

Review

Functional ligands and complexes for new structures, homogeneous catalysts and nanomaterials

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Abstract

In this account, we focus on results from our laboratory to illustrate recent developments in various fields of organometallic chemistry. Studies on hemilabile P,N donor ligands and on the ion-pair behaviour of cationic Pd(II) complexes have led to the full characterization of complexes with η^1 -allyl ligands. This still rare bonding mode for the allyl ligand in palladium chemistry allows facile insertion of CO into the Pd–C σ -bond, in contrast to the situation in related η^3 -allyl Pd(II) complexes. In order to develop new homogeneous catalysts for the selective dimerization and oligomerization of ethylene, a range of Ni(II) complexes have been prepared with new chelating P,N ligands where P represents a phosphine, phosphinite or phosphonite donor group and N a pyridine or oxazoline moiety. Finally, we shall examine bottom-up approaches to the formation of new nanomaterials of magnetic or catalytic interest by covalent anchoring of metal complexes and clusters into mesoporous materials using functional phosphine or alkyne ligands containing an alkoxysilyl group.

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1. Introduction

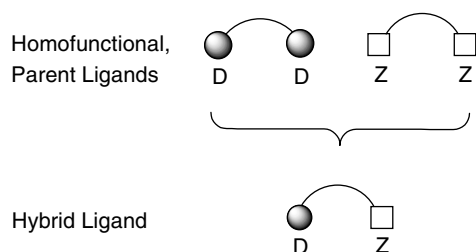
Over the past 40 years, organometallic chemistry has experienced major developments and given rise to numerous breakthroughs of considerable academic and industrial importance. Its scope and relevance to other areas of chemistry as well as the depth of understanding of its numerous facets are very impressive. Structural investigations and advanced theoretical studies make it now possible to analyze much more complex structures and reactivity patterns than ever before. However, a complete understanding of the interplay between electronic and steric properties and between structures (generally determined in the solid state for a collection of

molecules) and reactivity (observed in solution at the molecular level) often remains a challenge. This is largely due to the considerable diversity encountered within the Periodic Table and the fact that relatively small energy differences can translate into large variations of reactivity, particularly in catalysis.

Owing to the continuous developments in synthetic organic methodologies and discovery of new efficient tools, increasingly involving the (catalytic) use of metals, ligand design has become a major component of synthetic chemistry, including toward the search for new chemical or physical properties [1]. This is not limited to molecular chemistry and the templating effect of ligands is now commonly used for the preparation of mesoporous materials and new solid-state architectures [2]. Such an endeavour is motivated by the subtle control that ligands exert on the structure and reactivity of the

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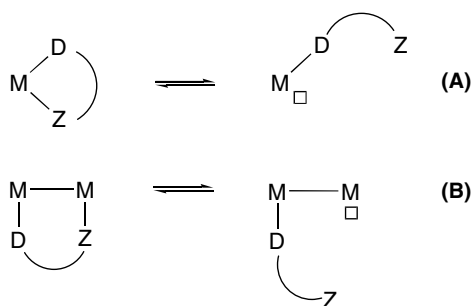


Scheme 1. A hybrid ligand contains at least two chemically different donor functions.

metal coordination sphere. In particular, ligands which contain significantly different chemical functions, such as hard and soft donors (often called hybrid ligands) find increasing use in chemistry because of the selectivity introduced in the metal–ligand interactions and their possible dynamic behaviour (see below) (Scheme 1) [3–6]. Such ligands may also be considered as derived from a pair of parent homofunctional ligands and it is usually observed that the “child” has gained new properties when compared to either of its “parents”.

New molecular interactions and properties may – even if discovered serendipitously – allow the emergence of useful concepts that help tailor molecular structures oriented towards a given property. This is for example the case with the concept of ligand hemilability, which finds numerous illustrations with hybrid ligands, and refers to systems containing at least one substitutionally labile donor function Z while the other donor group(s) D remain firmly bound to the metal(s) (Scheme 2) [3–6].

The term “hemilabile” was introduced ca. 25 years ago [7], although the phenomenon itself had been observed earlier [8]. It was first investigated in mononuclear metal complexes but this concept can easily be extended to dinuclear complexes [9] and metal clusters [10] where the labile coordination site does not need be at the metal ligated by the strong donor D but could be at an adjacent site [Scheme 2(B)]. It should be emphasized that hemilability is not an intrinsic property of the sole ligand but implies the metal–ligand couple. Although the reversibility of the formation/displacement of the Z → metal interaction represents an essential criterion of hemilability, the irreversible “opening” or



Scheme 2. Hemilabile behaviour of a hybrid ligand interacting with one or two metal centres.

“closing” of a chelate with participation of an external reagent is nevertheless a sign of chemical reactivity [3]. This aspect will be illustrated below.

The identification of the conditions for the occurrence of new bonding patterns, even for well-known ligands, is also of considerable importance since it may explain unusual situations or lead to new reactivity. Ligand design has been particularly effective in promoting catalytic reactions and fine-tuning of the stereoelectronic properties of the active site has met with considerable success, as exemplified with – but not limited to – the fields of olefin oligomerization and polymerization. More than 80 million tons polyethylene and polypropylene are produced annually and if most of them are prepared by Ziegler or Phillips polymerization catalysts based on early transition metals, complexes of the late transition metals arouse increasing interest in olefin oligomerization and polymerization [11].

