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Kinetic Evaluation of Ligand Hemilability in Transition Metal Complexes

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Hemilability is the property of hybrid ligands to undergo a reversible metal chelate opening process by rupture of the weakest coordinative bond, yielding a coordinatively unsaturated complex. While experimental evidences of the process rely on the observation of fluxional behavior in the metal complex or on the spectroscopic detection of the species with different chelating bites, various effects are speculatively attributed to hemilability. In this review, this property is discussed in the context of its effects on the rate and mechanisms of bimolecular reactions. Examples of kinetics performed on ligand substitution, oxidative addition, alkyne tautomerization, and dehydrobromination reactions illustrate that the ligand hemilability process can be detected through simple kinetic analyses and can be quantitatively evaluated with respect to alternative reaction pathways. Since this concept affects various fields of chemistry, e.g. catalysis, supramolecular chemistry, molecular sensing, and materials, the kinetic approach may assist the rational design of ligands with the expected properties.

1. Introduction

Bidentate or polydentate ligands characterized by the presence of different donor atoms (X) bind to metal centers forming complexes with one or more metallacyclic rings. Because of the different strengths of the metal–heteroatom bonds, the metal complex may undergo a ring-opening process by the preferential rupture of the weakest coordinative bond. When the ligand free arm is easily recoordinated, the process becomes reversible (Scheme 1).[1,2]

Scheme 1. Hemilability of a bifunctional ligand X^1–X^2.

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This feature, defined as hemilability, arises from the mixed bonding characteristics of hybrid ligands. It should be emphasized that while the term hybrid identifies the bifunctional structure of the ligand, the term hemilabile refers to the property of undergoing selective metal-donor bond breaking in the corresponding metal complex.[3]

Hemilability has been discussed in excellent reviews written in the last few years, which have focussed on definition and properties, and have described either the different classes of ligands according to the donor atoms involved in the chelate[1] or specific ligand systems with hemilabile character.[2] The use of potentially hemilabile ligands in catalysis has also been reviewed.[4]

The expression "hemilabile ligands" was first formulated by Jeffrey and Rauchfuss,[5] following from the early examples of transition metal complexes with bifunctional ligands.[6] These investigations were motivated by the expectation that bifunctional, for instance phosphane-amine or phosphane-ether, ligands would bind strongly enough to form chelate complexes but would readily dissociate the hard (N or O) ligand component in order to create a vacant site for substrate binding. Since then, the transition metal

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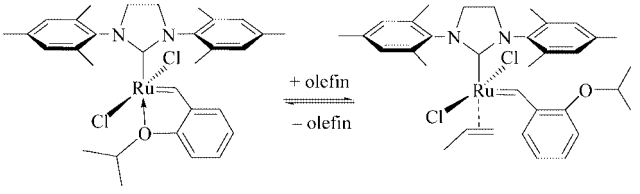
coordination chemistry of hemilabile ligands has expanded impressively and, while the initial motivation still remains the essential leitmotiv, hemilability is now considered a useful approach to induce molecular activation and create new systems for homogeneous catalysis and functional materials. Ligand design, synthesis of transition metal complexes with enhanced reactivities, biomimetic modelling, enantioselective catalysis, supramolecular coordination chemistry, and sensing of small molecules are some of the topics which have been affected by this concept.[1,2]

As a striking example of the impact that may arise from the strategic use of hemilability in catalysis, it is worth mentioning the case of the Hoveyda–Grubbs catalysts, which have significantly expanded the application profile of olefin metathesis in organic chemistry,[7] a subject now at the forefront of the chemical scenario.[8]

The key feature of these ruthenium complexes is the presence of the bidentate *o*-isopropyloxybenzylidene ligand, which binds to ruthenium through both the carbene functionality and the ethereal oxygen atom. When in action, the molecule allows the coordination of the olefinic substrate by substitution of the bound oxygen moiety (Scheme 2). On the other hand, the ethereal group stabilizes the complex when dormant in solution, thus reducing the decomposition pathways that occur more easily in the corresponding benzylidene phosphane complexes. In addition, this stabilizing effect allows for the recovery of the complex at the end of the reaction by column chromatography.

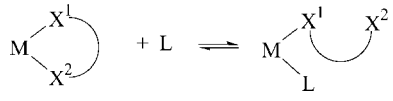


Scheme 2. Activation of a Hoveyda–Grubbs metathesis catalyst by substitution of the oxygen-bound chelate by an olefin.

The combination of a strong, substitutionally inert, and a weak, substitutionally labile, donor atom within the ligand molecular frame is the rationale for obtaining hemilability, which results from the relative metal–donor bond strengths in the complex. In fact, the strong bond ensures stability to the system when monocoordinated, while the weak bond allows for ring opening and closing of the metallacycle. Although it can be generically stated that the net effect arises from a combination of steric and electronic properties, it is nowadays difficult to predict a hemilabile character because of the variety of factors coming into play, for instance relative donicity toward a specific metal ion, interplay of soft and hard donor properties, ring size of the chelate, influence of ancillary ligands, ring substituents, solution effects, etc. The net outcome is that the game of hemilability is ruled by subtle and elusive energy differences, still difficult to control. It is with regard to this that an understanding of this property at a kinetic level may assist a rational design of ligands and complexes with the expected functions.

2. Properties of Hemilabile Complexes

The most significant feature exhibited by transition metal complexes of bifunctional ligands with hemilabile character is a fluxional behavior arising from the dissociation and rebinding of the weakly bonding moiety by intramolecular ligand exchange processes (Scheme 1).[9] The exchange involves a transient species which is either coordinatively unsaturated if formed from a dissociative pathway or saturated by solvent or by a counterion molecule. The intimate mechanistic features of fluxional processes of hemilabile systems have been documented in detail and are understood in depth, with a corresponding development of appropriate spectroscopic techniques and evaluative criteria.[1] A second important feature that may arise from hemilability in the complex is the facility to undergo ligand displacement reactions with external molecules, in which a monodentate ligand, a small molecule, or an organic substrate coordinates to the metal ion via the door opened by the substitutionally labile group. Reversible decoordination followed by chelate formation corresponds to hemilability (Scheme 3).[10]



Scheme 3. Substitution reaction in the complex with a hemilabile ligand.

This property moves hemilability from a strictly intramolecular process toward a bimolecular phenomenon, with the obvious implications for molecular sensing, supramolecular design, and enhanced catalytic activity. However, in addition to the isolation of the corresponding substituted complexes and the qualitative observation of intriguing effects in stoichiometric or catalytic reactions, attributed to hemilability, the reaction mechanisms of transition metal complexes with bifunctional ligands in bimolecular reactions have not been studied extensively from the point of view of hemilability. In this regard, since the ring opening represents an easy access to a structural isomer of the chelate complex with altered reactivity, kinetic studies can provide an additional criterion for the identification of hemilability and a quantitative evaluation of its role along the reaction coordinate. In fact, it is within the exclusive realm of chemical kinetics that many reactive species are detected and evaluated, specifically when these are elusive toward any spectroscopic detection.

