observed NOE contacts allowed the relative anion−cation orientation in solution to be determined, and it was found to be independent of the counterion (Figure 11).

The counterion occupies the apical positions even if it is shifted toward the N,N-ligand and, in particular, it stays close to the N-arm trans to the Pd−C σ bond. The exact role of the counterion in the catalytic performance is not known, but it seems that it competes with the substrate for the fifth coordination position. In agreement with this hypothesis, recent results for the CO/*p*-Me-styrene copolymerization catalyzed by $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)((2,6\text{-}(R)_2\text{-}C_6H_3)N{=}C(R')\text{-}C(R'){=}N((2,6\text{-}(R)_2\text{-}C_6H_3))]PF_6$ carried out in methylene chloride indicate that the catalytic activity decreases when the steric hindrance in the apical position increases.[332] By investigating the relative anion−cation orientation through NOE NMR methodologies it was also possible to evaluate the minimum steric hindrance above and below the square-planar coordination plane (introduced by varying the 2,6-R substituents), which causes the counterion to avoid the apical positions. By a proper selection of the substituents (R = R′ = Me) such palladium catalysts bearing achiral C_{2v}-symmetric α-diimine ligands catalyze the isospecific CO/*p*-Me-styrene copolymerization.[333] The counterion significantly affects the stereoregularity of the copolymers: the isotactic content tracks with the coordination ability of the anion. While the use of $BARF^-$ and PF_6^- resulted in a similar percentage of the *ll*-triad (72% and 75%, respectively), the catalyst having the more coordinating $CF_3SO_3^-$ anion affords a polyketone containing 80% *ll*-triad.[333]

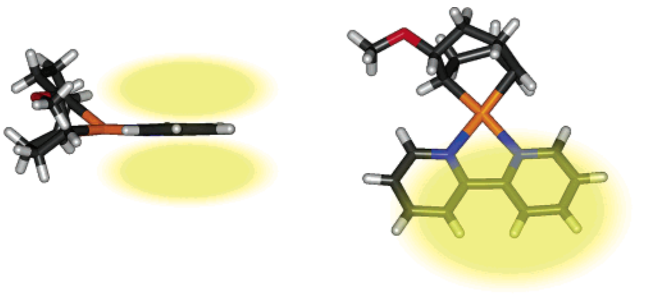
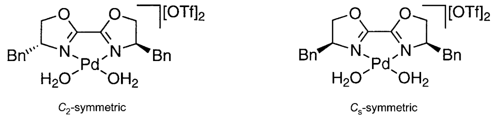


Figure 11. Two views of the interionic solution structure of $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(bipy)]X$ complexes where the two clouds represent the action space of the X^- counteranion. The two positions above and below the coordination plane are equally populated, and the anion is shifted on the side of the bipy ligand with a slight preference for the ring trans to the Pd−C σ bond. (Reprinted with permission from ref 31. Copyright 2003 Wiley-VCH.)

Scheme 36

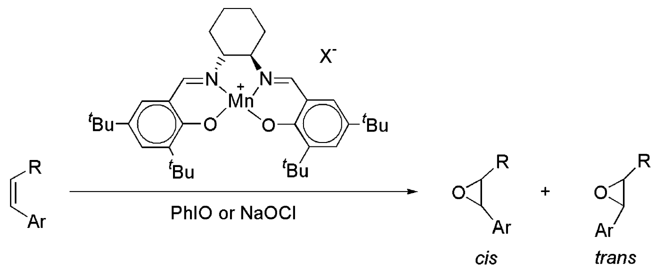


Very interesting results concerning solvent control of the stereoselectivity of alternating CO/styrene copolymerization were reported by Consiglio and coworkers[334] using the bicationic bis-aquo catalysts shown in Scheme 36.

When the reaction was carried out in a mixture of methylene chloride/MeOH (10:1), not only the C_2-symmetric but also, unexpectedly, the C_s-symmetric catalyst afforded isotactic copolymer.[335] When only MeOH was used as solvent, syndiotactic copolymer was prevalently produced with the C_s-symmetric catalyst. The authors hypothesize that the change in the microstructure of the copolymer produced with MeOH as the only solvent is probably due to the effects of ion pairing on the stereoselectivity of the copolymerization.