Functional ligands are also central to the emergence of new mesoporous materials containing binding sites that allow the specific incorporation of metal complexes and thereby opening up new avenues for organic–inorganic hybrid materials and the bottom-up design of nanomaterials [2b]. The latter find increasing applications in various scientific areas ranging from biology and catalysis to molecular electronics [12].

The fields of current international research mentioned above should just be taken as illustrative of recent developments and cannot of course reflect the whole diversity of organometallic chemistry. The present account will focus on recent research in our laboratory that pertains to these aspects. We will discuss (i) how studies on the hemilability of P,N ligands led to the isolation and full characterization of rare Pd(II) complexes with η^1 -allyl ligands, (ii) the use of new hybrid P,N ligands in the selective Ni-catalyzed oligomerization of ethylene and (iii) a bottom-up approach to the covalent anchoring of metal complexes and clusters into mesoporous materials by using functional phosphine or alkyne ligands and the subsequent formation of new nanomaterials of magnetic or catalytic interest. We will therefore not intend to provide a complete coverage of the subjects but rather refer to more specific literature references that the interested reader will be invited to consult.

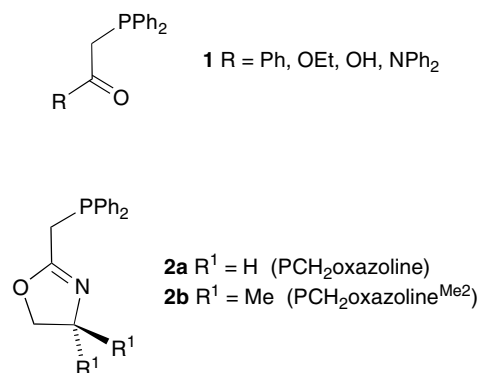
2. Functional, hemilabile P,N Ligands and Pd(II) η^1 -allyl complexes

Early motivations for studying metal complexes displaying hemilabile behaviour of their ligands mostly dealt with the reversible coordination, stoichiometric and catalytic activation and transport of small molecules [3–6]. This is related to the ability of hemilabile ligands to provide open coordination sites at the metal

during reaction, while their “masking” in the ground-state structure allows stabilization of reactive intermediates. Hemilability has been a very useful concept for the design of new systems oriented toward molecular activation and homogeneous catalysis, including hydrogenation, carbonylation or its reverse, hydroformylation, allylation, epoxidation, olefin (co)dimerization and copolymerization [3,4,6], functional materials and small molecule selective sensing, in particular of CO [5,13]. The difficulty in designing systems endowed with specific properties is largely due to the small activation energy involved in the dynamic processes which form the basis of hemilability, often of the order of 50 kJ/mol.

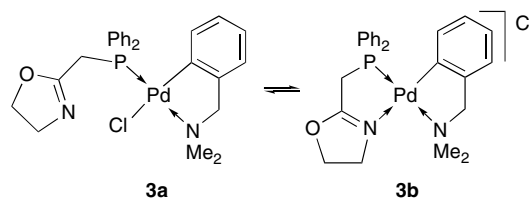
In a recent review article, we have examined some extensions of the hemilability concept, and illustrated properties of phosphorus ligands containing one or more oxazoline moieties and shown why the combination of these two categories of donor groups appeared particularly fruitful [3].

As part of our studies on the coordination chemistry and catalysis with functional phosphine ligands such as β -phosphino-ketones [14], -ester [8], -acids [15], or -amides [16] of type **1**, we became interested in incorporating oxazoline moieties in such systems, as shown with **2**.

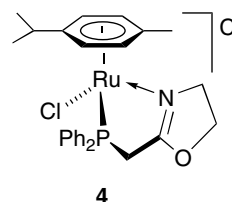


For an evaluation of their coordination properties, we first considered four-coordinated palladium(II) complexes and generally observed the formation of strong P,N chelates in complexes such as [PdMe(Cl)(PCH₂oxazoline)] and [PdMe(SMe₂)(PCH₂oxazoline)] (O₃SCF₃) [17]. The bidentate coordination of the ligand strongly differentiates the position *trans* to P and N and, as observed in the copolymerization of CO and ethylene [18], orients the incoming substrate and the growing polymeric chain in a mutual *cis* arrangement [17].

Whereas a fast dynamic equilibrium was observed between the Pd(II) complexes **3a** and **3b** (Scheme 3) [19], the PCH₂oxazoline ligand in compound **4**, which contains a stereogenic metal centre, does not exhibit any hemilabile behaviour although the chloride ion could have competed for coordination to the metal [19].

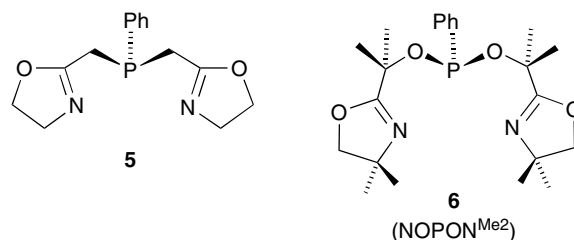


Scheme 3. Reversible chelation of the PCH₂oxazoline ligand.

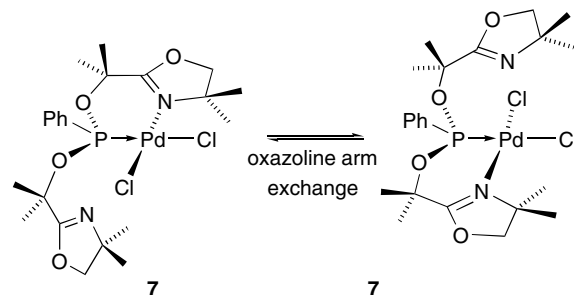


These differences further illustrate the tuning of the coordination behaviour of the phosphinooxazoline ligand by the choice of the metal.