3. Kinetic Studies

Although the mechanisms of metal-chelate ring-opening processes of polydentate ligands have been studied extensively from a kinetic viewpoint,[11] the first article dealing

with the reaction of a metal complex of a bifunctional ligand was described by Knebel and Angelici in 1974.[12] The purpose of the work was to study the effect of the chelate ring structure on the rates of ring opening for reactions in which the product contained a bidentate ligand in the monocoordinated mode. This effect was obtained using a series of bifunctional ligands $Ph_2P(CH_2)_2NR_2$ (R = Me, Et, H) and $Ph_2P(CH_2)_3NMe_2$ (P-N) in the reaction of the complexes $[M(CO)_4(\kappa^2\text{-}P,N)]$ (**1**) with carbon monoxide, by taking advantage of the different binding abilities of a relatively inert phosphorus-donor and a labile nitrogen-donor atom. In fact, the substitution reactions of analogous bidentate N–N, S–S, CS–CS, As–As ligands in Cr, Mo, and W complexes had always proceeded with complete displacement of the bidentate ligand, affording no experimental evidence for the ring-opened monodentate species.

The reactions of complexes **1** with CO to give $[Mo(CO)_5(\kappa^1\text{-}P,N)]$ (**2**) were found to be first order in the metal complex and in CO, and second order overall. Such a relatively simple kinetic behavior is in agreement with at least two mechanisms, implying either direct attack of CO on the starting complex or reversible dissociation of the N-donor group followed by CO attack on the five-coordinate intermediate $[Mo(CO)_4(\kappa^1\text{-}P,N)]$ (**3**), this latter case being outlined in Scheme 4.

With the assumption that k_{-2} is negligible, application of the steady-state approximation to the open intermediate yields the rate expression (1) (L = CO), which implies a first-order dependence on the CO concentration in the reasonable case that $k_{-1} >> k_2[CO]$. This is in agreement with the observed linear dependence of the k_{obs} values on the concentration of carbon monoxide.

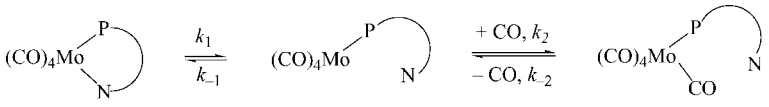
$$k_{obs} = \frac{k_1 k_2[L]}{k_{-1} + k_2[L]} \quad (1)$$

Since the second-order behavior does not give direct evidence for the existence of an intermediate along the reaction pathway, discrimination between the two mechanisms was possible from the observation that the reactivity, expressed by k_{obs}, became independent of [CO], hence zero order, upon performing the reaction in the presence of trifluoroacetic acid. This is because of the fast protonation of the nitrogen atom of the intermediate, which prevents any possibility of ring closing, resulting in the starting complex, and allows rapid trapping of the five-coordinate species by CO to give the product $[Mo(CO)_5(\kappa^1\text{-}P,NH^+)]$ (**4**) (Scheme 5).

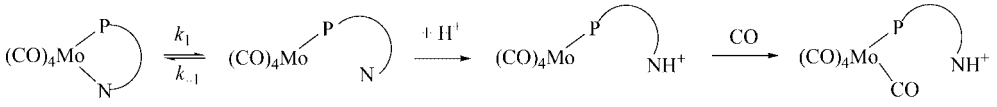
Under these conditions, the rate is only limited by the value of k_1. Therefore, the kinetics in the presence of acid allowed the rate constant of the ring-opening process to be obtained, i.e. the Mo–N bond breaking, being $k_{obs} = k_1$. The operation of a purely dissociative mechanism yielding the "open arm" five-coordinate intermediate $[Mo(CO)_4(\kappa^1\text{-}P,NH^+)]$ was supported from the evidence of zero-order dependence on [CO] for the substitution reactions of corresponding monodentate N-ligand complexes under analogous conditions, with a lack of rate enhancements in the presence of acid. The k_1 values were found to increase by an order of magnitude with the bulkiness of the N substituents (H = Me > Et) in the five-membered chelate complexes $[Mo(CO)_5(\kappa^2\text{-}P,N)\text{-}Ph_2P(CH_2)_2NR_2]$, while a 50-fold rate increase was observed in the corresponding six-membered chelate (R = Me) as the result of the larger release of ring strain in the transition state.

Having established from kinetic data the hemilabile character of the P–N complexes, the k_{obs}/[CO] values in the absence of acid yield k_1k_2/k_{-1}, from which the ratio k_2/k_{-1} can be derived. This value represents the competition for the intermediate species between ring closure and reaction with CO. The data indicated that ring closure (k_{-1}) is approximately one thousand times faster than the uptake of CO (k_2) and that the five-coordinate intermediate is insensitive to the nature of the N donor group or to the size of the incipient ring. Thermodynamic parameters in addition to kinetic data were determined for the reactions of complexes $[M(CO)_4(\kappa^2\text{-}P,N)]$ with carbon monoxide, P–N being a series of *o*-phosphanepyridyl ligands.[13]

These articles represented the most informative kinetic studies on the reaction of a bifunctional system proceeding by substitution of the weakly bound donor moiety with an external ligand, and showing in quantitative terms the competition of the monodentate intermediate between ring closure (k_{-1}) and the bimolecular reaction (k_2). In these cases, (i) the only reactive pathway is provided by chelate-ring opening, and (ii) the incoming ligand does not participate in further reactions. The backward reaction can be suppressed by trapping the ligand free arm into a group that is



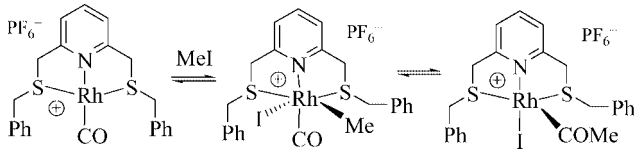
Scheme 4. Mechanism of the substitution reaction of complexes $[M(CO)_4(\kappa^2\text{-}P,N)]$ with carbon monoxide.



Scheme 5. Mechanism of the substitution reaction of complexes $[M(CO)_4(\kappa^2\text{-}P,N)]$ with carbon monoxide in the presence of acid.

unsuitable for rebinding, such as by protonation. Kinetics of the acid-promoted chelate-ring opening have often been reported for a variety of transition metal complexes with hybrid ligands.[14]

The case of competitive reactivity of the chelate molecule and of the open monodentate species has emerged during our studies on the reaction of the rhodium(I) carbonyl complex [Rh(κ^3-L)(CO)]PF_6 (**5**) with methyl iodide, in which L is the tridentate NS_2 ligand 2,6-bis(benzylthiomethyl)pyridine binding to rhodium in a square-planar geometry through a *trans*-dithioether coordination. The complex, as well others from the same family containing the NS_2 ligand set, exhibits a fluxional behavior at room temperature arising from configurational inversion at the stereogenic sulfur centers and occurring by the debinding and rebinding of the sulfur donor groups.[15] The reaction of **5** with methyl iodide proceeds by consecutive oxidative addition–carbonyl insertion reactions, which is typical of many monodentate and bidentate rhodium(I) carbonyl complexes, and results in the isolation of the final Rh^{III} acyl complex [Rh(κ^3-L)(COMe)I]PF_6 (**6**) (Scheme 6).[16]



Scheme 6. Consecutive oxidative addition–migratory insertion steps in the reaction of complex **5** with methyl iodide.

Rate studies on the oxidative addition step, giving the intermediate Rh^{III} methyl species [Rh(L)(CO)(Me)I]PF_6 (first stage in Scheme 6), have been carried out in solvents of different polarity. The data indicated the presence of two parallel routes, one involving the four-coordinate complex **5**, and one involving a rearranged form of this complex. This evidence emerged from a relatively simple kinetic behavior expressed from the plots of k_{obs} vs. the concentration of MeI in acetonitrile, acetone, and dichloromethane (Figure 1), which showed a linear dependence on MeI and a nonzero intercept on the *y* axis. While the linear dependence identifies a reaction route characterized by the presence of both the rhodium complex and the electrophile in the rate-determining step, overall second-order, the nonzero intercept indicates an alternative pathway that is first order in the rhodium complex but zero order in MeI, in which the electrophile comes into play after the rate-limiting step.