Recently, Consiglio and co-workers also reported that in the asymmetric cyclocarbonylation of 4,4′-bis(carboethoxy)hept-6-en-1-yne with carbon monoxide, catalyzed by [Rh(1,5-COD)BIPHEMP]X, the anion effect on the reaction yield inversely correlates with the coordinating tendency: $OTf^- > BF_4^- > PF_6^-$.[336] PGSE and HOESY NMR measurements by Pregosin et al. on the catalytic precursors indicated that OTf^-, surprisingly, has a slightly lower tendency to ion pairing.[337] This could explain the higher perfor-

Scheme 37



mances of the salt. An alternative explanation could involve the partial coordination of OTf⁻ to the catalytically active species, which kinetic investigations indicated to be [RhBIPHEMP(S)$_2$]X (S = solvent). OTf⁻ is not only more coordinating than BF_4^- and PF_6^- but it also usually shows smaller decomposition tendency with respect to BF_4^- and, especially, PF_6^-.

Selection of the Brønsted acid and the deriving anion was found to be critical for CO/ethene copolymerization even in a “green” medium such as water, where the reaction was catalyzed by palladium(II) complexes bearing water-soluble C_3H_6-1,3-[P(C_6H_4-m-SO_3Na)$_2$]$_2$ phosphine.[338] Anions $CF_3CO_2^-$ or TsO⁻ afforded highly active catalysts, while with the strongly coordinating iodide anion, no catalytic activity was observed. Again, a compromise must be reached in selecting the Brønsted acid cocatalyst that has to be coordinating enough to avoid catalyst decomposition but not too coordinating so as to inhibit coordination of the substrates.

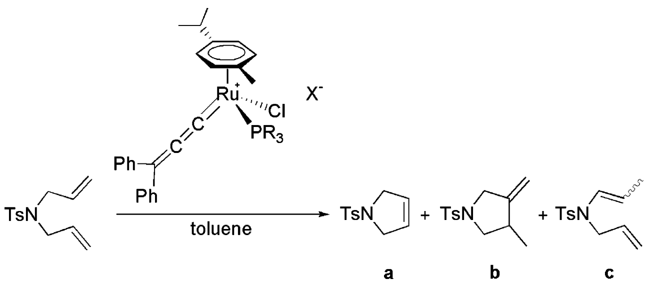
ILs are another environmentally friendly medium where CO/styrene copolymerization may occur. In ILs cationic catalysts obviously exchange the counteranion with that of the solvent. Both of them must be weakly coordinating in order to obtain a reasonable catalytic activity. Interestingly, Klingshirn et al. showed that [n-C_6H_{13}-pyridinium]NTf_2 is an effective solvent for the palladium-catalyzed copolymerization of CO and styrene.[339] Catalyst productivity approached that obtained in polar noncoordinating solvents, while higher molecular weights and improved catalyst stability were observed compared with methanol.

3.5. Other Reactions

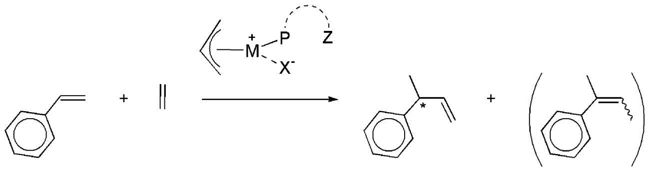
An interesting ion-pairing effect was reported by Adam and co-workers[340,341] for the Mn(III)(salen)-catalyzed *epoxidation* of phenyl-substituted *cis*-alkenes (Scheme 37).

The diastereoselectivity (cis/trans ratio) strongly depends on the counterion: more coordinating counterions (Cl⁻, Br⁻, or MeCOO⁻) afford extensive isomerization (cis/trans ratio ca. 30/70) while isomerization with weakly coordinating counterions (BF_4^-, PF_6^-, or SbF_6^-) is reduced (cis/trans ratio ca. 75/25). Theoretical calculations indicate that the singlet, triplet, and quintet states are all accessible in both the Mn(V)(oxo) complex and Mn(III)(epoxide) adduct.[342,343] The energies of these spin states are different for the coordinating anions, which afford neutral Mn species, and little-coordinating anions, which lead to cationic Mn species. In the latter case the epoxidation is expected to proceed mainly on the quintet surface where Mn(V)(oxo)$^+$ should transfer its oxygen atom concertedly in a diastereoselective manner. When more coordinating anions are considered, all three states of Mn(V)(oxo)X participate in the oxygen-transfer processes with a consequent enhancement in the isomerization.[341]