Since the PCH₂oxazoline ligand **2a** shows a strong propensity to form stable chelates and is fairly inert toward competition from external ligands, we introduced the possibility of an intramolecular competition between the two equivalent oxazoline moieties in the new N,P,N type ligand bis(oxazoliny)phenylphosphine **5** [20].



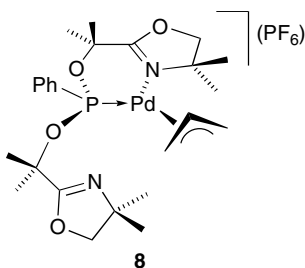
This idea was extended to the case of the bis(oxazoline)phenylphosphonite ligand **6** which exhibits a dynamic bidentate coordination mode in compound **7** where the two oxazoline arms are in fast exchange, as shown by variable temperature NMR spectroscopy (Scheme 4) [21]. Introduction of the oxygen spacer between the P and C atoms of **5** not only modifies the size of the chelate ring formed by coordination of **6** but also affects the electronic properties of the P donor.



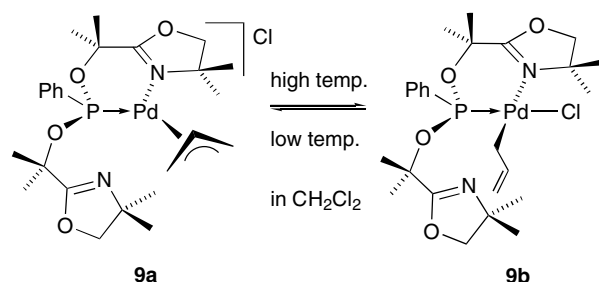
Scheme 4.

This dynamic process prompted us to investigate the behaviour of $\text{NOPON}^{\text{Me}_2}$ complexes in which an additional ligand can also display changes in hapticity. This is the case of the allyl ligand which can adopt either a η^1 - or η^3 -bonding mode. Its transition metal complexes display a rich chemistry and have a considerable importance in homogeneous catalysis because they often represent key intermediates in C–C coupling reactions [22]. Whereas the η^3 bonding mode is the most general for this ligand, some η^1 -allyl complexes have been isolated, mainly with platinum [23], rhodium [24], iridium [25], or early transition metals [26]. This η^1 -allyl type of bonding to a transition metal affects the stereochemistry of reactions proceeding via allyl intermediates and it is well known in Pd-allyl chemistry that a η^3 - η^1 - η^3 dynamic behaviour may be operative which can be either detrimental to, or required for enantioselection [22]. It is therefore essential to unambiguously identify the bonding mode of the allyl ligand in a complex in order to understand or rationalize its reactivity. In Pd chemistry, the η^3 -bonding mode of the allyl ligand is the rule and when we began our investigations, few Pd complexes containing η^1 -allyl ligands had been characterized in solution [27], and even fewer in the solid state [28]. Although the idea that a strong and rigid tridentate ancillary ligand coordinated to a Pd(II) centre should trigger the occurrence of the rare η^1 -bonding mode of the allyl ligand is completely logical [27,28], we could show that this is not a prerequisite [21].

To study the mutual influence of the allyl ligand and $\text{NOPON}^{\text{Me}_2}$ **6**, we first investigated the behaviour of complex **8** obtained from the reaction of $\text{NOPON}^{\text{Me}_2}$ with 0.5 equivalent of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})_2]$ and one equivalent of NH_4PF_6 . A dynamic exchange occurs in **8** between the two oxazolines, the allyl ligand remaining coordinated in an η^3 -fashion over the temperature range 200–395 K [21].



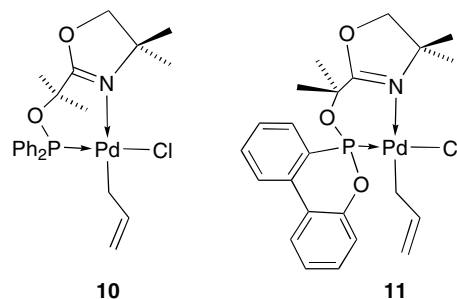
We then examined the situation where the chloride ligand from the Pd precursor ($[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})_2]$) has not been replaced by PF_6^- and could therefore influence the dynamic behaviour of the ligands by coordination to the metal. Spectroscopic data showed that in complex **9**, the $\text{NOPON}^{\text{Me}_2}$ ligand remains a dynamic P,N chelate, while the additional fluxional behaviour of the allyl is related to the presence of the chloride ion (Scheme 5).



Scheme 5. Hapticity change of the allyl ligand induced by chloride coordination.

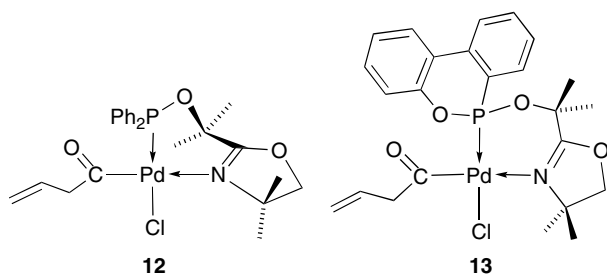
Competition between the preferred η^3 -bonding mode of the allyl ligand and chloride coordination occurs. This dynamic behaviour is solvent-dependent and going from CH_2Cl_2 to toluene displaces the equilibrium toward a static η^1 -bonded allyl ligand [21].