The concept arising from the observed kinetic behavior, represented graphically in Scheme 7, corresponds to the case of a generic substrate S that can react as such (second-order route) or in the form of a more reactive species S* (first-order route) to give the same final product P.[17] The transient molecule S* is either captured by the reagent R with rate k_2 or transformed back into the original complex with rate k_{-1}. Since both of these steps are faster than its formation, this rearranged form of the starting material is subject only to kinetic but not to spectroscopic detection.

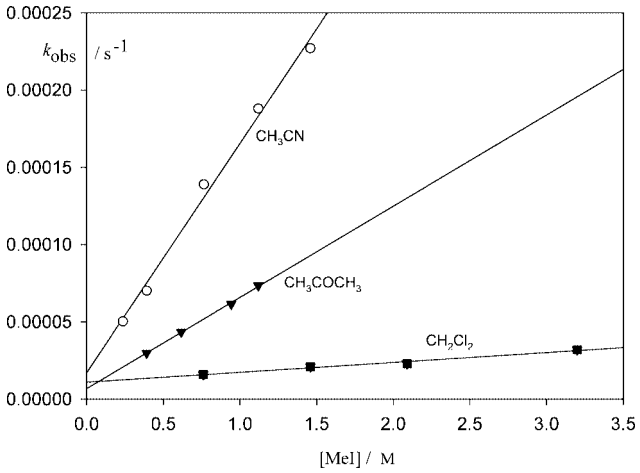
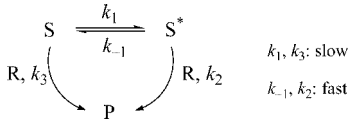


Figure 1. Plot of k_{obs} values for the oxidative addition of methyl iodide to complex [Rh(κ^3-L)(CO)]PF_6 (**5**) [L = 2,6-bis(benzylthiomethyl)pyridine] in acetonitrile, acetone, and dichloromethane, at 31 °C.



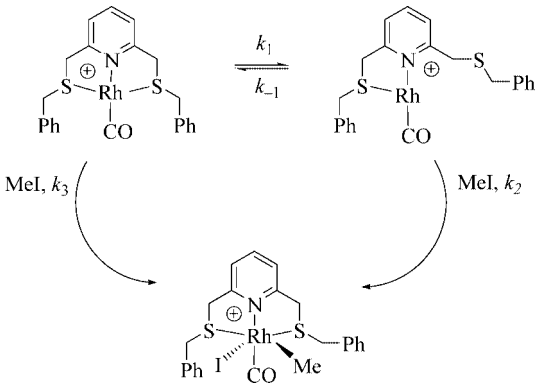
Scheme 7. Schematic representation of parallel first- and second-order routes in the reaction of substrate S with reagent R to give product P.

The kinetic analysis of Scheme 7 yields Equation (2) from the application of the steady-state approximation to the intermediate S*.

$$k_{obs} = k_1 + k_3[R] \quad (2)$$

At this stage, the next step takes us from facts to interpretation. Although various speculations can be done as to the origin of a highly reactive species arising from the tridentate complex, logic and indirect evidences suggest that hemilability of the NS_2 ligand plays a role in the pathway which is zero order in MeI. In fact, the fluxional character of this system indicates the presence of an equilibration process specifically involving the methylene groups of the ligand. The dissociation of one ligand arm by rupture of the sulfur–rhodium bond would provide a 14 electron and coordinatively unsaturated complex, expected to be highly reactive toward the electrophilic methyl iodide. The mechanistic version of Scheme 7 in terms of the structural features of complex **5** is represented in Scheme 8.

The intercept on the *y* axis represents the rate of formation of the κ^2-*N*,*S* complex (k_1), which is slower than the reaction with MeI (k_2) or the rebinding of the thioether group (k_{-1}). Analysis of the first-order rate constants, k_1, reveals a small dependence on the nature of the solvent, which is typical for a limiting-ligand dissociative step from a platinum group metal.[18] This is in sharp contrast with the values of the second-order rate constants, k_3, which vary by a factor of 20 between the polar solvent acetonitrile and the less polar dichloromethane, implying separation of charge in the attack of rhodium to the methyl group during



Scheme 8. First (k_1: slow; k_2: fast) and second-order (k_3) routes for the reaction of complex **5** with methyl iodide.

the slowest step, clearly associated with methyl iodide bond rupture.[19] Values of k_1 and k_3, along with the ratios $k_1/([MeI]\times k_3)$, which represent the relative weight of the two pathways at different concentrations of methyl iodide, are reported in Table 1.

Table 1. Values of rate constants for the reaction of complex $[Rh(\kappa^3\text{-}NS_2)(CO)]PF_6$ (**5**) with MeI in different solvents (31 °C).

Solvent	ε[a]	k_1 / s^{-1}	k_3 / $M^{-1}s^{-1}$	$k_1/k_3\times$[MeI][b]	$k_1/k_3\times$[MeI][c]
CH_2Cl_2	9.1	1.1×10^{-5}	6.4×10^{-6}	3.4	1.7
Me_2CO	20.7	6.7×10^{-6}	5.9×10^{-5}	0.23	0.11
MeCN	37.5	1.7×10^{-5}	1.4×10^{-4}	0.24	0.12

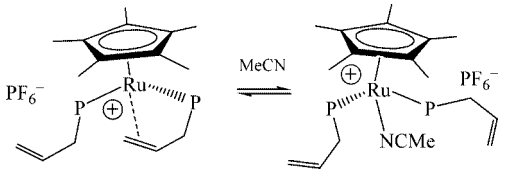
[a] Dielectric constant. [b] c = 0.5 M. [c] c = 1.0 M.

In addition to the fluxional character of complex **5**, a convincing indirect evidence that supports the interpretation based on hemilability is that the reactions of rhodium(I) complexes with MeI, as well as those of platinum group metal complexes in general, display kinetic plots characterized by linear dependence on the electrophilic concentrations and zero intercepts on the y axis, indicating the availability of only one reactive route.[20] Moreover, significant solvent effects are observed in these reactions, which proceed by means of an SN2 pathway, in contrast to the lack of any correlation with the solvent donor ability in the clockwise route (k_1) of Scheme 8. A kinetic pattern showing a nonzero intercept was found once in the case of the rhodium(I) complex [Rh(cupf)(CO)(PPh_3)], containing the bidentate anionic ligand *N*-nitrosophenyloxyamine PhN(NO)-O^- (cupf).[21] In this case, the presence of mixed first- and second-order pathways was interpreted as the result of an intramolecular rearrangement of the complex induced by the attack of solvent and involving a change of the coordinative mode of the bifunctional ligand, thus generating a reactive species in equilibrium with the starting material. Linear plots with a positive intercept on the y axis and described by an equation formally identical to 2 are found for equilibrium processes in which substrate and product remain spectroscopically observable at the end of the reaction. Such a case can be found in the oxidative addition of methyl iodide to the iodocarbonyl complex [Rh(CO)-$(L_{Me})_2$I] containing the N-heterocyclic carbene 3,5-dimethylimidazoline-2-ylidene (L_{Me}) ligand.[22] It is usually easy to differentiate between parallel and reversible processes from the final spectra.