Scheme 38



Scheme 39



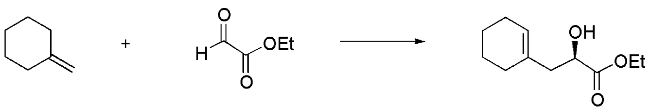
Ring-closing metathesis (RCM) catalyzed by cationic ruthenium(II) allenylidene complexes was also affected by the counteranion in terms of both reaction rate and selectivity. In particular, Dixneuf and coworkers initially discovered that the RCM reaction shown in Scheme 38 exclusively affords product **a** when X⁻ = OTf⁻ counterion, while it leads to a mixture of **a** (31%), **b** (43%), and **c** (16%) with a slower reaction rate when X⁻ = BF_4^-.[344,345]

Although mechanistic studies have been carried out,[346] a rationale for the counteranion effect has not been given. It has been suggested that the more coordinating OTf⁻ counterion could assist the decomplexation of *p*-cymene ligand and stabilize the 14-electron Ru(II) species in solution, which would be the catalytically active species.

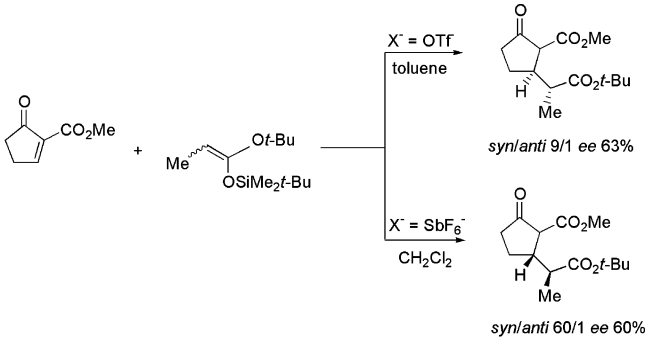
The counterion affects the conversion and enantioselectivity of *asymmetric hydrovinylation* of vinylarenes.[347] In such a reaction Ni(II) or Pd(II) catalysts, shown in Scheme 39, are prevalently employed.

As far as the catalyst activity is concerned, two different situations have been observed depending on whether monophosphine or P,Z hemilabile bidentate ligands are used. In the former case greater activity has been accomplished with more coordinating anions. As an example, RajanBabu showed that hydrovinylation of styrene, catalyzed by Ni(II) with monophosphine, does not proceed unless a weakly coordinating anion such as OTf⁻ or ClO_4^- is used.[348] Almost no reaction occurs under the same conditions with BF_4^-, BPh_4^-, NTf_2^-, SbF_6^-, or BARF⁻. A slight coordinative tendency seems to be necessary to afford enough thermodynamic stability to the catalytic system. When this stability is furnished by the labile Z-arm of the hemilabile P,Z ligand,[349] better results are obtained with the least coordinating anions such as SbF_6^- or BARF⁻.[348,350,351] Interestingly, Vogt and co-workers showed that the counteranion has a

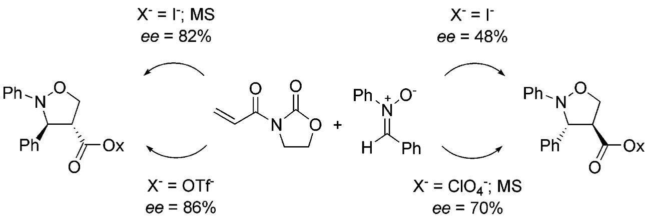
Scheme 40



Scheme 41

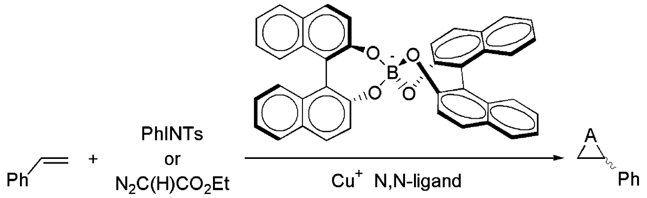


Scheme 42[a]



[a] Adapted from ref 362.