The ligand arrangement and geometry of complex **9b** was confirmed by solid-state ^{13}C NMR spectroscopy and X-ray diffraction. This represented the first crystal structure of a *cis* chloro η^1 -allyl transition metal complex [21]. Since the dangling oxazoline arm in **7** or **8** was responsible for the dynamic behaviour of the complex, we wanted to examine whether it played any significant role in promoting the η^1 -allyl bonding mode in **9b**. We therefore replaced one arm of the ligand with a phenyl group and obtained with the new bidentate ligand 1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-1-methyl diphenyl phosphonite [29], abbreviated NOP^{Me_2} , the new η^1 -allyl chloro Pd(II) complex **10** in high yield. This complex was fully characterized by an X-ray diffraction study [30].



A similar bonding situation of the allyl ligand could also be generated in the Pd(II) complex **11** with the new bidentate, racemic ligand, abbreviated $\text{NOPO}^{\text{Me}_2}$, which was prepared by reaction between 6-chloro-6H-dibenz[*c,e*][1,2]oxaphosphorin and the lithium alcoholate derived from 4,4-dimethyl-2-(1-hydroxy-1-methylethyl)-4,5-dihydrooxazole [31]. Consistent with Pearson's anti-symbiotic effect [32], in all three structures (**9b**, **10**, **11**) the η^1 -allyl ligand is in a *trans* position with respect to the nitrogen donor, a ligand of weaker *trans* influence than phosphorus. A similar situation was also recently observed by Kollmar and Helmchen [33].

Bubbling of CO through a solution of **10** or **11** in toluene led to the formation of the insertion products **12** and **13**, respectively [30,31].



These carbonylation reactions under very mild conditions provide an interesting contrast with the inactivity of $[\text{Pd}(\eta^3\text{-2-MeC}_3\text{H}_4)\text{PdCl}(\text{PMe}_3)]$ [34] and support the view that CO insertion into η^3 -allyl palladium cationic complexes occurs via first coordination of the counterion to form an η^1 -allyl intermediate. This hypothesis was presented by Ozawa et al. [34], although they had not succeeded in isolating such η^1 -allyl intermediates. In contrast to e.g. *trans*- $[\text{Pd}\{\text{C}(\text{O})\text{CH}_2\text{CH}=\text{CH}_2\}\text{Br}(\text{PMePh}_2)_2]$, complex **12** exhibits a remarkable stability towards decarbonylation or decomposition, which is slightly less pronounced for **13**.

The considerable influence that the counterion and solvents exert on the bonding mode and reactivity of the allyl ligand was clearly demonstrated by these carbonylation reactions. The halide ligand plays a central role in stabilizing the η^1 -allyl bonding mode and its abstraction immediately leads to formation of η^3 -allyl palladium cationic complexes [21,30,31]. Other strongly bound ligands, such as alkyl or aryl ligands, could lead to similar stabilization of the η^1 -allyl bonding mode. Appropriate bidentate chelating ligands are therefore suitable to stabilize η^1 -allyl Pd complexes and this still rare bonding situation [21,28,30,31,33] may occur more often than previously expected in numerous stoichiometric or catalytic transformations involving Pd(II) allyl complexes. These studies have established that the paradigm for a strong tridentate ligand being required for a stable η^1 -allyl bonding mode in Pd(II) chemistry should be reconsidered.

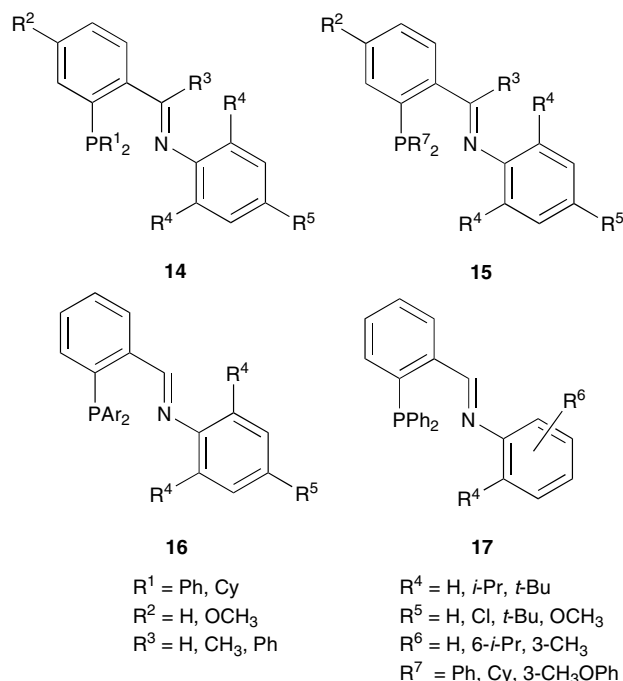
3. Nickel complexes with functional P,N chelates for the catalytic oligomerization of ethylene

The electronic and steric properties of the donor groups in P,N ligands can be easily varied and this versatility explains why they are much used in coordination chemistry and homogenous catalysis [3,4,22a,35]. We have seen above examples of their hemilabile behaviour and of their influence on the nature of the bonding of their coligands, such as the allyl group. We will now dis-