An interesting kinetic pattern was observed for the reaction of complex **5** in methanol, in which the k_{obs} values as a function of [MeI] exhibit a saturation behavior, i.e. tend toward a limiting value with increasing concentration of the electrophile.[15] This situation corresponds to the formation of a reactive species in equilibrium with the substrate, often induced by solvent, with comparable values of the forward reaction with the reagent and of the step leading back to the starting material.[23] The kinetic analysis on treatment of the intermediate under steady-state conditions yields the same Equation (1) (L = MeI) which was derived from the case of the P–N complexes **1**, the saturation effect here arising from the similarity of k_{-1} and k_2. Although the separate values cannot be determined, the analysis yields the ratio k_{-1}/k_2 and the rate constant k_1. In the present case, these correspond to 1.8, and to the same rate of methyl iodide attack and ring closure at [MeI] = 1.8 M, and to 1.7×10^{-4} s^{-1}, respectively. Therefore, it appears that in methanol the preferred route is the one involving a methanol solvated bidentate κ^2-*N*,*S* complex, along the clockwise pathway of Scheme 8, with no evidence for the second-order route. For the sake of comparison with the reaction of the bidentate P–N complexes **1** with carbon monoxide, the ratio of ring closure to CO attack (k_{-1}/k_2) from the five-coordinate intermediate [Mo(CO)$_4$(κ^1-*P*,N)] is about one thousand at the conditions employed ([CO] = 5×10^{-3} M, 69.6 °C in 1,2-dichlorobutane), while extrapolation at a concentration of carbon monoxide of about 1 M yields a similar ratio to the one observed for the reaction of **5** in methanol.

We have performed rate studies on the second step of the reaction of complex **5** with MeI (Scheme 6), which is the migratory insertion process giving the isolable product $[Rh(\kappa^3\text{-}L)(COMe)I]PF_6$ (**6**). The reaction is characterized by no rate dependence on the MeI concentration as expected for an intramolecular process, and we had no experimental evidence for any role of hemilability. However, in light of more information now available about the reactivity of rhodium(I) complexes with tridentate ligands, it appears that the presence of harder donor atoms or of less flexible ligand structures inhibit the migratory-insertion step. In fact, the oxidative addition of MeI stops at the methyl carbonyl rhodium(I) species for [N–N–N] complexes of 2,6-bis(oxazoline)pyridine,[24] bis(imino)carbazolide,[20q] or of [C–N–C] 2,6-bis(alkylimidazol-2-ylidene)pyridine ligands,[20r] while it proceeds to spontaneous migratory CO insertion for rhodium(III) complexes of hybrid [P–N–O] or [N–O–N] ligands.[25–26] The contribution of the association/dissociation process of a dangling ligand arm in carbonylation reactions was proposed for rhodium(I) complexes of mixed phosphane-phosphite or phosphane-ether bidentate ligands.[2a,c,20e,27]

Analogous cases of parallel first- and second-order kinetics were found in the study of the reactions of ruthenium complexes coordinated by the hybrid allylphosphane ligand, $Ph_2PCH_2CH=CH_2$, which acts in a bidentate fashion through the coordination of both the phosphorus atom and the allylic double bond to the metal center. Mixed alkenyl-phosphane or alkynyl-phosphane ligands have attracted a large interest because of the potential hemilabile character in the corresponding transition metal complexes.[28] The Cp* ruthenium complex $[Ru(\eta^5\text{-}C_5Me_5)\{\kappa^1\text{-}P\text{-}Ph_2PCH_2CH=CH_2\}\{\kappa^3\text{-}P,C,C\text{-}Ph_2PCH_2CH=CH_2\}][PF_6]$ (**7**), containing two molecules of allylphosphane in different, monodentate and bidentate, coordinative modes, reacts with nucleophiles (L = NaNCS, CO, PhC≡CH) yielding corresponding neutral or cationic complexes in which both molecules are monodentate. In addition, complex **7** reversibly binds acetonitrile (Scheme 9).[29]



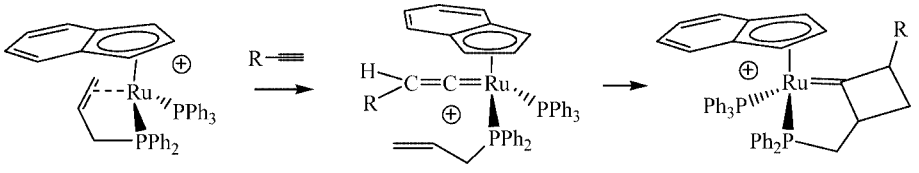
Scheme 9. Reversible coordination of acetonitrile to complex **7**.

These reactions occur readily by substitution of the coordinated alkenyl group, which forms a weaker bond to the metal than the phosphorus donor. The specific hemilabile character of allylphosphane was suggested by a fluxional behavior exhibited by complex **7** at room temperature, and confirmed by variable temperature NMR spectroscopic studies. Substitution reactions and dynamic properties have been interpreted as the result of a dissociative mechanism involving binding and rebinding of the allylic moiety, typical of hemilability. In analogy, the cationic indenyl complexes $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)\{\kappa^3\text{-}P,C,C\text{-}Ph_2PCHRCH=CH_2\}]PF_6$ (**8**, R = H; **9**, R = Me) containing allylphosphane derivatives undergo substitution reactions of the allylic double bond by nitriles (MeCN, BzCN) or by sodium azide yielding the corresponding monodentate cationic or neutral complexes.[30] In contrast with the behavior of the Cp* complex **7**, dynamic processes were not observed in the ^1H or ^{31}P NMR spectra of complexes **8** or **9**, performed between –90 and 50 °C. Because of their rich chemistry, rate studies were performed on the reactions of these indenyl complexes.

In particular, complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3\text{-}(P,C,C)\text{-}PPh_2(CH_2CH=CH_2)\}(PPh_3)][PF_6]$ (**8**) reacts with terminal alkynes RC≡CH (R = Ph, *p*-MeC_6H_4, $SiMe_3$) yielding bicyclic cyclobutadienylidene compounds.[31] This reaction stems from the action of the allylphosphane ligand, which first decoordinates the allylic double bond allowing the incoming alkyne to π-coordinate to ruthenium and then undergoes an unprecedented [2+2] cycloaddition with the tautomerized vinylidene moiety (Scheme 10). The reaction is highly diastereoselective yielding only one isomer of the bicyclic derivative, which contains three stereogenic centers.

In the case of aryl alkynes, the intermediate vinylidene species, observable by ^{31}P NMR spectroscopy, were also independently prepared from the corresponding alkynyl derivatives and shown to proceed under thermal activation to the same bicyclic products. In addition to the novelty of such a [2+2] cycloaddition occurring smoothly just above room temperature, the process appears peculiar among those of complexes with hybrid ligands since it involves both a transformation of the alkyne at the metal center and its further reaction with the dissociated arm of the bifunctional molecule.

