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Reviews

The chemistry of carbonyl clusters of transition metals containing labile and hemilabile ligands. Synthesis, reactivity, and prospects for application

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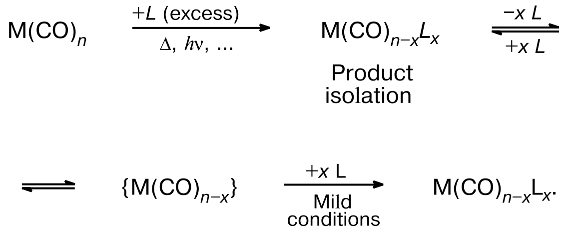
The methods of synthesis, structural features, and the reactivity of substituted carbonyl clusters of transition metals containing labile and hemilabile ligands are considered.

Key words: carbonyl clusters, transition metals, labile ligand, hemilabile ligands, synthesis, structure, reactivity, mechanism of substituted reactions, catalysis.

1. Introduction

Labile, or weakly bound ligands have been extensively used for rather long time in the organometallic chemistry of mononuclear transition metal complexes. The strong bonds between the metal atom and ligands, for example, carbon monoxide molecules (~120—180 kJ mol^{-1}),[1] are responsible for low reactivity (inertness) of these compounds in ligand substitution reactions. The use of harsh conditions for activation of inert complexes (thermal or photochemical treatment) may prove to be impossible or undesirable for many reasons when certain chemical reactions are performed. Therefore, the introduction of one or several weakly bound (labile) ligands in the composition of complexes is a mild and elegant method for affecting the reactivity of inert compounds; using this method, it is possible to markedly extend the scope of applicability of these compounds in synthetic chemistry and catalysis. This approach becomes fundamentally important when dealing with thermo- and photosensitive substituting substrates (L). Therefore, the use of $M(CO)_nL_x$ type complexes (hereinafter, labile ligands *L* are *italicized*) contributes to solution of many synthetic problems within the framework of a rather simple approach described by the following sequence of reactions:



By isolation of labile complexes $M(CO)_nL_x$, it is possible to break the synthetic sequence and to change appreciably the conditions of substitution reactions, which gives rise to final products under mild conditions in nearly

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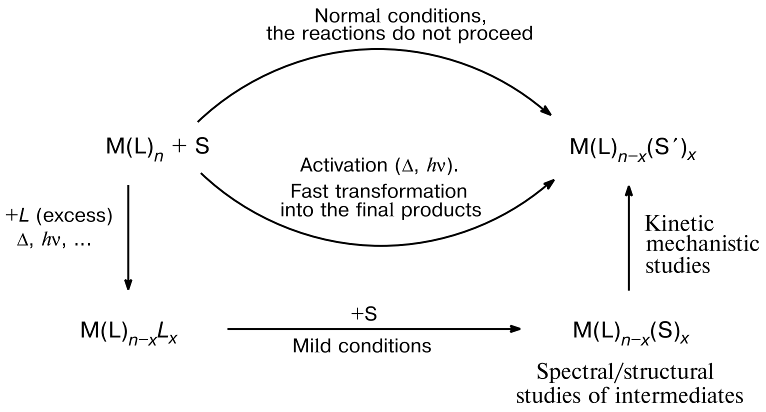
Scheme 1



quantitative yields (in relation to both the complex and the ligand). This may be significant in the case of expensive ligands, for example, chiral phosphines. A specific application of labile complexes consists in the study the mechanisms of multistep reactions involving intra- or intermolecular rearrangements of the coordinated ligands. In the complexes containing labile ligands, one can retard the transformations of the intermediates or even isolate the intermdiates by conducting the primary coordination steps at room or lower temperatures. Study of the spectral/structural characteristics of these species provides valuable information on the reaction mechanism and, in some cases, allows independent kinetic measurements (the mechanism and the kinetic parameters) for the transformation of intermediates into the final products (Scheme 1).

Labile ligands and the substituted derivatives containing these ligands are also widely and successfully used in the chemistry of transition metal carbonyl clusters both in the synthesis and in the study of the reactivity of inert cluster complexes. In this field of organometallic chemistry, the use of labile ligands has one more important aspect related directly to the nature of cluster compounds. The presence of weak metal—metal bonds (~50—100 kJ mol^{-1})[1,2] opens an additional, often undesirable channel of chemical transformations, namely, reactions related to destruction or enlargement of the cluster cores. The introduction of labile ligands into clusters and, as a consequence, the possibility of conducting substitution reactions under mild conditions eliminate the complications related to the rearrangement of the cluster cores, which makes it possible to study the coordination and transformations of organic substrates on a polymetallic coordinating center "just as they are". The advantages provided by this approach can be successfully utilized in the synthetic cluster chemistry the goal of which is to prepare polynuclear complexes of a particular stoichiometry regarding both the ligand environment and the composition of the cluster framework. This approach is also useful in the investigation of the mechanisms of reactions of carbonyl clusters, which is highly significant for homogeneous and heterogeneous catalysis.

Equally interesting is the chemistry of cluster complexes related to the presence, in their coordination sphere, of so-called hemilabile heterobidentate (XY) ligands. These ligands possess a coordinating function (X), which may be labile. This labile function can be involved in the fully reversible dissociative equilibrium without leaving the coordination sphere due to the strong bond between the other coordinating function and the metal center(s). An important feature of this equilibrium, usually referred to as the hemilabile behavior, is that the ligand generally has a pronounced influence on the electronic, steric, and especially stereochemical characteristics of the dissociative intermediates generated upon dissociation of the function X. For this reason, hemilabile mononuclear transition metal complexes have found extensive use in the homogeneous, especially asymmetric catalysis of various organic reactions.[3] Clusters with hemilabile ligands are now of lesser utility than mononuclear complexes; however, their synthesis and structural and catalytic properties provoke considerable interest.[4—6] Moreover, the stereochemical features of the structures of polynuclear complexes containing bridging heterobidentate ligands XY (these structural fragments can be formed only in polynuclear complexes) imply attractive opportunities of using them in asymmetric synthesis.[6,7]

This review is devoted to some aspects of the synthesis and reactivity of the transition metal carbonyl clusters containing labile and hemilabile ligands, which are either widely used in fundamental research or are promising for practical application. The review does not claim to be exhaustive, being largely based on the results obtained by author´s research group during the last 10 years. Nevertheless, when analyzing the key issues of this field of organometallic chemistry, we discussed also fundamental works of other research groups.