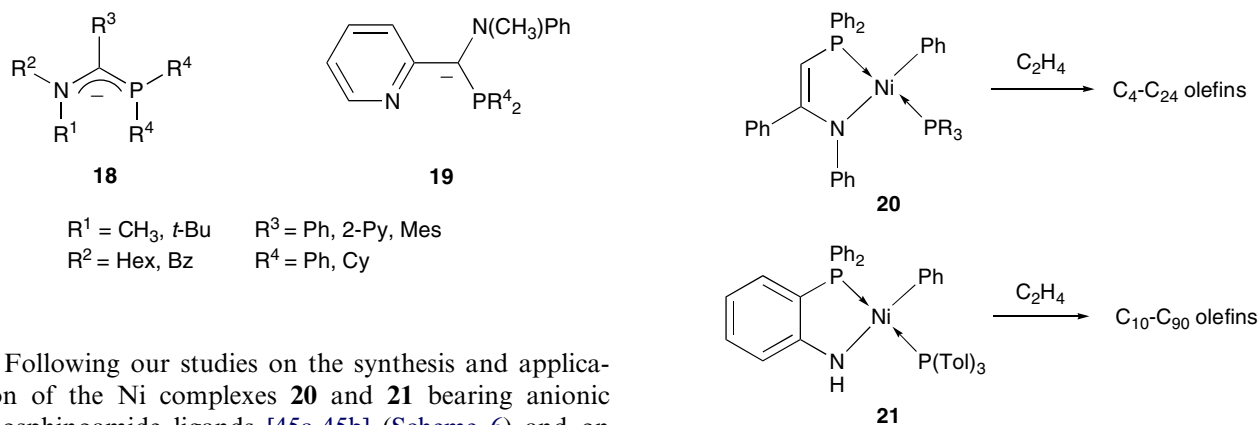
cuss, with selected examples, properties of their Ni(II) complexes for the catalytic dimerization and oligomerization of ethylene, which we studied in collaboration with the Institut Français du Pétrole.

This reaction is the basis of major industrial processes developed by BP Amoco and Shell (SHOP process) using aluminium alkyls and neutral nickel phosphine complexes as catalysts, respectively [11,36]. α -Olefins in the C_4 – C_{16} range are particularly desirable because they are used for the preparation of detergents (C_{12} – C_{16}), lubricants (C_{10} – C_{12}), plasticizers (C_6 – C_{10}), and as comonomers for the synthesis of linear low density polyethylene (C_4 – C_6). The dimerization of olefins catalyzed by transition metal complexes has therefore gained considerable industrial relevance as also exemplified by the IFP Dimersol[®] process [37]. The biphasic nature of the SHOP process generates increasing interest for the use of ionic liquids in the catalytic dimerization and oligomerization of ethylene [38].

Phosphinoimine ligands have only recently attracted attention for the late transition metal-catalyzed oligomerization, polymerization and copolymerization of ethylene [11,39]. The neutral phosphinoimine ligands **14**–**17** were developed by the Eastman Chemical Corporation **14** [40], Shell **15** [41], Rush et al. **16** [42] with different substituents on either the phosphorus or the nitrogen donor and Asahi Industries **17** [43] with only one bulky substituent in the *ortho* position to the imine nitrogen.



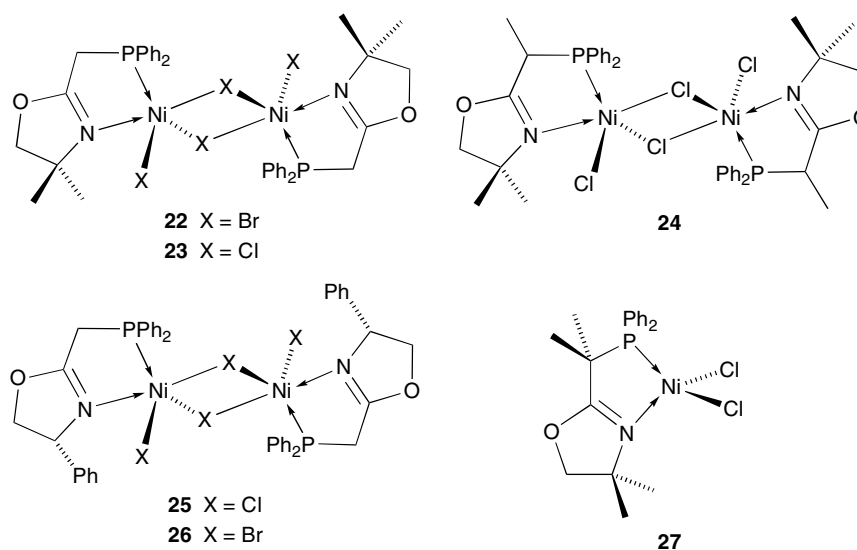
The anionic P,N systems **18** and **19** were used by Symyx Technologies in the oligomerization or polymerization of α -olefins [44].



Scheme 6.

Following our studies on the synthesis and application of the Ni complexes **20** and **21** bearing anionic phosphinoamide ligands [45a,45b] (Scheme 6) and on SHOP-type P,O systems [36,45a,45c] for the oligomerization of ethylene, we were interested in obtaining short chain oligomers using Ni complexes with other P,N donor ligands while using the smallest possible amount of added cocatalyst. The stronger binding ability of the phosphine group should lead to improved thermal sta-

the strong influence of a substituent on the carbon atom α to P. The coordination geometry around the Ni(II) centre in solution was determined by the Evans method to be trigonal bipyramidal in **22–26** and tetrahedral in **27** [46].



bility of the catalysts. Furthermore, the use of nonenzymizable imine donors should also be beneficial to catalyst thermal stability [39c,39f]. For the nitrogen donor function, we have focused on oxazoline and pyridine rings which fulfill these requirements.