Although the first step of this process, i.e. the formation of the vinylidene intermediates, is associated with a change of the binding mode of the allylphosphane ligand from κ^3-*P,C,C* to monodentate κ^1-*P* coordination, a case of hemilability cannot be identified due to the lack of fluxional behaviour. Kinetic experiments were performed by ^{31}P NMR spectroscopy for the formation of the vinylidene species from complex **8** and the aryl alkynes *p*-$XC_6H_4C{\equiv}CH$ (X = H, Cl) in chloroform-*d* solution.[32] The reactions were found to be first order in **8** and the values of k_{obs} were obtained at different concentrations of the alkynes. Figure 2 shows the corresponding plots. Analogous to the results obtained for the rhodium complex **5**, the graph reveals finite intercepts on the *y* axis and points to the mechanistic hypothesis of Scheme 7, which when adapted to the structural features of complex **8** yields Scheme 11. In this case the positive values of the intercepts on the *y* axis represent the rate of dissociation of the allylic double bond from ruthenium (k_1). These were found to be $k_1 = 9(\pm2.5)\times10^{-5}\ s^{-1}$ for phenylacetylene and $7(\pm1.5)\times10^{-5}\ s^{-1}$ for *p*-chlorophenylacetylene, corresponding to the rate of formation of the vinylidene species $[Ru(\eta^5\text{-}C_9H_7)(=C=CHC_6H_4\text{-}p\text{-}X)\{\kappa^1\text{-}(P)\text{-}PPh_2(CH_2CH=CH_2)\}(PPh_3)]^+$, existing in equilibrium with the chelate complex. It is worth mentioning that a chelate complex analogous to **8** coordinated by the homoallylphosphane ligand $PPh_2(CH_2CH_2CH=CH_2)$ is inert to-



Scheme 10. Reaction of complex **8** with terminal alkynes.

ward reactions with either nitrile or alkynes.[28] This information indicates that enlarging the chelate by one additional methylene group in the carbon chain imparts greater stability to the ring and to the ruthenium–olefin bond, which does not undergo either spontaneous or induced ring opening.

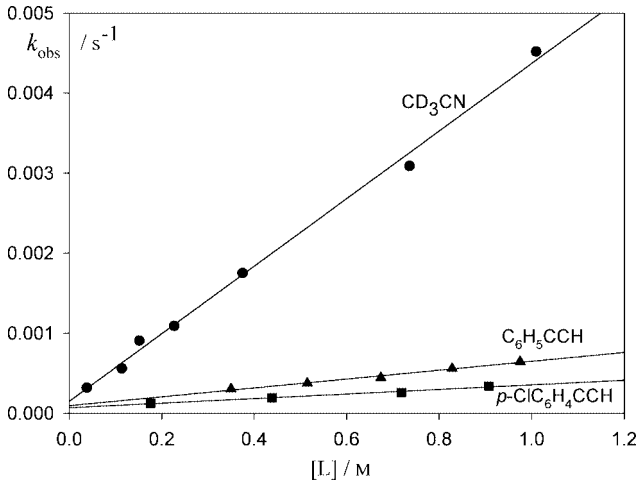
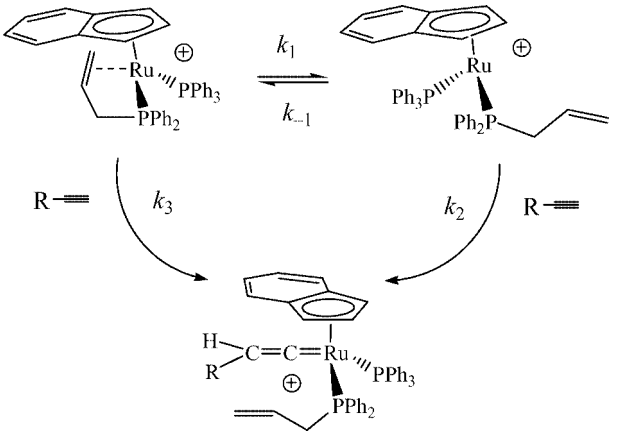


Figure 2. Plot of k_{obs} values for the substitution reaction of complex $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^3\text{-}(P,C,C)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][PF_6]$ (**8**) with CD_3CN (●), compared with the k_{obs} values for the reactions with PhC≡CH (▲) and p-$ClC_6H_4C{\equiv}CH$ (■), in [D_1]chloroform at 38.1 °C.

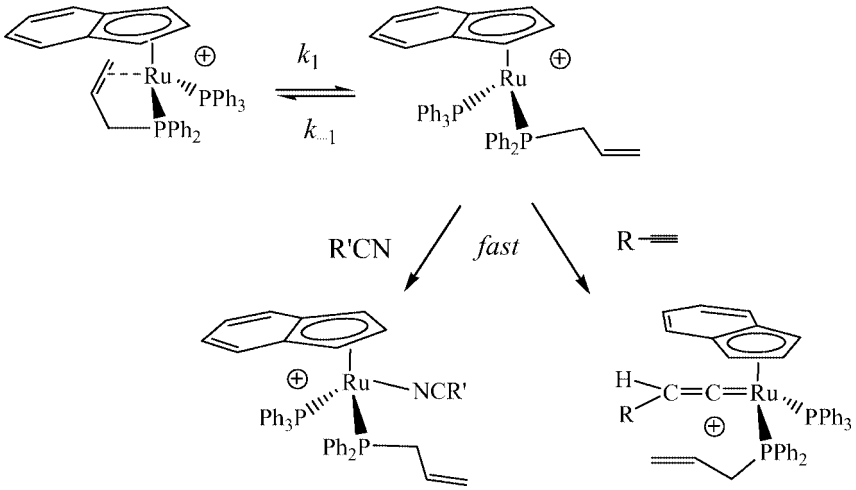


Scheme 11. Direct SN2 attack of the alkyne at complex **8** (k_3, slow) or at the transient $[Ru(\eta^5\text{-}C_9H_7)\{\kappa^1\text{-}(P)\text{-}PPh_2(CH_2CH{=}CH_2)\}(PPh_3)][PF_6]$ (k_2, fast).

With regard to the mechanistic analysis presented for the reaction of complex **5**, there is an additional feature of relevance in the concept of kinetic detection of hemilability. In fact, the rate data in the case of the NS_2 rhodium complex $[Rh(\kappa^3\text{-}L)(CO)]PF_6$ were obtained for the reaction with the same MeI in different solvents, while here different alkynes have been made to react with the indenyl ruthenium complex. The zero-order dependence on the alkyne implicit in the finite y intercept and the observation of Scheme 11 points out that k_1 values must be independent not only of the concentration of the alkyne but also of its nature, since the alkyne is supposed to interact with the ruthenium complex after the rate-determining dissociation of the allylic double bond. In agreement with this consideration, the values of the intercept on the y axis obtained from phenylacetylene and p-chlorophenylacetylene are the same within experimental error of the measurements. In line with the basic principle of chemical kinetics for which information is attainable only up to the rate-limiting step along the reaction coordinate, the rate of dissociation of the weakest bond of the hybrid ligand is not affected by the evolution of the resulting intermediate. In contrast, the values of the second-order rate constants obtained from the slopes of the linear plots, which are $k_2 = 5.5(\pm0.4)\times10^{-4}$ for phenylacetylene and $2.8(\pm0.3)\times10^{-4}$ $M^{-1}s^{-1}$ for p-chlorophenylacetylene, depend on the nature of the alkyne interacting with the metal complex in the slowest step of this pathway. In particular, the smaller value for the p-chloro derivative indicates that an electron-withdrawing ring substituent reduces the electron density on the triple bond and its reactivity toward the ruthenium center.