2. Labile ligands in the chemistry of carbonyl clusters

2.1. Methods for the synthesis of clusters containing labile ligands. The lability of the ligand in transition metal complexes is determined, first of all, by the strength of the metal—ligand bond and, to a certain extent, by nonbonding interactions of the ligand with the coordination sphere of the complex as a whole. In carbonyl complexes, in particular, in transition metal clusters, the strength of these bonds depends, as a rule, on the nature of the donor center of the ligand, which can generally be classified as either soft or hard Lewis base. Soft Lewis bases such as CO and phosphorus(III) compounds (phosphines and phosphites) form rather strong bonds with the central metal atoms in low oxidation states, and they are not labile (in the sense we are using this term) in transition metal carbonyl clusters (TMC) and their derivatives. In contrast, the ligands which contain hard coordination functions such as ether, alcohol, carbonyl or phosphine oxide oxygen atom, thioether or sulfoxide sulfur atom, and the nitrogen atom of a nonaromatic amino group form weak bonds with transition metal ions in low oxidation states and are typical labile ligands in the corresponding complexes. This class of labile ligands includes also "insufficiently soft" Lewis bases, for example, organic nitriles (RCN), is a typical example widely used (Table 1) as such a ligand in organometallic chemistry. Even alkenes (cyclooctene, cyclooctadiene, see Table 1) demonstrate in some cases labile properties and can be used for synthetic purposes to prepare substituted derivatives of mono- and polynuclear organometallic complexes. Halide ions can also exhibit lability in the coordination sphere of TMC; however, the anionic nature of these ligands imposes some limitations on the scope of their application in this field. Typical labile ligands used in the chemistry of transition metal clusters are listed in Table 1. It is worth noting that labile ligands have found the most extensive application in the chemistry of inert clusters such as $Os_3(CO)_{12}$, $Ir_4(CO)_{12}$ and $Rh_6(CO)_{16}$. The inertness of these clusters in CO substitution reactions is combined with the high strength of metal—metal bonds, which keeps intact the polynuclear nature of the coordinating center in these complexes even under relatively harsh (temperature and pressure) conditions. This is why inert clusters and their labile derivatives are used most often as model compounds in the studies of fundamentally important characteristics of reactions that occur on polynuclear metal centers. For example, they can simulate the transformations of organic substrates on metal particles of heterogeneous catalysts. Nevertheless, the general features of the chemical behavior of labile ligands in the coordination sphere of clusters allow one to use these ligands to modify the reactivity of virtually any cluster, and the array of complexes listed in Table 1 can be substantially extended. Moreover, labile ligands (see Table 1) cover a broad range of donor-acceptor properties of the coordinating functions, that provides the possibility of fine tuning of the

Table 1. Main types of labile ligands in transition metal clusters (TMC)

Labile ligand	Examples of substituted TMC derivatives containing labile ligands	Methods of synthesis*	Ref.
NCMe	$Os_3(CO)_{12-x}(NCMe)_x$ ($x = 1, 2$)	*A*	8
	$Ru_3(CO)_{12-x}(NCMe)_x$ ($x = 1, 2$)	*A*	9
	$Rh_6(CO)_{16-x}(NCMe)_x$ ($x = 1, 2$)	*A*, *B*	10
	$Re_3(\mu\text{-}H)_3(CO)_{12-n}(NCMe)_n$ ($n = 1—3$)	*A*	11
	$RCCo_3(CO)_{9-x}(NCMe)_x$ ($n = 1, 2$)	*A*	12
	$Os_5(CO)_{15}(NCMe)$	*A*	13
	$Os_7(CO)_{19}(NCMe)_2$	*A*	14
Alkenes			
Cyclooctene	$Os_3(CO)_{10}(C_8H_{14})_2$	*C*	15
	$Rh_6(CO)_{15}(C_8H_{14})$	*D*	16
Cycloocta-1,5-diene	$PtRe_2(\mu\text{-}H)_2(CO)_8(1,5\text{-}C_8H_{12})$	*E*	17
Hal^-	$[Ir_4(CO)_{11}Br]^-$	*F*	18
NMe_3	$HMCo_3(CO)_{11}(NMe_3)$ (M = Fe, Ru)	*A*	19
Dimethyl sulfoxide	$Rh_6(CO)_{15}(DMSO)$	*D*	16
Tetrahydrofuran	$Rh_6(CO)_{15}(thf)$	*D*	16

* Methods of synthesis: *A*. $M_n(CO)_p + x\ Me_3NO\ (\text{excess}\ L) \rightarrow M_n(CO)_{p-x}(L)_x$; *B*. Photochemical reaction in the presence of ligand excess; *C*. The reaction of $H_2Os_3(CO)_{10}$ with an excess of cyclooctene; *D*. The reaction of $Rh_6(CO)_{15}(NCMe)$ with excess cyclooctene; *E*. The reaction of $Re_2(H)_2(CO)_8$ with $Pt(1,5\text{-}C_8H_{12})_2$; *F*. The reaction with excess ligand on heating.

reactivity of the coordination sphere of a TMC for particular purposes.

Labile ligands usually replace strongly bound carbonyl groups in the coordination sphere of TMC. Therefore, the substitution requires rather tough action on an inert complex in the presence of an excess of the substituting ligand. Thermal activation has been used, for example, to synthesize bromide-substituted tetranuclear iridium clusters.[18] Unlike the carbonyl ligands in the starting clusters, the bromide ions are easily replaced by ligands of various types to give neutral complexes $Ir_4(CO)_{12-n}L_n$ (see the next section).

$$Ir_4(CO)_{12} \xrightarrow{i} [Ir_4(CO)_{11}Br]^-$$

i. THF, Δ, Br^- (excess).

The photochemical reaction of hexanuclear rhodium cluster with an excess of acetonitrile

$$Rh_6(CO)_{16} \xrightarrow[CHCl_3]{h\nu} \{Rh_6(CO)_{15}\} \xrightarrow{+NCMe}$$

$$\longrightarrow Rh_6(CO)_{15}(NCMe)$$

also gives[10] the monosubstituted actonitrile derivative of the $Rh_6(CO)_{16}$ cluster in a high yield.

Among the methods of introduction of labile ligands well-reputed in the chemistry of carbonyl clusters, the approach making use of oxidation of coordinated carbon monoxide with trimethylamine *N*-oxide in the presence of excess labile ligand is used most extensively.[8—10,20]

$$M_n(CO)_p \xrightarrow[-x\ CO_2]{+x\ Me_3NO} \{M_n(CO)_{p-x}\} \xrightarrow{+NCMe}$$

$$\longrightarrow M_n(CO)_{p-x}(NCMe)_x$$

$M_n(CO)_p = Os_3(CO)_{12}, Ru_3(CO)_{12}, Rh_6(CO)_{16}$

This method enables targeted control of the stoichiometry of the reaction products and allows researchers to attain very high yields of target products for clusters of various nature. All methods listed above can be employed to introduce labile ligands into carbonyl clusters and to isolate substituted products containing labile ligands as pure compounds. In this case, it is possible to replace one labile ligand by another.[16]

$$Rh_6(CO)_{15}(NCMe) \xrightarrow[-NCMe]{+L\ (excess)} Rh_6(CO)_{15}(L)$$

L = DMSO, cyclooctene, THF, EtOH

The chemical characteristics of the labile ligand and, hence, the cluster reactivity can thus be varied in a desired manner.