3.1. Phosphino-oxazoline Ni(II) complexes

An additional advantage of phosphinooxazolines is that their stereoelectronic properties can be modulated in a systematic manner [46]. The oxazoline heterocycle provides a rigid backbone with the possibility of introducing chirality and steric hindrance.

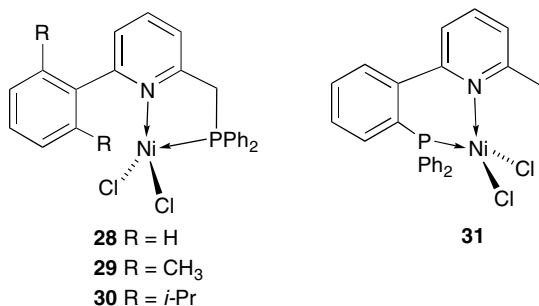
Whereas complexes **22–24** are dinuclear complexes with distorted trigonal bipyramidal Ni(II) centres, **27** is a mononuclear, tetrahedral complex, which underlines

In the catalytic conversion of ethylene, these complexes afforded mostly dimers and trimers [46]. Complex **22** yielded a turnover frequency of 36 300 mol C₂H₄/mol Ni·h in the presence of 14 equiv of AlEtCl₂ as cocatalyst. In the presence of only 6 equiv of AlEtCl₂, the Ni complexes **24** and **27** afforded TOF values of 38 100 and 45 900, respectively, higher than that of 27 200 mol C₂H₄/mol Ni·h obtained with [NiCl₂(PCy₃)₂] taken as a reference. In the presence of MAO, complexes **22–26** and [NiCl₂(PCy₃)₂] were inactive whereas **27** showed a TOF of 7900 mol C₂H₄/mol Ni·h and a selectivity for 1-butene within the C₄ fraction of 38%. It was suggested that some incorporation of the butene formed occurs during chain growth (consecutive reaction) [46]. The limited selectivity for α -olefins could result from (i) reversible β -H elimination after ethylene insertion,

followed by reinsertion with the opposite regiochemistry and chain transfer to give 2-butene, or (ii) a re-uptake mechanism leading to isomerization of 1-butene. The ability of Ni(II) complexes to isomerize α -olefins is well known [47] and has again been recently evidenced in the case of phosphino-pyridine chelates [48].

3.2. Phosphino-pyridine Ni(II) complexes

Only few complexes containing phosphino-pyridines have been reported for their application in the oligomerization or polymerization of α -olefins [11,49,50]. In view of the decisive influence of the ligands and, in particular, of the steric hindrance of their substituents in controlling oligomerization versus polymerization, we prepared the mononuclear Ni(II) complexes **28–31** containing phosphino-pyridines which possess the rigid and chemically inert structure characteristic of a pyridine heterocycle and, at the same time, allow easy variation of the steric hindrance around the metal centre [49]. Modifying the ligand basicity also provides an excellent tool to influence the catalytic properties. These ligands have different substituents in the *ortho* position of the pyridine ring whereas in another study we have focused on substituent effects in the one carbon connection between the *ortho*-pyridine carbon and the PPh₂ group [49a].

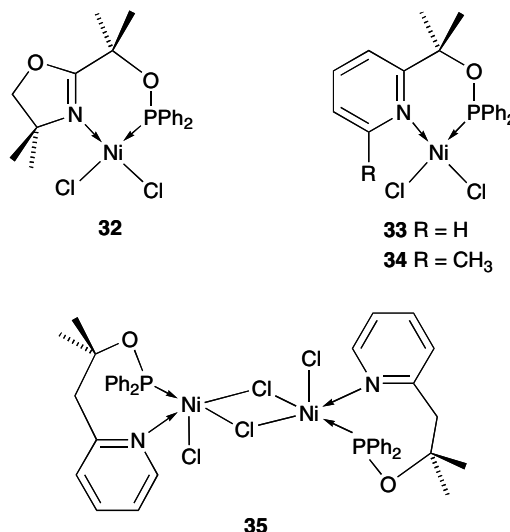


Complexes **28–31** are paramagnetic in solution, as determined by the Evans method. Whereas they were inactive in the presence of MAO as a cocatalyst, they provided activities up to 61 000 mol C₂H₄/mol Ni·h (**30**) in the presence of only 6 equivalents of AlEtCl₂. The selectivities for C₄ oligomers were as high as 92% for **31** in the presence of 2 equivalents of AlEtCl₂. Similar activities were obtained by other groups in the dimerization of ethylene and propene, but only when using between 200 and 400 equiv of cocatalyst [51].

3.3. P,N-type phosphinite Ni(II) complexes

In order to investigate the potential of P,N-type phosphinite ligands in the catalytic oligomerization of ethylene and compare them with phosphino-oxazolines and phosphino-pyridines discussed above, we prepared

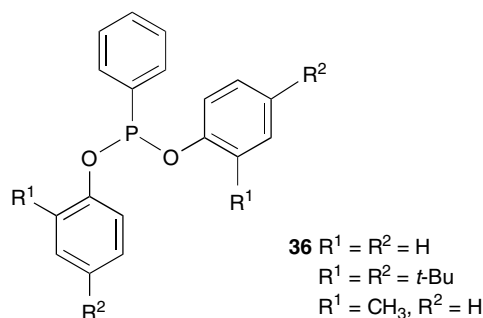
the Ni-complexes **32–35** [29a]. The basicity of the nitrogen donor is increased by replacing the oxazoline heterocycle with a pyridine and the ring size of the metal chelate increases from six in **33** to seven in **35**.