Scheme 43



significant effect on the enantioselectivity in the Pd(II)-catalyzed hydrovinylation of styrene. Different from previous reports,[352,353] they found that the asymmetric induction tracked with the noncoordinating tendency of the counteranion: $SbF_6^- = PF_6^- > BF_4^- \gg OTf^-$.[354]

The *carbonyl–ene* reaction illustrated in Scheme 40 was also found to be sensitive to ion pairing.[355,356] These reactions are usually catalyzed by the same catalysts employed in Diels–Alder reactions, and similar considerations can be given to explain the counterion effect on rate and asymmetric induction of the reaction.

An interesting observation has been made by Gagné regarding the reaction reported in Scheme 40 catalyzed by [((*S*)-MeOBiphep)Pt]X_2 complexes.[357] Not unexpectedly, the reactivity as a function of the counterion followed the order $SbF_6^- > BF_4^- \gg OTf^-$, while the enantioselectivity was only marginally affected by the nature of the counterion. Interestingly, the presence in the catalytic medium of weakly coordinating protic additives[358] affected the catalyst turnover and the effect was counterion dependent. While Lewis basic additives such as *t*-BuOH and water inhibit the reaction, acidic alcohols and phenols accelerate it without altering the ee. The effect is even more marked with a more coordinating counterion such as OTf^-. These results indicate the break up of contact ion pairs between P_2Pt^{2+} and X^- as a turnover event in catalysis. The acidic additives could increase the rate of associative anion–substrate exchange (kinetic effect) and/or reduce the coordinating power of the counterion through hydrogen bonding and, consequently, stabilize the solvent-separated ion pair (thermodynamic effect). Additives also play an important role in rendering the catalyst less sensitive to traces of water by sequestering them through hydrogen bonding.

An inversion of the absolute configuration of the product was observed by Bernardi and Scolastico[359] for the *Mukaiyama–Michael reaction* (Scheme 41) catalyzed by (*t*-Bu-box)Cu(X)$_2$ when the counterions and solvents were changed.

For the addition reactions of enolsilanes to alkylidene malonates catalyzed by similar Cu(II) catalysts it was essential to use hexafluoro-2-propanol as an additive in order to induce catalyst turnover.[360]

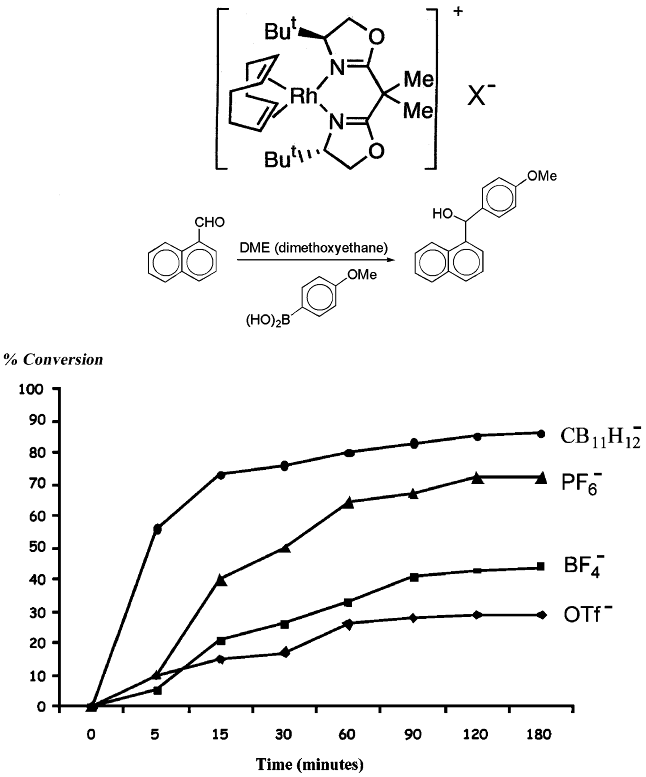
An analogous change of enantioselectivity was observed for the *1,3-dipolar cycloadditions of nitrones*[361] catalyzed by [(*R*)-Ph-box)Mg]X_2 complexes as a function of the counterion[362] and, interestingly, the presence of molecular sieves (Scheme 42; Ox = oxazolinic ring; MS = molecular sieves).[363]

As can be seen from Scheme 42, by simply changing the counterion from I^- to OTf^- or performing the reaction in the presence of MS the chiral selection can be reversed.