2.2. The mechanism and kinetics of substitution of labile ligands. The ability of both clusters and mononuclear complexes containing labile ligands (L) to generate coordination vacancies through elimination of L giving rise to a coordination site for incoming ligands/substrates underlies the use of these compounds in the synthesis and study of reaction mechanisms. The kinetics of substitution of L by phosphines and phosphites (typical representatives of two-electron ligands) have been studied in detail for trinuclear acetonitrile clusters of osmium,[21] rhenium,[22] and substituted derivatives of the hexanuclear rhodium cluster[16] containing labile ligands with the nitrile, sulfoxide, ether, and alkene coordinating functions. The mechanism of substitution for all these clusters can be summarized in the general form as equilibrium dissociation of the labile ligand and subsequent addition of the substituting ligand at the newly formed coordination vacancy.

$$M_x(CO)_y(L) \underset{+L \atop k_{-1}}{\overset{k_1 \atop -L}{\rightleftarrows}} \{M_x(CO)_y\} \xrightarrow[k_2]{+PR_3} M_x(CO)_y(PR_3)$$

As shown by kinetic studies, the elimination of the labile ligand is the rate-determining step, its rate constant (k_1) determines the course of the whole process and characterizes the lability of the ligand. The kinetic parameters characterizing dissociation of labile ligands from tri- and hexanuclear osmium and rhodium clusters are listed in Table 2. The data on the dissociative substitution of CO in the binary carbonyl $Os_3(CO)_{12}$ cluster, given for comparison, clearly illustrate the efficiency of labilization, which gives rise to the difference between the rates of CO and acetonitrile substitution by more than eight orders of magnitude. The series of $Rh_6(CO)_{15}(L)$ clusters is also a demonstrative example. At room temperature in the ab-

Table 2. Rate constants and activation parameters for the substitution of labile ligands in transition metal clusters

Complex	$k_1 \cdot 10^3/s^{-1}$	$\Delta H^{\#\ a}$	$\Delta S^{\#\ b}$
$Os_3(CO)_{12-x}(NCMe)_x$[21]			
$Os_3(CO)_{12}$	$2 \cdot 10^{-7\ c}$	137.5	31.8
$Os_3(CO)_{11}(NCMe)$	80^c	112.4	92.2
$Os_3(CO)_{10}(NCMe)_2$	19^c	91.3	28.5
$H_3Re_3(CO)_{11}(NCMe)$[22]	0.21^d	115.9	70.3
$Rh_6(CO)_{15}(L)$[16]			
$Rh_6(CO)_{15}(NCMe)$	109^e	83.7	17.1
$Rh_6(CO)_{15}(DMSO)$	6.43^e	87.3	−4.5
$Rh_6(CO)_{15}(C_8H_{14})$	898^e	—	—
$Rh_6(CO)_{15}(thf)$	$301 \cdot 10^{3\ e}$	—	—
$Rh_6(CO)_{15}(EtOH)$	$529 \cdot 10^{3\ e}$	—	—

[a] In kJ mol^{-1}.

[b] In kJ mol^{-1} K^{-1}.

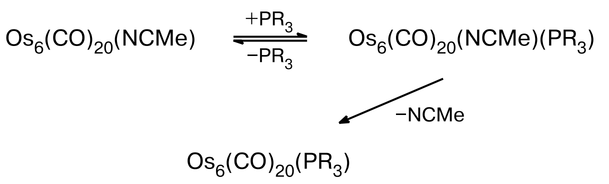
[c] 25.0 °C.

[d] 28.0 °C.

[e] 25.4 °C.

sence of oxygen, the substitution of CO in $Rh_6(CO)_{16}$ by, for example, phosphines does not occur for several days, whereas acetonitrile substitution by any phosphine is irreversibly completed over a period of several minutes.[16] In addition, for the substituted clusters (L = NCMe, DMSO, cyclooctene) isolated in a pure state, the difference in the rate constants for ligand dissociation covers two orders of magnitude, which makes it possible to change the substitution rate over fairly broad limits in a controlled manner. The clusters containing labile solvent molecules (L = THF, EtOH,[16] $CHCl_3$, CH_2Cl_2 [23]) are extremely unstable in themselves. They are formed *in situ* on substitution of a solvent molecule for acetonitrile or under photostimulated dissociation of CO from the $Rh_6(CO)_{16}$ cluster and can hardly be used for synthetic purposes. However, their discovery and characterization[16,23] has largely contributed to the understanding of the role of weak interactions of the active forms of clusters with the solvent and to elucidation of the mechanisms of the corresponding reactions in solutions. In particular, spectroscopic analysis of the intermediates formed in the photochemical reaction of $Rh_6(CO)_{16}$ has shown[23] that the coordination vacancies generated upon CO dissociation are first occupied by solvent molecules, including very weak donors like chloroform and dichloromethane. The solvents are then substituted by other ligands present in the reaction mixture in much lower concentrations.

The dissociative mechanism of the substitution of a labile ligand can be somewhat different, as, for example, for the $Os_6(CO)_{20}(NCMe)$ cluster, which has an unusual planar structure of the coordination unit, so-called raft cluster. In this case, the slow (rate-determining) dissociation of the labile ligand is preceded by fast associative pre-equilibrium.[24]

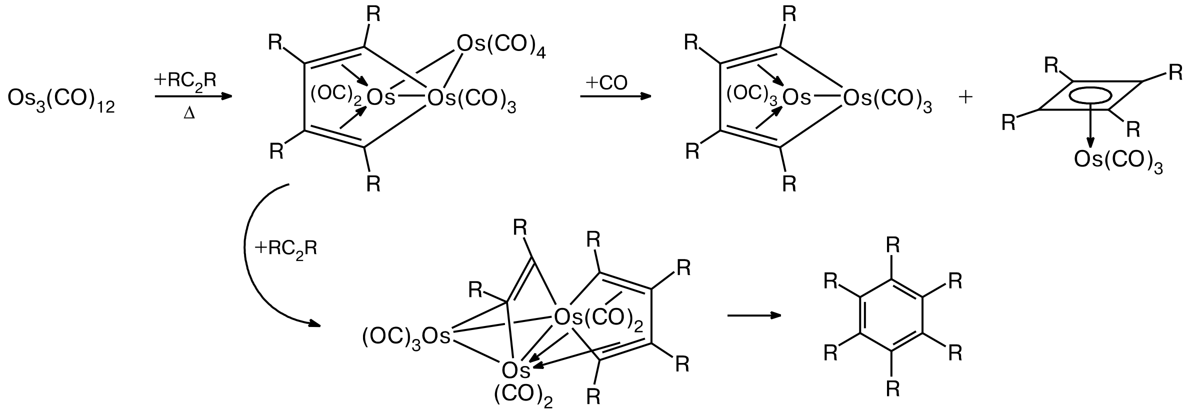


The outcome of this reaction is determined by the low strength of the osmium—acetonitrile bond, which accounts for the substitution of the acetonitrile rather than the carbonyl ligand. The presence of associative pre-equilibrium is due to the open structure of the cluster core in which the phosphine addition proceeds without essential steric hindrance, being stimulated by the electronic unsaturation of the cluster. Thus, for most of substitution reactions of labile ligands in transition metal clusters, dissociation of the leaving ligand is the rate-determining step. The kinetic studies showed that in this case, unlike the reactions of unsubstituted carbonyl clusters, the contribution of the associative pathway to the reaction rate is negligibly small if at all present. As a result, destruction or isomerization of the cluster skeleton related to this reaction channel does not affect the reaction course and the result of the substitution reaction.