The concept that the rate of formation of a monodentate intermediate arising from ring opening must be independent of the concentration and nature of the reagent found a further example in the reactions of complex **8** with nitriles (L), proceeding quantitatively to the formation of the substituted complexes $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)\{\kappa^1(P)\text{-}Ph_2PCH_2CH{=}CH_2\}(L)]PF_6$ (L = MeCN, BzCN),[30] differently from that of the equilibrium observed for the bisallyl Cp* complex **7** (Scheme 9). The kinetics for the reaction with [D_3]acetonitrile exhibited mixed first- and second-order routes, with the second-order rate constant $k_2 = 4.2(\pm0.1)\times10^{-3}$ $M^{-1}s^{-1}$, in agreement with a larger nucleophilic character of a nitrile with respect to an arylalkyne. In contrast, the first-order rate constant $k_1 = 1.5(\pm0.6)\times10^{-4}$ s^{-1} was within experimental error of the values obtained from the reactions with p-$XC_6H_4C{\equiv}CH$ (X = H, Cl). Therefore, because of the nature of k_1 its value is independent of the reaction in which the coordinatively unsaturated intermediate becomes involved, i.e. of its final destiny. This concept is represented graphically in Scheme 12.

As previously pointed out, consistent circumstantial evidence should assist the proposal of a reaction mechanism, especially when highly reactive or spectroscopically undetectable species are involved. The possibility of an intermediate arising from the dissociation of PPh_3 instead of the allylic double bond was excluded by the observation that the rate of the reaction of complex **8** with phenylacetylene was not depressed in the presence of a large excess of the monodentate phosphane. In addition, the attribution of the first-order pathway to a rate-limiting η^5-η^3 shift of the indenyl ring can be excluded from the fact that substitution reactions of indenyl complexes exhibit second-order behavior.[33] The substitution reaction in the indenyl complex is first-order overall when the rate-determining dissociation of another ligand generates a 16-electron coordinatively unsaturated species and the free ligand, the indenyl group remains η^5-bound.[34] What occurs in the case of complex **8** is exactly the intramolecular version of this phenomenon,



Scheme 12. The reactivity of complex [Ru(η^5-C_9H_7){κ^3-(*P*,*C*,*C*)-$PPh_2(CH_2CH{=}CH_2)$}(PPh_3)][PF_6] is dominated by the rate of dissociation of the allylic double bond (k_1).

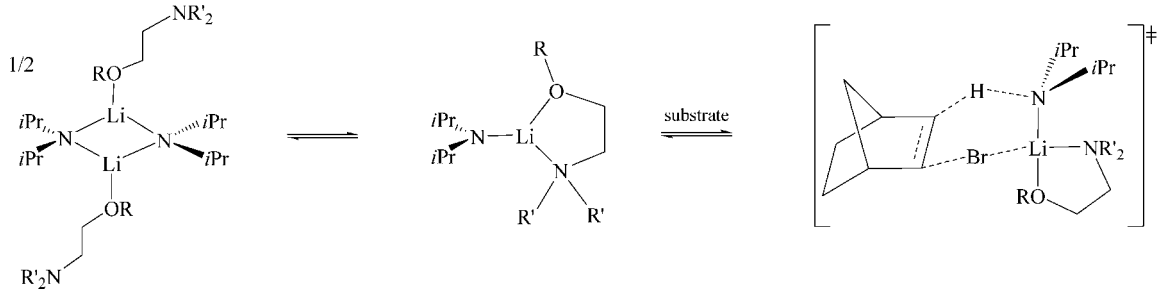
with the allylphosphane ligand remaining bound to the ruthenium through the phosphorus atom. Cases of parallel first- and second-order kinetics involving monodentate ligands and exhibiting the same kinetic pattern observed here were also reported.[35]

A simple analysis of the plots in Figure 1 and Figure 2 allows the contribution of the arm-off mechanism to the overall reactivity to be estimated. This is done graphically from the ratio of k_1 over the interpolated k_{obs} value on the *y* axis at a given concentration of the reagent. For instance, the rhodium complex **5** reacts with MeI via the κ^2-*N*,*S* intermediate for about 10% in acetone or in acetonitrile, and for about 60% in dichloromethane, at [MeI] ≈ 1 M. The contribution of hemilability increases to about 19% in the more polar solvents and to 78% in dichloromethane at [MeI] ≈ 0.5 M. The reaction of the indenyl ruthenium complex **9** proceeds via the monodentate intermediate for about 25% in the case of phenylacetylene and 33% in the case of the *p*-chloroderivative, at an alkyne concentration of 0.5 M. At the same concentration of phenylacetylene, only 5% of the reaction with [D_3]acetonitrile occurs via the open arm intermediate of the allylphosphane complex. The effect of hemilability is minimized under those conditions of solvent or reagent that favor the SN2 attack to the chelate complex, while it tends to become dominant at concentrations of the reagent approaching zero.

The substitution reactions of the homoditopic S–S ligands of [Pt(Ph)$_2${κ^2-(*S*,*S*)-$Ph_2S(CH_2)_nSPh_2$}] (*n* = 2,3) by a diphosphane were found to proceed according to Equation (2), indicating the formation of a monodentate κ^1-*S* transient species.[36] Parallel first- and second-order kinetics were also observed for the acid-promoted ring opening and displacement by chloride of the bidentate chelate ligand from dichloro[pyridine-2-(α-methoxymethanolato)]-gold(III).[14d]

The effect of hemilabile ligands on the rates of 1,2-dehydrobromination reactions mediated by lithium diisopropylamide (LDA) were studied in detail by Collum and coworkers. The process itself served as the reference reaction for addressing key issues in organolithium chemistry, in particular aggregation and solvation effects.[37] The reaction in the presence of hemilabile O–N ligands instead of BuOMe can be accelerated by up to four orders of magnitude because of the intervention of monomer and dimer based pathways. Kinetic and spectroscopic experiments carried out using either BuOMe, bidentate ethers such as dimethoxyethane, or different hybrid aminoethers have shown that ground state structures are dimeric complexes bearing a monodentate ligand, while transition state structures are chelated monomeric species (Scheme 13).

The subject has been investigated with various approaches, including thermodynamic, kinetic, and computa-



Scheme 13. Equilibrium between dimeric monodentate and monomeric bidentate complexes, and the transition state structure in the 1,2-dehydrobromination of (±)-2-*exo*-bromonorbornane, mediated by lithium diisopropylamide complexes.

tional work, which has allowed the authors to show and prove some fundamental mechanistic concepts. In particular, effects on relative reaction rates were dissected into the rate retarding influence due to ground state stabilization and the rate accelerating influence due to transition state stabilization. The rate acceleration imparted by dimethoxyethane and related aminoethers is due to selective stabilization of the transition state structure arising from a chelate effect of the hybrid ligands, and not to an increased solvation ability with respect to a monodentate ligand. This case, when compared with the examples described previously, shows an opposite situation among the effects, which hybrid hemilabile ligands may exert on the reactivity of a metal center. In fact, while complexes **1**, **5**, and **8** are chelated in the ground state and change into monocoordinated complexes by the arm-off mechanism to become reactive toward a substrate, the lithium diisopropylamide complexes are dimeric monodentate species in solution but use bidentation at the transition state to access lower energy pathways for the reaction. The transition state stabilization and hence the reaction rates can be tuned by changing the structure of the hybrid ligand in the following ways: (i) altering the length of the hydrocarbon chain and so the chelate ring size, (ii) varying the alkyl substituents on both the oxygen and nitrogen donors, (iii) introducing ramification on the carbon chain. A recent work addressing the last issue has concluded that rate accelerations based on the *gem*-dimethyl effect are nonexistent for lithium ion chelation.[38] The *gem*-dimethyl effect applies when destabililizing effects due to unfavorable steric interactions of alkyl substituents in an open carbon chain are alleviated by ring closure and can give pronounced substituent-dependent rate accelerations.[39]

Although many hybrid ligands have been used successfully in catalysis,[2,4] the establishment of contributions from the reversible association/dissociation of one labile function during the catalytic cycle remains a key question, which appears more difficult to address than it is for stoichiometric reactions.[40] Because of the interchange of various metal species, the alternation of dangling or chelate ligand modes may occur frequently during the cycle and affect the relative stability/reactivity in each step. To devise kinetic experiments that are as informative for catalysis as they are for stoichiometric reactions represents an important challenge, however, it is fundamental for understanding the role of hemilability in cyclic multistep processes.