Aziridination[364,365] *and cyclopropanation*[365,366] *reactions* catalyzed by cationic Cu(II) complexes bearing bisoxazoline ligands also undergo counterion modulation of reactivity. Interesting results have been reported by Arndtsen an co-workers for the reaction indicated in Scheme 43 (where A = NTs or $CHCO_2Et$) in which achiral and chiral counterions were used.

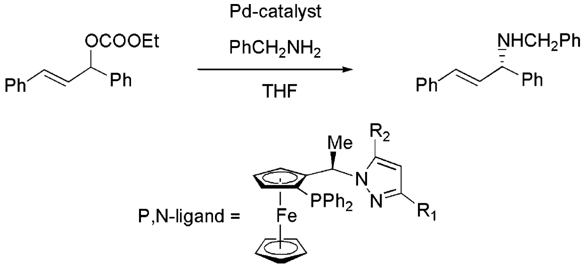
Variation of achiral weakly coordinating counteranion (OTf^-, ClO_4^-, PF_6^-) in the catalyzed aziridination of styrene in the presence of (*R*)-Ph-box and (*S*)-*t*-Bu-box ligands led to changes in the ee of over 30% in benzene. No apparent trend was found between the influence in enantioselectivity and the coordinating tendency of the anions. The combination of chiral Cu(I) complexes with chiral anions, as indicated in Scheme 43 (only the *R* isomer is shown, but both enantiomers were isolated and employed in catalysis), showed that while the chirality of the counterion has a minor influence on the enantioselectivity of aziridination (variation of ca. 2% ee) it dramatically alters the enantioinduction of cyclopropanation. Examination of the *cis*-isomer of cyclopropane reveals that changing the anion chirality from *R* to *S* not only influences enantioselectivity (from 28% to 6%) but also actually changes the preferred enantiomer generated. Some aziridination catalytic reactions were carried out with achiral bidentate ligands and the above-indicated chiral anions, and a small enantiomeric excess (7%) was observed whose configuration is inverted by changing that of the counterion. This represents an interesting first example of an enantioselective transition-metal-cata-

Scheme 44[a]



[a] Reprinted with permission from ref 368. Copyright 2001 Elsevier.

Scheme 45



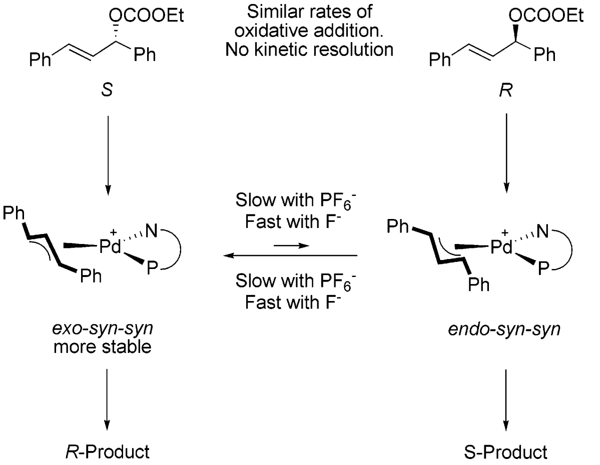
lyzed reaction where the sole source of chirality is the counterion. The possibility of inducing asymmetric reactions through ion pairing of cationic prostereogenic or racemic reagents with chiral anions was reviewed recently by Lacour and Viton.[367]

New Rh(I) catalysts for the *arylation of aldehydes* with good activity at low catalyst loadings were developed.[368] The best results, for the reaction shown in Scheme 44, were obtained by employing the catalysts based on the (*S*)-t-Bu-box ligand.

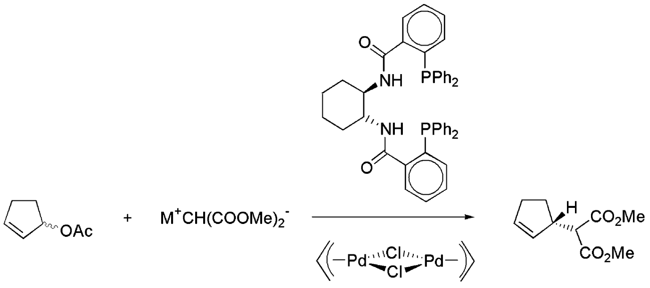
With all other variables being constant, the counterion had a dramatic effect on the reaction rate (Scheme 44). The trend reflects the increasing Lewis acidity of the metal center with weaker coordinating anions.