2.3. The use of clusters containing labile ligands for synthetic purposes. The preparation of substituted derivatives of carbonyl clusters according to Scheme 1 is a classical example of synthetic application of TMC containing labile ligands. A basic drawback of thermal substitution in inert TMC is the formation of a mixture of thermodynamic products (which was to be expected under these conditions). For example, for $Os_3(CO)_{12}$ and phosphine ligands, these are polysubstituted derivatives ($Os_3(CO)_{12-x}(PR_3)_x$) and the products of oxidative addition of hydrocarbon substituents in phosphines to the cluster core.[25—29] In the case of $Rh_6(CO)_{16}$, which is inert toward substitution, the tetrasubstituted $Rh_6(CO)_{12}(P(OPh)_3)_4$ derivative is the only product isolated after the thermal reaction with triphenyl phosphite.[30,31] Even the use of stoichiometric amounts of the substituting ligand often does not give a satisfactory result, because the system is shifted toward the thermodynamic sink due to the labilization of CO ligands upon the introduction of phosphines into the cluster coordination sphere. The mechanism of successive CO substitution during the reaction of $Ir_4(CO)_{12}$ with PPh_3 is mainly dissociative, the ratio of the rates of first, second, and third substitution steps being 1 : 220 : 3500,[32,33] which practically excludes stabilization or isolation of the intermediate mono- and disubstituted products. For $Ru_3(CO)_{12}$, these rates differ to a lesser extent (1 : 55 : 40),[33,34] but the presence of a noticeable concentration of the monosubstituted derivative among the products can hardly be expected. It is worth noting that it is the polynuclear nature of the clusters and the possibility of coordination of the incoming ligands to various metal atoms on the cluster core that eliminate the steric hindrance to polysubstitution, which serves as a natural controller of the product stoichiometry in mononuclear complexes. Thus, the use of thermal reactions in the targeted synthesis of substituted derivatives of inert carbonyl clusters has limited applicability; these situations call for more directed methods for the introduction of substituting ligands.

The vast majority of compounds considered in a previous review,[35] which is devoted to various modes of binding of phosphorus-containing ligands to the Os_3 cluster core, have been synthesized starting from mono- and disubstituited acetonitrile clusters, $Os_3(CO)_{12-x}(NCMe)_x$. The use of labile TMC made possible the synthesis of a broad range of substituted derivatives of trinuclear osmium clusters, which often cannot be obtained in thermal or photochemical reactions for thermodynamic reasons. The same strategy (based on the use of the $Rh_6(CO)_{16-x}(NCMe)_x$ labile clusters) allowed the preparation of a family of substituted derivatives of $Rh_6(CO)_{16}$ containing ligands with a broad spectrum of donor prop-

Scheme 2



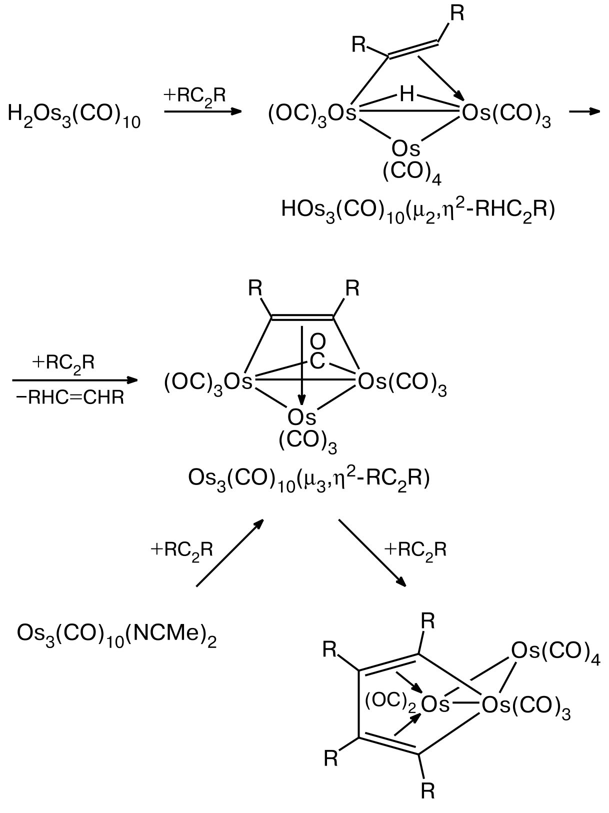
erties and steric characteristics. The studies of structural parameters[36,37] of these compounds and the mechanism and kinetics of the carbonyl ligand exchange between nonequivalent positions on a cluster core[38—40] made it possible to perform the first systematic analysis of the static and dynamic ligand effects in the octahedral rhodium carbonyl clusters. Similarly, the use of the labile $[Ir_4(CO)_{11}Br]^-$ anion for the synthesis of substituted derivatives of the tetrairidium clusters resulted in a detailed study of the influence of a wide range of heteroligands on the intramolecular dynamics of the carbonyl environment for more than two dozens of compounds and determination of the key features of these processes, which are highly important, in particular, for the simulation of catalytic reactions involving CO on the surface of heterogeneous catalyst particles (see reviews[41,42] and references cited therein).

Another example of the kinetic substitution products isolated and characterized using the labile ligand strategy is represented by alkyne and diyne derivatives of osmium and ruthenium trinuclear clusters. The pioneering studies dealing with the reactions of $Os_3(CO)_{12}$ with alkynes under thermal[43—50] or photochemical activation[51] have showed oligomerization of these organic substrates in the cluster coordination sphere (Scheme 2).

Depending on the reaction conditions, the diene derivatives of $Os_3(CO)_{12}$ formed upon dimerization of alkynes can either undergo fragmentation to give low-molecular-weight complexes or perfom alkyne trimerization to give substituted benzenes.[47] It is quite obvious that diene formation in the coordination sphere of the cluster is a multistep process. The intermediate (kinetic) product of this reaction, the $Os_3(CO)_{10}(\mu_3,\eta^2\text{-}RC_2R)$ cluster, was isolated and characterized after the two-step reaction of $H_2Os_3(CO)_{10}$ with monoalkynes (Scheme 3).[52,53]

However, the use of the bis(acetonitrile) derivative, $Os_3(CO)_{10}(NCMe)_2$, as the starting reagent[15] gives the same result in one step, and this it does not require the presence of excess alkyne (Scheme 4).