4. Concluding Remarks

This review describes the information attainable from kinetic studies about the hemilability of hybrid ligands coordinated to transition metal complexes. In particular, it shows that the kinetic method allows for the detection of the reversible association/dissociation process of the hemilabile ligand function, even in the absence of fluxional behavior, as well as a quantitative evaluation of its weight along the coordinate of a bimolecular reaction. Cases in which the only available reaction pathway involves a transient species arising from dissociation of the ligand arm, cases in which such species reacts in parallel with the chelate complex, and opposite cases in which only the chelate is reactive are described. The kinetic approach may serve as a basis for the rational design of hemilabile systems and for the development of targeted applications.

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[1] C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Progr. Inorg. Chem. Vol. 48* (Ed.: K. D. Karlin), Wiley, New York, **1999**, pp. 233–350.
[2] a) P. Braunstein, F. Naud, *Angew. Chem. Int. Ed.* **2001**, *40*, 680–699; b) P. Espinet, K. Soulantica, *Coord. Chem. Rev.* **1999**, *193–195*, 499–556; c) A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27–110.
[3] In principle, while a metal complex of a hybrid ligand may not display hemilability, a chelate complex of a homofunctional polydentate ligand can exhibit reversible decoordination of one ligand arm, e.g., G. Kiss, I. T. Horváth, *Organometallics* **1991**, *10*, 3798–3799.
[4] a) J. J. Schneider, *Nachr. Chem.* **2000**, *48*, 614–616; J. J. Schneider, *Nachr. Chem.* **2000**, *48*, 618–620; b) K. N. Gavrilov, A. I. Polosukhin, *Russ. Chem. Rev.* **2000**, *69*, 661–682; c) G. Delapierre, G. Buono, *Actualite Chimique* **2003**, *2*, 3–11.
[5] J. C. Jeffrey, T. B. Rauchfuss, *Inorg. Chem.* **1979**, *18*, 2658–2666.
[6] a) J. F. Sieckhaus, T. Layloff, *Inorg. Chem.* **1967**, *6*, 2185–2190; b) M. Bacci, S. Midollini, *Inorg. Chim. Acta* **1971**, *5*, 220–222; c) D. H. Payne, Z. A. Payne, R. Rohmer, H. Frye, *Inorg. Chem.* **1973**, *12*, 2540–2543; d) T. B. Rauchfuss, D. M. Roundhill, *J. Am. Chem. Soc.* **1974**, *96*, 3098–3105; e) S. O. Grim, L. C. Satek, C. A. Tolman, J. P. Jesson, *Inorg. Chem.* **1975**, *14*, 656–660; f) P. Braunstein, D. Matt, F. Mathey, D. Thavard, *J. Chem. Res. Synop.* **1978**, 232–233.
[7] J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791–799; S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 868–8179.
[8] R. H. Grubbs, *Tetrahedron* **2004**, *60*, 7117–7140.
[9] In the study of the exchange processes associated with hemilability, various expressions have been introduced to represent the reversible decoordination of one ligand arm: interchange, tick-tock, wind-screen wiper, opening and closing, arm-off mechanism (see ref.[1]).
[10] The formation of a stable monochelate product indicates that selective decoordination of one ligand arm has occurred, but does not imply that the bis-chelate complex was involved in the reversible motion which identifies hemilability.
[11] For example: T. R. Webb, T. Y. Dong, *Inorg. Chem.* **1982**, *21*, 114–116; S. Siddiqui, R. E. Shepherd, *Inorg. Chem.* **1983**, *22*, 3726–3733; G. R. Dobson, S. S. Basson, C. B. Dobson, *Inorg. Chim. Acta* **1985**, *105*, L17–L19; D. A. Buckingham, C. R. Clark, *Inorg. Chem.* **1994**, *33*, 6171–6179.
[12] W. J. Knebel, R. J. Angelici, *Inorg. Chem.* **1974**, *13*, 627–631.
[13] W. J. Knebel, R. J. Angelici, *Inorg. Chem.* **1974**, *13*, 632–637.
[14] For example: a) A. Peloso, *J. Chem. Soc. Dalton Trans.* **1979**, 2033–2036; b) E. Kita, M. Laczna, *Transition Met. Chem.* **2001**, *26*, 510–516; c) J. Favier, M. Gómez, J. Granell, M. Martínez, X. Solans, M. Font-Bardía, *Dalton Trans.* **2005**, 123–132;

d) G. Marangoni, B. Pitteri, G. Annibale, M. Bortoluzzi, *Eur. J. Inorg. Chem.* **2006**, 765–771.

[15] M. Bassetti, A. Capone, M. Salamone, *Organometallics* **2004**, *23*, 247–252.

[16] M. Bassetti, A. Capone, L. Mastrofrancesco, M. Salamone, *Organometallics* **2003**, *22*, 2535–2538.

[17] J. D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*, Brooks/Cole Publishing Company, Monterey, CA, **1985**, p. 14.

[18] M. R. Plutino, L. Monsù Scolaro, R. Romeo, A. Grassi, *Inorg. Chem.* **2000**, *39*, 2712–2720, and references therein.

[19] a) A. J. Hart-Davis, W. A. G. Graham, *Inorg. Chem.* **1970**, *9*, 2658–2663; b) T. R. Griffin, D. B. Cook, A. Haynes, J. M. Pearson, D. Monti, G. E. Morris, *J. Am. Chem. Soc.* **1996**, *118*, 3029–3030; c) G. Aullon, S. Alvarez, *Inorg. Chem.* **1996**, *35*, 3137–3144; d) D. Lamprecht, G. J. Lamprecht, *J. Comput. Chem.* **2000**, *21*, 692–703.