Allylic substitution reactions are affected by the ion-pairing phenomena. A remarkable example of the anion effect was reported by Togni and co-workers for the allylic amination reaction catalyzed by allyl Pd(II) complexes bearing bidentate P,N-ligands (Scheme 45).[369] It was found that F^- and PF_6^- present either as counterion or added in small amounts as ammonium salts were highly beneficial (ee > 95%) or drastically detrimental (almost no selectivity, ee < 10%), respectively. Other small, hard anions such as BH_4^- or OH^- behaved analogously to F^-.

Scheme 46



Scheme 47



It is known that the racemic substrates oxidatively add to the catalyst with similar rates, affording equal amounts of diastereoisomeric π-allyl complexes with opposite configuration at the allylic termini (Scheme 46).[370] Their reaction with the nucleophile at the position trans to the P-arm would generate opposite product enantiomers. Consequently, fast equilibration rates between the diastereoisomers must be rapidly established in order to obtain high ee's. The authors suggest that different equilibration rates with different anions, either by virtue of ion pairing or, in the case of F^- and BH_4^-, coordination to Pd(II), would be responsible for the anion effect on ee.

When allylic substitution reactions employ anionic entering nucleophiles, ion-pairing effects due to the countercation of the nucleophile become important. These phenomena have been observed in allylic alkylations[371−377]and aminations.[378] For the allylic alkylation reaction shown in Scheme 47, Trost observed a marked dependence of the ee on the nature of the ion pair of the attacking nucleophile.[371]

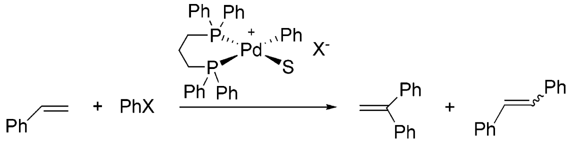
In particular, increasing the size of the countercation (M^+) increases the ee within a homologous series, i.e., within the tetraalkylammonium and alkali metal series (Table 4). On the contrary, the anion that actually bonds to the substrate has a minor effect on ee.

To explain the effect of ion pairing on enantioselectivity, it has been proposed that the leaving group forms an intimate ion pair with the cationic (π-allyl)-palladium intermediate in which it retains some memory of the starting material stereochemistry due

Table 4. Dependence of Enantiomeric Excess on the Nature of Ion Pairs for the Reaction Shown in Scheme 47 (from refs 373 and 374)

M^+	solvent	yield (%)	ee (%)
Me_4N^+	THF	88	41
Bu_4N^+	THF	74	57
Hex_4N^+	THF	92	68
Hex_4N^+	CH_2Cl_2	81	98
Oct_4N^+	THF	74	66
Li^+	THF	75	63
Na^+	THF	77	38
K^+	THF	90	51
Cs^+	THF	76	76
Cs^+	CH_2Cl_2	98	>99

Scheme 48



to the asymmetric configuration of the ion pair.[375] An alternative process in which the ionization of the mismatched enantiomer of substrate is accompanied by the dissociation of one of the P donors has been proposed by Lloyd-Jones to explain the memory effect.[379] The same author studied the alkylation reactions of pivalate with $NaCH(CO_2Me)_2$ in THF catalyzed by Pd complexes of MOP (2-(diphenylphosphanyl)-2′-methoxy-1,1′-binaphthalene) and MAP (2′-(dimethylamino)-2-(diphenylphosphanyl)-1,1′-binaphthalene) ligands and found that they proceed with powerful stereochemical memory effects. The latter were attributed to the rapid capture of the initially formed diastereoisomeric ion-paired complex $[(\pi\text{-cycloalkenyl})Pd(P,C\text{-}L)]X$[380,381] (L = MAP or MOP) by the nucleophile before ion-pair collapse or equilibration occur.[382]

By investigating the allylic alkylation reaction of dienyl acetates as a function of M^+ it was found that the distribution of different regioisomers also depends on the countercation.[383,384,376] Cs^+ and Hex_4N^+, i.e., the cations that were found to afford the highest ee's for the asymmetric reaction shown in Scheme 47, were found to slow the rate of nucleophilic addition relative to the intermediate equilibration and allow the complete equilibration of (π-allyl)palladium intermediates prior to nucleophilic addition.