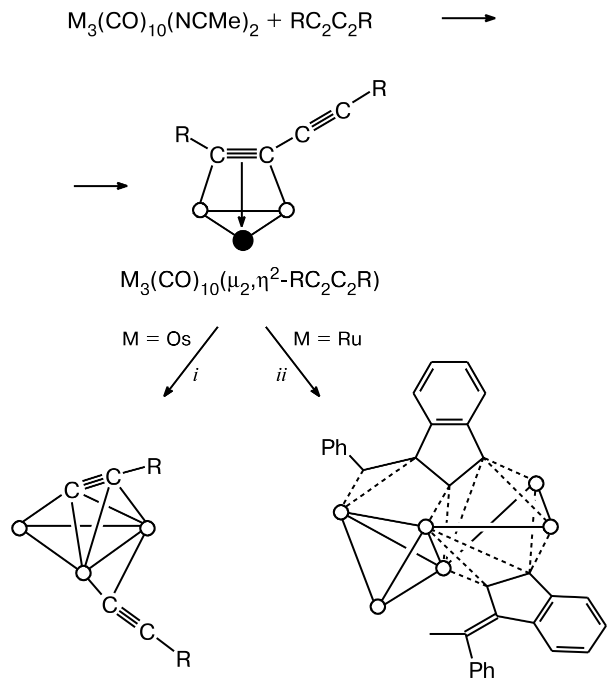
Scheme 3



It is evident that isolation of the kinetic intermediates of rather complex multistep reactions in this and other similar cases may provide important information on the possible routes of transformation of organic ligands containing triple bonds,[54,55] especially diynes.[56,57]

The thermal treatment of the kinetic μ_3,η^2-products containing diynes induces an intramolecular rearrangement of these ligands[56,57] to give coordinated organic fragments absolutely atypical of classical organic chemistry of these compounds. Therefore, the information con-

Scheme 4



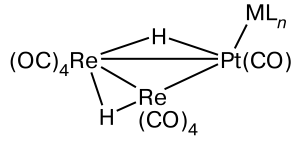
M = Ru, Os

i. Octane, refluxing; *ii*. Xylene, refluxing.

cerning intermediate products of these complex transformations may serve as a background for directed design of the corresponding catalytic processes.

The reaction of the GaCp* metal-containing ligand with the $Rh_6(CO)_{16}$ cluster yields[58] polysubstituted derivatives, $Rh_6(CO)_{13}(GaCp^*)_3$ and $Rh_6(CO)_{12}(GaCp^*)_4$, as thermodynamic products. The only strategy that resulted in the isolation of less substituted kinetic products proved to be the use of the labile cluster, $Rh_6(CO)_{15}(NCMe)$, whose reaction with 1 equiv. of GaCp* gave mono- ($Rh_6(CO)_{15}(GaCp^*)$, 14%) and disubstituted ($Rh_6(CO)_{14}(GaCp^*)_2$, 71%) clusters in reasonable yields.

The substitution of the labile cyclooctadiene (COD) ligand in $Re_2Pt(\mu\text{-}H)_2(CO)_8(COD)$ by metal-containing fragments ML_n = $[Mn(CO)_5]^-$, $[WCp(CO)_3]^-$, $[Co(CO)_4]^-$, and $HRe(CO)_4(PPh_3)$ was shown to be efficient method for the synthesis of heterometallic clusters containing three different transition metal atoms.[59] Not only the stoichiometry of the products, $[Re_2Pt(\mu\text{-}H)_2(CO)_9ML_n]^-$, but also the synthesis regioselectivity can be controlled in this case. The Mn, Re, W, and Co atoms in the complex are connected to the platinum center which was bound to the leaving cyclooctadiene ligand in the starting compound.



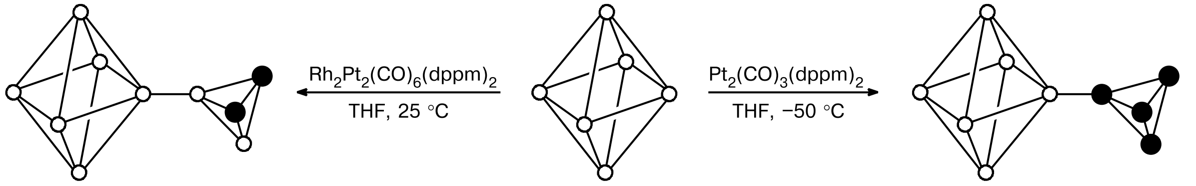
The above examples clearly illustrate the expansion of the synthetic potential and the enhancement of the control over the substitution reactions in clusters by the use of labile TMC derivatives.

The use of labile clusters is even more efficient in those cases where the temperature of the chemical experiment plays a crucial role in stabilization of unusual structures of cluster complexes. An example of this sort is the synthesis of $Rh_6(CO)_{16}$ derivatives in which the Rh_6 cluster core is bound through donor-acceptor interaction to the polynuclear Rh_2Pt_2 and Pt_4 fragments (Scheme 5).[60,61]

The use of the labile $Rh_6(CO)_{15}(NCMe)$ cluster as the starting compound and conduction of the second reaction at a reduced temperature enabled the high-yield synthesis of unique heterometallic clusters with an unusual type of bonding between the constituent fragments. Detailed investigation of the effect of the experimental conditions in the latter case has shown that the assembly of the $Pt_4(dppm)_3$ framework and stabilization of this tetraplatinum fragment are possible only at reduced temperatures, most likely, due to the thermal instability of the intermediates formed during the successive addition of Pt_2 fragments to the hexanuclear rhodium cluster. The same reaction carried out at room temperature induces degradation of the starting platinum compounds and diphosphine transfer onto the Rh_6 core and does not afford any heterometallic complexes, which have been successfully obtained and isolated when the reaction was carried out at −50 °C.

Heterometallic clusters containing different transition metals are of considerable interest as regards their reactivity[62,63] and catalytic activity.[64–66] These properties of clus-

Scheme 5



$Rh_6(CO)_{14}(\mu\text{-}CO)_2Rh_2Pt_2(CO)_5(dppm)_2$ $Rh_6(CO)_{15}(NCMe)$ $Rh_6(CO)_{14}(\mu\text{-}CO)_2Pt_4(CO)_5(dppm)_3$

ter compounds are those where synergistic effects are most clearly displayed because of the presence of several atoms of different metals bonded to one another in the coordinating core of the cluster. Compounds of this type are also of primary importance for the preparation of heterometallic phases of a particular composition,[66,67] which can be dictated by the stoichiometry of the starting compounds in this particular case. Therefore, development of synthetic approaches that allow directed variation of the metal ratio in the target product is an important practical task of modern cluster chemistry. The above examples demonstrate how labile clusters help to solve this problem in the synthesis of compounds containing atoms of different metals that are connected by direct metal—metal interactions. The range of available heterometallic clusters can be substantially extended by using the strategy of bonding of cluster fragments by a polydentate ligand, for example, a diphosphine. In this case, mono- or polymetallic fragments in the target compounds are linked due to the interaction with the phosphorus donor fragments of the same ligand. A basically important aspect is the consecutive (in time) coordination of the metal fragments to diphosphine to avoid the formation of randomly distributed "homo" and "hetero" products. This approach is successfully implemented within the strategy of successive reactions of the diphosphine with labile clusters and/or mononuclear complexes. A typical example of this type of reaction is the synthesis of the diphosphine Rh_6—Os_3 heterometallic cluster[68] shown in Scheme 6.