In the presence of MAO and AlEt₃ only decomposition of the complexes was observed. However, complexes **32–35** provided activities up to 50 000 mol C₂H₄/mol Ni·h (**34, 35**) in the presence of 6 equivalents of AlEtCl₂, superior to that of [NiCl₂(PCy₃)₂]. The selectivities for ethylene dimers were as high as 92% (**32, 33**) [29a].

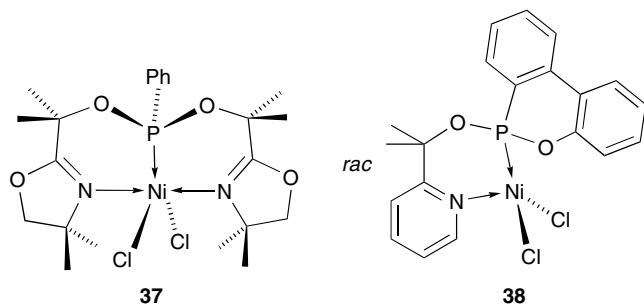
3.4. P,N-type phosphonite Ni(II) complexes

Only few examples of phosphonite complexes have been reported for the catalytic oligomerization or polymerization of α -olefins [11,52]. These include studies by the Mitsubishi Chemical Corporation with nickel complexes prepared in situ with the monodentate phosphonites **36** for the dimerization of *trans*-2-butene [53].



The new nickel phosphonite complexes **37** and **38** were synthesized in 75% and 80% yields and the X-ray structure determination of **37** established the trigonal bipyramidal coordination geometry around the Ni(II)

centre, which is in accordance with the paramagnetism of the complex [52].



In the presence of 1.3 equivalents of AlEtCl_2 , complex **37** showed an activity of 17000 mol C_2H_4 /mol $\text{Ni}\cdot\text{h}$ whereas **38** was inactive. With 2 equivalents of AlEtCl_2 , turnover frequencies of 26500 mol C_2H_4 /mol $\text{Ni}\cdot\text{h}$ (**37**) and 44200 mol C_2H_4 /mol $\text{Ni}\cdot\text{h}$ (**38**) were obtained. Activities of up to 31400 mol C_2H_4 /mol $\text{Ni}\cdot\text{h}$ (**37**) and 57300 mol C_2H_4 /mol $\text{Ni}\cdot\text{h}$ (**38**) were observed when using 6 equivalents of cocatalyst. These complexes showed high selectivities, up to 76% (**37**) and 82% (**38**) for ethylene dimers in the presence of only 2 equivalents of AlEtCl_2 . Selectivities of 94% or 90% for the ethylene dimers and of 19% or 17% for 1-butene within the C_4 fraction were observed when MAO was used as cocatalyst with complexes **37** and **38**, respectively.

Comparative studies with Ni(II) complexes of N,O ligands of the type pyridine-alcohol or oxazoline-alcohol have shown that a less basic nitrogen moiety (oxazoline vs. pyridine) led to an increased α -olefin selectivity and to higher turnover frequencies [54]. The fact that complex **38** with a pyridine donor is more active and selective for 1-butene than **37** which contains an oxazoline donor could be due to the presence of a cyclic phosphonite moiety in the former. However, it remains difficult to draw general conclusions and it was recently found with other Ni(II) complexes that phosphinito-pyridine chelates led to more active catalysts than phosphinito-oxazolines, in which the nitrogen donor is less basic [29a].

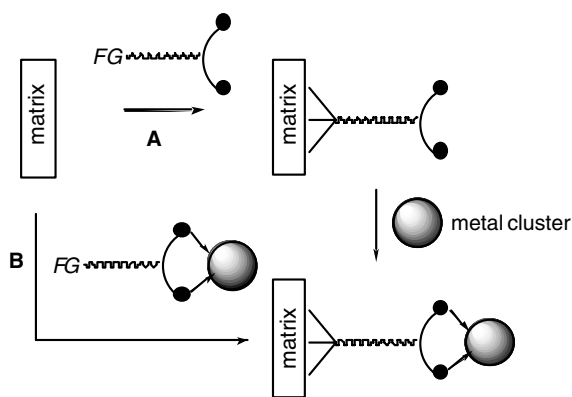
The ligand or packing effects that are responsible for structural variations in the solid state cannot be easily extrapolated to the structures in solution and make it difficult to strictly relate the catalytic performances of a Ni(II) complex to its coordination geometry, in particular since structures intermediate between square-planar and tetrahedral are often encountered. Recent theoretical studies on the structures and energies of the transition states for the insertion of the $\text{C}=\text{C}$ bond of various (functional) olefins into the metal-carbon bond of generic models for Ni(II) and Pd(II) complexes with diimine (Brookhart) and salicylaldiminato (Grubbs)

ligands have shown that nickel systems show lower insertion barriers than their palladium counterparts owing to their easier access to the required tetrahedral transition state [55].