Finally, Ludwig and Åkermark found that the counterion strongly affects the regioselectivity of the *Heck reaction*.[385] The investigated reaction is reported in Scheme 48. Using DMF as solvent (S), the selectivity for 1,2-diphenylethene was reduced by weakly coordinating anions: 82% for $X^- = OAc^-$, 80% for $X^- = I^-$, 65% for $X^- = OTf^-$, 58% for $X^- = BF_4^-$, 57% for $X^- = PF_6^-$. Minor or no changes were observed in the cis/trans ratio for 1,2-diphenylethene, which was always less than 2/98, depending on the nature of the anion. Consistent with the counterion effect on the selectivity, when the solvent polarity increased (MeCN), arylation at the terminal position decreased, while when the polarity decreased (DMF/CH_2Cl_2 or THF), high percentages (>90%) of 1,2-diphenylethene were obtained. The cationic character of the phenylpalladium species led to an increase in the relative phenylation at the less substituted position, favoring formation of stilbene.

4. Conclusions and Future Perspectives

The principal conclusion of the present review is that ion pairing greatly affects many chemical reactions mediated by ionic transition-metal organometallic compounds. Consequently, the counterion cannot be considered as a mere spectator but rather it is one of the actors in both stoichiometric and catalytic processes involving organometallic salts. The capacity to control anion–cation interactions is key to optimizing yield, chemoselectivity, regioselectivity, and stereoselectivity of chemical processes that, in some cases, are of primary importance for academics as well as chemical industry.

Clearly, the counterion competes with the substrate, which has to be activated, for coordination to the metal center. Consequently, counterions that have a marked tendency to form ion pairs *usually* inhibit chemical reactions mediated by transition-metal salts. In *a few cases* counterions having a greater tendency to form ion pairs favor reactions through associative processes that may occur when the counterion enters into the first coordination sphere of the metal (affording a little thermodynamic stability to otherwise unstable, highly unsaturated systems) or when the counterion interacts with functional groups of the ligands that are directly involved in the transformations.

Ion pairing may also influence stereochemistry, but the trend is usually the opposite of that observed for yield and conversion. Counterions that favor ion pairing *usually* afford higher stereoselectivity even though some examples of the opposite have been observed.

Another important point is the strict interplay between counterions and solvent in determining the effects of ion pairing. The nature of the solvent does not usually alter the scale of counterion tendency to form ion pairs but can flatten or expand the counterion effect. For example, in methanol, where CO/olefin copolymerizations are usually carried out using cationic Pd catalysts, counterions that have a lesser tendency than OTf^- to afford ion pairs are considered weakly coordinating. No relevant changes in reactivity are observed if, for instance, OTf^- or $B(C_6F_5)_4^-$ is used as counterion. On the other hand, in benzene or toluene, where olefin polymerizations catalyzed by metallocenes occur, OTf^- completely inhibits catalysis because it is so much more coordinating than $B(C_6F_5)_4^-$.

If solvents of a similar nature are considered, the tendency to form ion pairs normally decreases when the relative permittivity of the solvent increases. However, it is now clear that the presence of transition-metal organometallic ion pairs is not only limited to low-polarity solvents ($\epsilon_r < 10$) but also significant in solvents with moderate ($10 < \epsilon_r < 20$) to high relative permittivity ($\epsilon_r > 30$). It is not easy to predict the tendency of transition-metal organometallic ion pairs to form in solvents of different nature, even if they have the same relative permittivity. For instance, in studies on some arene ruthenium(II) salts higher percentages of ion pairs were found in protic solvents (2-propanol and methanol) than in aprotic ones that had about the same relative permittivity (acetone and nitromethane).[386] The level of ion pairing in 2-propanol ($\epsilon_r^{20°C} = 19.92$) was found to be comparable to that in methylene chloride ($\epsilon_r^{20°C} = 8.93$).[386]