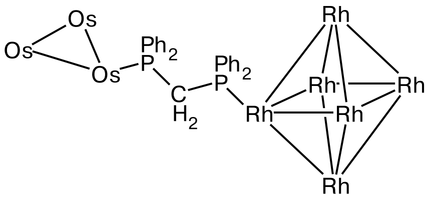
Scheme 6

$$Os_3(CO)_{11}(NCMe) + Ph_2PCH_2PPh_2 \xrightarrow[-NCMe]{}$$

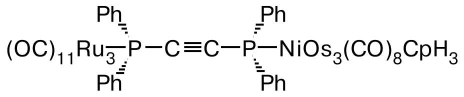
$$\longrightarrow Os_3(CO)_{11}(\eta^1\text{-}Ph_2PCH_2PPh_2)$$

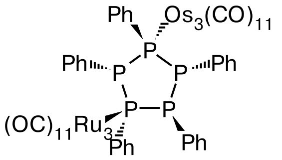
$$Os_3(CO)_{11}(\eta^1\text{-}Ph_2PCH_2PPh_2) + Rh_6(CO)_{15}(NCMe) \longrightarrow$$

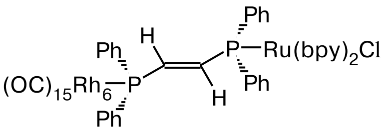
$$\longrightarrow Os_3(CO)_{11}(\eta^1{:}\eta^1\text{-}Ph_2PCH_2PPh_2)Rh_6(CO)_{15}$$



The Ru_3—$NiOs_3$,[69] Os_3—Ru_3,[70] and Rh_6—Ru [71] clusters were prepared in a similar way.


$(OC)_{11}Ru_3-PPh_2-C\equiv C-PPh_2-NiOs_3(CO)_8CpH_3$

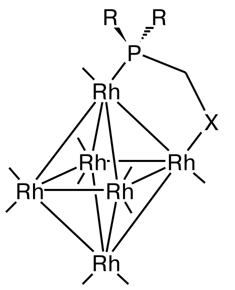


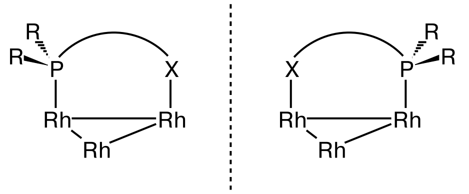


The same strategy based on the use of labile clusters can be successfully employed in the case of other potentially polydentate ligands, for example, diynes. Labile osmium and ruthenium clusters were used to synthesize heterometallic compounds containing simultaneously combinations of Os_3—Fe_2Se_2, Ru_3—Fe_2Se_2 [72] and Os_3—Mo_2, Ru_3—Mo_2, and Os_3—Co_2[73] cluster fragments, which are independently coordinated to the triple bonds of the diyne ligands.

2.4. The substitution of labile ligands for bidentate phosphines. The diversity of coordination modes of bi- and polydentate ligands in polynuclear transition metal complexes and the broad range of structures produced are remarkable and intriguing features of the synthetic cluster chemistry. In this respect, the structural chemistry of mononuclear complexes is (relatively!) poorer and provides less opportunity for imagination and implementation of unusual "day-dreams" of a synthetic chemist. The diversity of coordination modes of bidentate (even more so, polydentate) ligands raises the keen question of direction of the synthetic operations. If substitution is used, the introduction of a particular number of labile ligands into the cluster allows efficient control of the reaction course by providing a particular number of coordination vacancies for one or another mode of ligand bonding to the cluster core. For example, clusters containing two labile ligands in the coordination sphere can provide almost simultaneously a pair of coordination sites when react with functional phosphines for the formation of two bonds with one potentially bidentate ligand. This possibility facilitates the bidentate (chelate or bridging) coordination of the ligand. This is a convenient synthetic approach, which gives the target compounds almost instantaneously and in high yields even in those cases where the second coordinating function of the phosphine is able (for some reason) to form only a weak bond with the cluster core. Indeed, the use of the $Rh_6(CO)_{14}(NCMe)_2$ labile cluster made possible the synthesis (in nearly quantitative yields) of the $Rh_6(CO)_{16}$ derivatives with functionalized PX phosphines containing different coordinating functions X including thienyl, pyridyl, pyrrole, and alkenyl fragments.[7,40,74,75] Structural studies have shown that in all of these cases, the PX ligands form bridging structures in which the PX fragment is coordinated perpendicularly to a triangular face of the Rh_6 octahedron, thus giving a planar chiral center, $\{Rh_3(PX)\}$ [7].

$Rh_6(CO)_{14}(\mu,\kappa^2\text{-}R_2PX)$





Planar chiral fragment

From the general standpoint, the formation of these centers is important for cluster stereochemistry and may find application in the synthesis of cluster catalysts of asymmetric synthesis. To isolate these clusters in stereopure forms, the most efficient approach is based on the difference between the properties of diastereomers produced upon the introduction of a second chirality element into the cluster molecule. It is quite natural to use chiral functionalized phosphines, the coordination of which to a bridging position gives rise to diastereomeric products that can be separated by chromatography.[76] For expensive ligands, the efficiency of synthesis of the target products (which sharply increases when labile clusters are used) may be the crucial economic reason in determining the prospects of real application of asymmetric catalysts of this sort.

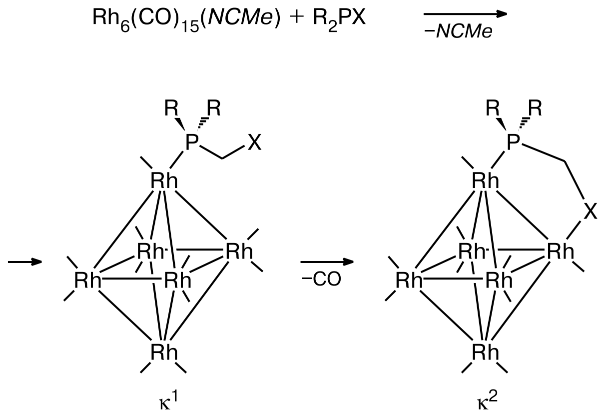
Study of the detailed mechanisms of the consecutive steps of coordination of bidentate ligands in polynuclear complexes is yet another interesting example of application of clusters containing labile ligands.

$$M_x(CO)_y(L) \xrightarrow[k_1]{+PX} M_x(CO)_y(\kappa^1\text{-PX}) \longrightarrow$$

$$\xrightarrow[k_2]{-CO} M_x(CO)_{y-1}(\kappa^2\text{-PX})$$

As noted above, the first step of these processes is fast and quantitative; nevertheless it is possible to measure the kinetics of substitution of labile ligands. The presence of the second coordinating group X in the functional phosphine results in the closure of a (di)metal ring into either the chelate or bridging position. The pronounced difference between the substitution rates of the labile ligand and CO leads to separation of these stages in time and allows independent measurement of their kinetics. Quite often, the reaction intermediates can be separated not only kinetically but synthetically; therefore, they can be isolated and studied by IR and NMR spectroscopy. Characteristics of the intermediates and the kinetics of dimetallic ring closure (bridging coordination) in the reactions of hexanuclear rhodium clusters with phosphines containing thienyl, pyridyl, alkene,[7] and pyrrole[74] substituents have been studied in this way (Scheme 7).