[20] a) P. B. Chock, J. Halpern, *J. Am. Chem. Soc.* **1966**, *88*, 3511–3514; b) R. Ugo, A. Pasini, A. Fusi, S. Cenini, *J. Am. Chem. Soc.* **1972**, *94*, 7364–7370; c) D. J. A. de Waal, T. I. A. Gerber, W. J. Louw, *Inorg. Chem.* **1982**, *21*, 1259–1260; d) J. P. Collman, J. I. Brauman, A. M. Madonik, *Organometallics* **1986**, *5*, 310–322; e) R. W. Wegman, A. G. Abatjoglou, A. M. Harrison, *J. Chem. Soc. Chem. Commun.* **1987**, 1891–1892; f) G. J. Vanzyl, G. J. Lamprecht, J. G. Leipoldt, T. W. Swaddle, *Inorg. Chim. Acta* **1988**, *143*, 223–227; g) A. Fulford, C. E. Hickey, P. M. Maitlis, *J. Organomet. Chem.* **1990**, *398*, 311–323; h) M. Bassetti, D. Monti, A. Haynes, J. M. Pearson, I. A. Stanbridge, P. M. Maitlis, *Gazz. Chim. Ital.* **1992**, *122*, 391–393; i) M. R. Wilson, H. Liu, A. Prock, W. P. Giering, *Organometallics* **1993**, *12*, 2044–2050; j) C. Dueker-Benfer, R. van Eldik, A. J. Canty, *Organometallics* **1994**, *13*, 2412–2414; k) L. Gonsalvi, H. Adams, G. J. Sunley, E. Ditzel, A. Haynes, *J. Am. Chem. Soc.* **1999**, *121*, 11233–11234; l) J. K. Jawad, F. N. K. Al-Obaidy, J. A. Hammud, F. Al-Azab, *J. Organomet. Chem.* **2000**, *599*, 166–169; m) A. Roodt, G. J. J. Steyn, *South Afr. J. Chem.* **2001**, *54*, 1–22; n) L. Gonsalvi, H. Adams, G. J. Sunley, E. Ditzel, A. Haynes, *J. Am. Chem. Soc.* **2002**, *124*, 13597–13612; o) V. Chauby, J.-C. Daran, C. Serra-Le Berre, F. Malbosc, P. Kalck, O. Delgado Gonzales, C. E. Haslam, A. Haynes, *Inorg. Chem.* **2002**, *41*, 3280–3290; p) L. Gonsalvi, J. A. Gaunt, H. Adams, A. Castro, G. J. Sunley, A. Haynes, *Organometallics* **2003**, *22*, 1047–1054; q) J. A. Gaunt, V. C. Gibson, A. Haynes, S. K. Spitzmesser, A. J. P. White, D. J. Williams, *Organometallics* **2004**, *23*, 1015–1023; r) J. M. Wilson, G. J. Sunley, H. Adams, A. Haynes, *J. Organomet. Chem.* **2005**, *690*, 6089–6095.

[21] S. S. Basson, J. G. Leipoldt, A. Roodt, J. A. Venter, *Inorg. Chim. Acta* **1987**, *128*, 31–37.

[22] H. C. Martin, N. H. James, J. Aitken, J. A. Gaunt, H. Adams, A. Haynes, *Organometallics* **2003**, *22*, 4451–4458.

[23] a) R. J. Mawby, F. Basolo, R. G. Pearson, *J. Am. Chem. Soc.* **1964**, *86*, 3994–3999; b) J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*; University Science Book, Mill Valley, CA, **1987**, p. 357.

[24] D. Cuervo, J. Díez, M. Pilar Gamasa, S. García-Granda, J. Gimeno, *Inorg. Chem.* **2002**, *41*, 4999–5001.

[25] P. Pelagatti, A. Bacchi, C. Bobbio, M. Carcelli, M. Costa, C. Pelizzi, C. Vivorio, *Organometallics* **2000**, *19*, 5440–5446.

[26] D. A. Cooper, S. J. Rettig, A. Storr, *Can. J. Chem.* **1986**, *64*, 566–574.

[27] P. Das, M. Sharma, N. Kumari, D. Konwar, D. K. Dutta, *Appl. Organomet. Chem.* **2002**, *16*, 302–306.

[28] J. Díez, M. P. Gamasa, J. Gimeno, E. Lastra, A. Villar, *Eur. J. Inorg. Chem.* **2006**, 78–87, and references therein.

[29] L. P. Barthel-Rosa, K. Maitra, J. H. Nelson, *Inorg. Chem.* **1998**, *37*, 633–639.

[30] P. Alvarez, E. Lastra, J. Gimeno, P. Braña, J. A. Sordo, J. Gomez, L. R. Falvello, M. Bassetti, *Organometallics* **2004**, *23*, 2956–2966.

[31] P. Alvarez, E. Lastra, J. Gimeno, M. Bassetti, L. R. Falvello, *J. Am. Chem. Soc.* **2003**, *125*, 2386–2387.

[32] M. Bassetti, P. Alvarez, E. Lastra, J. Gimeno, *Organometallics* **2004**, *23*, 5127–5134.

[33] a) M. E. Rerek, F. Basolo, *J. Am. Chem. Soc.* **1984**, *106*, 5908–5912; b) J. S. Merola, R. T. Kacmarcik, D. Van Engen, *J. Am. Chem. Soc.* **1986**, *108*, 329–331; c) A. K. Kakkar, N. J. Taylor, T. B. Marder, J. K. Shen, N. Hallinan, F. Basolo, *Inorg. Chim. Acta* **1992**, *198–200*, 219–231; d) T. Foo, R. G. Bergman, *Organometallics* **1992**, *11*, 1811–1819; e) C. Bonifaci, G. Carta, A. Ceccon, A. Gambaro, S. Santi, *Organometallics* **1996**, *15*, 1630–1636; f) M. Bassetti, P. Casellato, M. P. Gamasa, J. Gimeno, C. González-Bernardo, B. Martín-Vaca, *Organometallics* **1997**, *16*, 5470–5477; g) M. Bassetti, S. Marini, J. Díaz, M. P. Gamasa, J. Gimeno, Y. Rodriguez-Álvarez, *Organometallics* **2002**, *21*, 4815–4822.

[34] a) D. J. Jones, R. J. Mawby, *Inorg. Chim. Acta* **1972**, *6*, 157–160; b) K. A. Pevear, M. M. Banaszak Holl, G. B. Carpenter, A. L. Rieger, P. H. Rieger, D. A. Sweigart, *Organometallics* **1995**, *14*, 512–523; c) M. P. Gamasa, J. Gimeno, C. Gonzalez-Bernardo, B. Martín-Vaca, D. Monti, M. Bassetti, *Organometallics* **1996**, *15*, 302–308.

[35] a) A. J. Hart-Davis, C. White, R. J. Mawby, *Inorg. Chim. Acta* **1970**, *4*, 441–446; b) N. N. Turaki, J. M. Huggins, L. Lebioda, *Inorg. Chem.* **1988**, *27*, 424–427.

[36] R. Romeo, L. Monsù Scolaro, M. R. Plutino, A. Romeo, F. Nicolò, A. Del Zotto, *Eur. J. Inorg. Chem.* **2002**, 629–638.

[37] J. F. Remenar, D. B. Collum, *J. Am. Chem. Soc.* **1997**, *119*, 5573–5582.

[38] A. Ramírez, E. Lobkovsky, D. B. Collum, *J. Am. Chem. Soc.* **2003**, *125*, 15376–15387.

[39] R. F. Brown, N. M. Van Gulick, *J. Org. Chem.* **1956**, *21*, 1046–1049; C. Galli, G. Giovannelli, G. Illuminati, L. Mandolini, *J. Org. Chem.* **1978**, *44*, 1258–1261; C. Wang, G. A. Russell, *J. Org. Chem.* **1999**, *64*, 2066–2069; J. B. Sperry, D. L. Wright, *J. Am. Chem. Soc.* **2005**, *127*, 8034–8035.

[40] J. Andrieu, J.-M. Camus, P. Richard, R. Poli, L. Gonsalvi, F. Vizza, M. Peruzzini, *Eur. J. Inorg. Chem.* **2006**, 51–61, and references cited therein.

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