On the other hand, evidence of aggregates larger than ion pairs in organic solvents with low relative permittivity is increasing.[250,251,386,387] In particular, ion quadruples resulting from the association of two ion pairs can form in such apolar media where the existence of odd aggregates (free ions, ion triples, etc.) is highly improbable. If ion quadruples have enough thermodynamic stability to be significantly present in low-polarity solvents, then it also seems reasonable that neutral compounds can associate in solution into dimeric species. This has recently been demonstrated for arene ruthenium(II) precatalysts for transfer hydrogenation.[388] The possible effects of (1) ion pairing in polar media and (2) aggregates larger than ion pairs and dimeric neutral adducts in nonpolar solvents on the reactivity of ionic transition-metal organometallic compounds are almost completely unexplored and will presumably be addressed in the future. NOE and PGSE NMR measurements will surely play a key role in identifying and structurally characterizing ion pairs and ionic or neutral intermolecular adducts, in general. They will provide a clearer picture of the relative orientation of the noncovalently bonded units (NOE)[31−33] in solution and their aggregation level (PGSE).[32−34] Kinetic investigations will be required to determine if and how such intermolecular adducts affect any parameter of the chemical reactions.

Finally, many scientists, motivated by ecological and economic concerns, are now seeking new "green" reaction media that can be used as an alternative to organic solvents. Encouraging results have been obtained with ionic liquids,[389−391] supercritical CO_2,[309,392] and fluorous biphasic systems[393−397] used as media for reactions catalyzed by transition-metal organometallic complexes. The chemical nature and physical−chemical properties of such media are such that ionic aggregation phenomena should be present and significantly alter the chemical reactivity of the catalysts.

In conclusion, all the premises seem to indicate that soon the ion-pairing phenomenon will assume an even more central position in transition-metal catalysis carried out in both organic solvents and alternative "green" media.

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6. Abbreviations

$BARF^-$	$B(3,5\text{-}(CF_3)_2\text{−}C_6H_3)_4^-$
bdpp	2,4-bis(diphenylphosphino)pentane
$biimH_2$	2,2-biimidazole
binap	(*R*)- or (*S*)-2,2′-bis(diphenylphosphino)-1,l′-binaphthyl
biphemp	6,6′-dimethyl-2,2′-bis(diphenylphosphino)-1,1′-biphenyl
bipy	2, 2′-bipyridine
^{t}Bu-box	2,2′-isopropylidenebis[(4*S* or *R*)-4-*tert*-butyl-2-oxazoline]
^{t}Bu-pybox	2,6-pyridinebis[(4*S* or *R*)-4-*tert*-butyl-2-oxazoline]
CGC	$Me_2Si(\eta^5\text{-}Me_4C_5)(^tBuN)$
COD	cyclooctadiene
Cp	cyclopentadienide anion
Cp^*	pentamethylcyclopentadienide anion
Cy	cyclohexyl
depe	1,2-bis(diethylphosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
DMF	dimethylformammide
dmphen	2,9-dimethyl-1,10-phenanthroline
DMSO	dimethyl sulfoxide
dpa	bis-2-pyridylamine
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
dppp	1,2-bis(diphenylphosphino)propane
ϵ_r	relative permittivity
Flu	fluorenyl
ILs	ionic liquids
Ind	indenyl
ISIP	inner-sphere ion pair
LLDPE	linear low-density polyethylene
MAO	methyl-aluminoxane
MAP	2′-(dimethylamino)-2-(diphenylphosphanyl)-1,1′-binaphthalene
Me_4en	tetramethylethylendiamine
MOP	2-(diphenylphosphanyl)-2′-methoxy-1,1′-binaphthalene
MS	molecular sieves
NBD	norbornadiene
NTf_2^-	$N(CF_3SO_3)_2^-$
OSIP	outer-sphere ion pair
OTf^-	$CF_3SO_3^-$
$OTol^-$	$p\text{-}CH_3\text{−}C_6H_4\text{−}O^-$
OTs^-	$p\text{-}CH_3\text{−}C_6H_4\text{−}SO_3^-$
PBA^-	$FAl(2\text{-}C_6F_5C_6F_4)_3^-$
PBB	$B(2\text{-}C_6F_5C_6F_4)_3$
PGSE	pulsed field gradient spin−echo
Ph-box	2,2′-isopropylidenebis[(4*S* or *R*)-4-*tert*-phenyl-2-oxazoline]
phen	phenanthroline
py	pyridine
RCM	ring-closing metathesis
$scCO_2$	supercritical CO_2
T_1	longitudinal relaxation time
THF	tetrahydrofuran
TOF	turnover frequency
Tp	tris(pyrazolyl)borate

7. References

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