Scheme 7

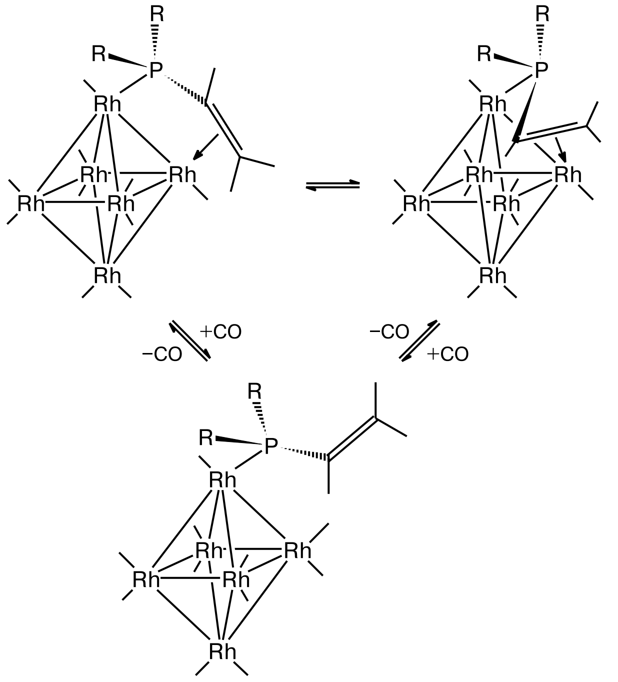


The rate constants and the activation parameters determined for the second stage of this reaction[7,74] indicate that dissociation of the carbonyl ligand from the κ^1-intermediate is the rate-determining step of the dimetal ring closure. An elegant proof of the dissociative mechanism for this reaction is the observation that the rates of formation of the dimetallic ring for three thienylphosphine ligands ($Ph_2P(C_4H_3S)$, $PhP(C_4H_3S)_2$, $P(C_4H_3S)_3$) with different local concentrations of the thienyl coordinating center in the κ^1-intermediates[7] are equal to each other within the experimental uncertainty, being determined only by the probability of formation of a coordination vacancy on the cluster core.

3. Hemilabile ligands in transition metal carbonyl clusters

It was found[7] that the thienyl and pyridyl substituents of the above-mentioned functionalized phosphines form strong bonds with rhodium atoms in the $Rh_6(CO)_{14}(\mu_2\text{-PX})$ cluster without exhibiting hemilability, which could have arisen due to reversible dissociation of the corresponding group with retention of the bond between the ligand and the cluster skeleton through the phosphorus atom. However, in similar clusters containing alkenylphosphine ligands ($Ph_2P((CH_2)_nCH=CH_2)$, $n = 0—3$),[40,75] the double bond of the alkenyl substituents dissociates reversibly to give a vacant coordination site, which can be occupied by other ligands (substrates), for example, CO, alkenes, and so on. We studied[40,75] the dynamic behavior of alkenylphosphine derivatives of $Rh_6(CO)_{16}$ in solutions by ^1H and ^{31}P NMR spectroscopy. The results show that the hemilability of alkenylphosphines is also manifested in the substitution of the coordinated double bond by two-electron ligands such as CO and in the change of the conformation of the coordinated alkenyl fragment. The conformations presented in the equilibrium are determined by the interaction of this fragment with the coordination environment of the phosphine. The change of the conformation in the $P—CH=CH_2$ fragment in the $Rh_6(CO)_{14}(\mu,\kappa^2-Ph_2P—CH=CH_2)$ cluster is a typical example of such equlibrium[40] (Scheme 8).

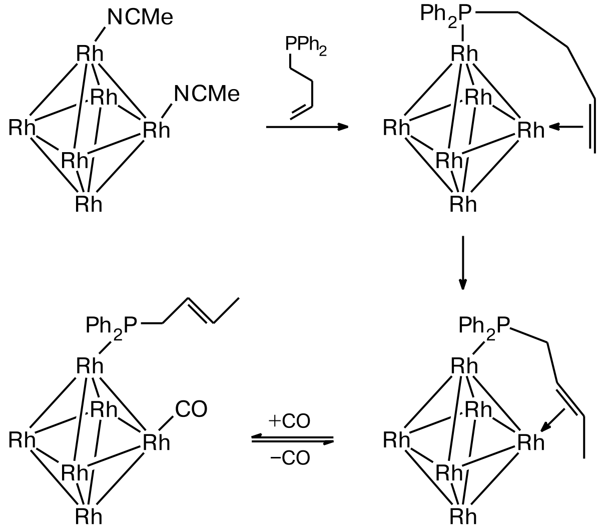
Scheme 8



When CO is present in the solution, both conformations rapidly arrive to the equilibrium with the cluster species containing the ligand coordinated only through phosphorus.

The hemilability phenomenon is manifested in a similar way (substitution of the alkenyl group by CO, conformational isomerization) in other alkenylphosphine ($Ph_2P((CH_2)_nCH=CH_2)$, $n = 1—3$) derivatives of $Rh_6(CO)_{16}$.[75] However, the reactivity of these compounds has a number of interesting features related to the high catalytic activity of rhodium carbonyl compounds. In particular, the terminal buten-3-yl and penten-4-yl substituents coordinated to the neighboring rhodium atom are readily and irreversibly isomerized into allylic fragments, thus giving the thermodynamically favorable conformation of the μ_2-alkenylphosphine bridge (Scheme 9).

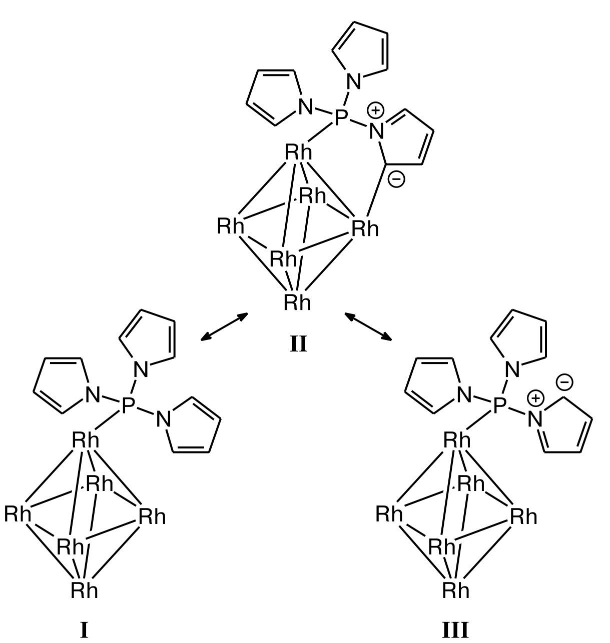
Scheme 9



The discovered isomerization of the coordinated terminal alkenyl substituent resembles to a certain extent the catalytic isomerization of hex-1-ene to hex-2-ene in the presence of the labile $Rh_6(CO)_{15}(NCMe)$ cluster,[77] indicating the possibility of using hemilabile $Rh_6(CO)_{16}$ derivatives in catalytic reactions of this type. Preliminary experiments on the catalytic isomerization of terminal alkenes with the hemilabile $Rh_6(CO)_{14}(\mu,\kappa^2-Ph_2PCH_2—CH=CH_2)$ cluster have shown that this compound actually exhibits a noticeable catalytic activity. The rate of catalytic isomerization is somewhat lower than that in the case of labile acetonitrile derivative, $Rh_6(CO)_{15}(NCMe)$,[77] but the catalyst activity remains almost constant for a rather long period of time. This behavior of the catalytic system points to a higher stability of the active form of the hemilabile catalyst, $\{Rh_6(CO)_{14}(\eta^1-Ph_2PCH_2—CH=CH_2)\}$, compared to the coordinatively unsaturated intermediate, $\{Rh_6(CO)_{15}\}$, generated upon dissociation of acetonitrile from $Rh_6(CO)_{15}(NCMe)$.

Noteworthy are also the unusual ways of coordination and hemilabile behavior of "usual" ligands, first discovered in rhodium[74] and ruthenium[6] clusters. The reaction of tris(pyrrolyl)phosphine with $Rh_6(CO)_{14}(NCMe)_2$[74] results in the bridging coordination of the ligand through the phosphorus atom and the carbon atom of a pyrrolyl group; one way of correct description of this interaction involves resonance structures (Scheme10).

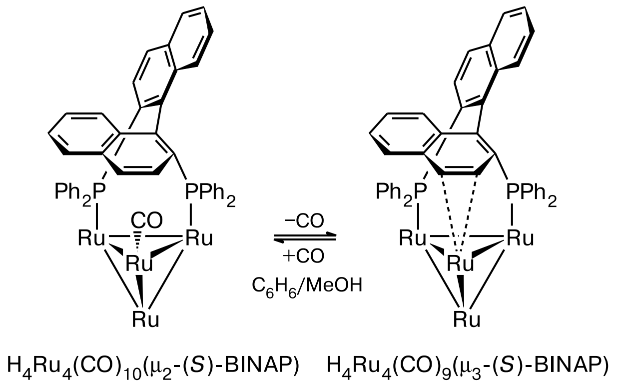
Scheme 10



In terms of this model, the donor-acceptor bond between the pyrrole substituent and the rhodium atom is determined by resonance structure **II** in which the carbon atom of the pyrrolyl fragment can serve as the two-electron donor to afford a stable 86-electron configuration of the octahedral cluster framework. The coordination of the pyrrolyl substituent to give the dimetallic ring is hemilabile; therefore, in the presence of CO in the solution, the structure with the phosphine ligand coordinated only through the phosphorus atom is regenerated reversibly and quantitatively. The kinetics and the mechanism of the reversible substitution of the hemilabile pyrrole group by a carbonyl ligand in the $Rh_6(CO)_{14}(PPyrr_3)$ cluster ($PPyrr_3$ is tris(pyrrolyl)phosphine) have been studied in the temperature range of 5—30 °C.[74] The forward and reverse reactions were found to yield a dissociative intermediate the nature of which is, however, not so simple as one might expect on the basis of the simplest model of formation of a coordination vacancy at the cluster core. The low entropy of formation of this intermediate implies a formation mechanism involving an essential rearrangement of the coordination sphere of the cluster, for example, the closure of additional carbonyl bridges, which decrease the entropy of this structure. The detailed investigation of the mechanism of this reaction has demonstrated, perhaps for the first time, the specific features of the kinetics of "usual" reactions in "unusual" clusters. From the viewpoint of application of hemilabile complexes of this type in catalysis, reliable information concerning the dissociative nature of the intermediates in the coordination—decoordination equilibria of group X appears highly significant. It is noteworthy that the formation of a coordination vacancy in the close vicinity of the hemilabile ligand upon dissociation of the group X ensures the possibility of effective influence of ligand characteristics on the product stereochemistry and opens up interesting prospects in the cluster asymmetric catalysis.

Another example of an unusual hemilabile coordination of a usual ligand is $H_4Ru_4(CO)_9(\mu_3$-(*S*)-BINAP) (BINAP is 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl),[6] obtained upon the removal of CO from the initial $H_4Ru_4(CO)_{10}(\mu_2$-(*S*)-BINAP) cluster, which contains a chiral diphosphine coordinated only through phosphorus (Scheme 11).

Scheme 11



Note that the presence of a typical labile ligand, MeOH, in the solution is a crucial condition for the preparation of the target product, which indicates once again an important role of ligands/substrates of this type in tuning the reactivity of carbonyl clusters.

The $H_4Ru_4(CO)_9(\mu_3$-(*S*)-BINAP) complex is the first example of a bridging μ_3-coordination of BINAP where a naphthyl fragment of the chiral ligand participates in the coordination. An interesting feature of the structure of this complex is the asymmetry of the tetrahedral Ru_4 cluster core in which all four ruthenium atoms have different ligand environments giving rise to a classical asymmetric tetrahedron. The stereoselectivity of the formation of the bridging μ_3-form is nearly quantitative, as only the *SS*-diastereomer with the *S*-configuration of the cluster core was detected among the reaction products. Note that such a stereoselectivity was found for the first time in reactions of cluster compounds. The interaction of the naphthyl fragment with the ruthenium atom can formally be considered as coordination of one double bond of this aromatic system. This bond is weak, in all probability, due to a substantial delocalization of the electron density within the naphthyl fragment as a whole and because of the deformation of the rather rigid binaphthyl fragment brought about by the bridging coordination of this ligand. As a consequence, ligands such as CO, acetonitrile, and alkenes readily replace the naphthyl fragment, thus returning the whole complex to a less strained conformation. According to the substitution stereochemistry, the incoming ligand (potential substrate of a catalytic reaction) appears in the close vicinity of the chiral binaphthyl helix of the ligand, which is typical, generally speaking, of reactions of hemilabile complexes. The asymmetry of the Ru_4 cluster core may be an additional factor influencing the chiral induction of this complex in catalytic reactions. The resultant action of the combination of these stereoinductions can hardly be predicted *a priori*; however, it is quite obvious that studies of this type of catalysts are topical. The catalytic activity and the chiral induction of the $H_4Ru_4(CO)_9(\mu_3$-(*S*)-BINAP) clusters in the hydrogenation of prochiral alkenes is now under study in our laboratory.

To summarize the brief review of the results obtained in the studies of cluster complexes containing labile and hemilabile ligands, a number of conclusions can be drawn.

1. The enhanced reactivity of these complexes in the substitution of labile ligands provides the possibility of their effective application for synthetic purposes, *e.g.*, in the directed synthesis of substances of a specified stoichiometry, in the preparation of kinetic products of ligand substitution, and in the assembly of unusual heterometallic cluster structures.

2. The possibility of stabilization of kinetic products using labile transition metal clusters makes it possible to study the structure and reactivity of the intermediates of these reactions, thus disclosing subtle details of the mechanisms of transformation of organic substrates in the coordination sphere of polynuclear complexes.

3. The chemistry of hemilabile transition metal clusters is still at its infancy; however, the prospects for using catalyst systems based on these clusters look rather interesting. The unusual ways of coordination of polydentate ligands in cluster compounds, in particular, heterometallic ones, and the asymmetry of the metal cluster core are new, in principle, structural properties, that may give rise to qualitatively new characteristics and enhance the known characteristics of the catalytic systems based on hemilabile cluster complexes.

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