4. Functional ligands for anchoring of metal clusters toward nanomaterials

Nanomaterials bridge the gap between the molecular scale and the solid state. Nanostructured metals, in particular bimetallic nanoparticles, are attracting considerable interest in view of their new and/or improved properties compared to conventional materials [12]. Numerous molecular clusters have at least one dimension in the nanometer range and are ideally suited for a bottom-up approach toward unique nanomaterials [56]. Such molecules may be confined in the cavities of meso- or nanoporous inorganic matrices, and subsequent thermal activation under inert atmosphere can lead to the stabilization of highly dispersed metal particles whose coalescence into larger, ill defined aggregates can thus be minimized or completely prevented. This has implications for the fabrication of optical materials, electronic devices [12f,12g,56,57] and the preparation of new generations of heterogeneous catalysts whose selectivity is expected to critically depend on the size and dispersion of the metal particles and also on the shape of the cavity in which they are embedded [12i–12l,58]. Early work on the impregnation of silica or alumina supports with organic solutions of structurally characterized Mo–Pd or Fe–Pd mixed-metal carbonyl clusters demonstrated for the first time that the particles resulting from thermal activation were bimetallic and endowed with catalytic properties superior to those of conventional catalysts containing these metals in the same atomic ratios [58c,58d]. The catalytic reaction investigated was the carbonylation of organic nitro derivatives to isocyanates, a method that avoids the use of phosgene.

More recently, we have focused our work on the preparation and characterization of molecular precursors based on cobalt-containing carbonyl clusters because of the anticipated interesting magnetic properties of the resulting nanomaterials. In collaboration with the Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS) and the Laboratoire de Matériaux Minéraux (Ecole Nationale Supérieure de Chimie de Mulhouse) we could show that impregnation of a mesoporous xerogel or of MCM-41 [59] with an organic solution of the heterometallic cluster $[\text{NEt}_4][\text{Co}_3\text{Ru}(\text{CO})_{12}]$, and subsequent thermal treatment led to highly dispersed magnetic nanoparticles under milder conditions than when conventional metal salts are used as precursors [60].



Scheme 7. Alternative approaches for the anchoring of metal clusters onto inorganic matrices. FG=functional group.

4.1. Covalent anchoring of the molecular clusters on matrices

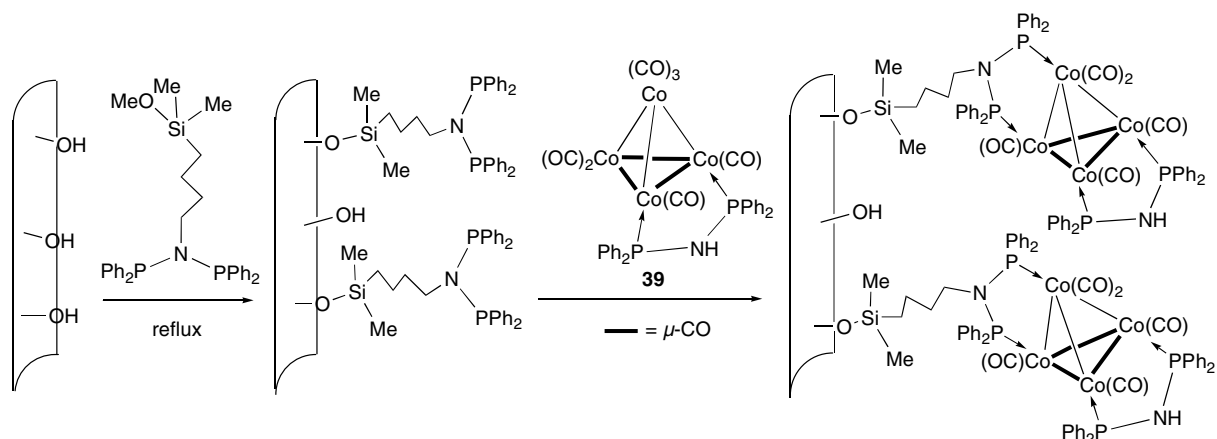
In addition to the impregnation techniques, it appears attractive to develop methods of chemical anchoring which by providing a stronger link between the molecular precursor and the host matrix could prevent leaching and lead to more homogeneous distributions. Bifunctional ligands may be used for grafting the molecular metal clusters into the pores of the matrix [61]. We have begun to explore and compare general approaches to this aim, by linking first one end of the ligand to the inorganic matrix and then react the other functional extremity with the molecular cluster, or first prepare a functionalized cluster and react it with the host matrix to generate the covalent linkage. These strategies are illustrated in Scheme 7, (A) and (B), respectively.

The short-bite alkoxy-silyl-functionalized diphosphine ligands $(\text{Ph}_2\text{P})_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ and $(\text{Ph}_2\text{P})_2\text{N}(\text{CH}_2)_4\text{SiMe}_2(\text{OMe})$ and $(\text{Ph}_2\text{P})_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ [62,63] derived from dppa (dppa = $\text{Ph}_2\text{PNHPPH}_2$) have been prepared and used to derivatize the pore walls of nano-

porous alumina membranes [62]. The considerable advantage of such short-bite diphosphines over monophosphines resides in the increased stability of the system owing to the formation of a $\overline{\text{MPNPM}}$ five-membered ring.

The covalent attachment of the diphosphine ligands to the inorganic matrix through formation of strong Si–O bonds allows subsequent reaction between the phosphorus donors and the cluster. The derivative $[\text{Co}_4(\text{CO})_{10}(\mu\text{-dppa})]$ (**39**) was selected because it is more stable than the parent $[\text{Co}_4(\text{CO})_{12}]$ and has a more selective substitution chemistry (i.e. the functional diphosphine and dppa bridge opposite metal–metal bonds, Scheme 8). We have observed that this approach [Scheme 7, (A)] was often more successful than method (B) because the larger size of the substituted cluster with its ligand shell may hinder its entering and filling the nanopores of the matrix.

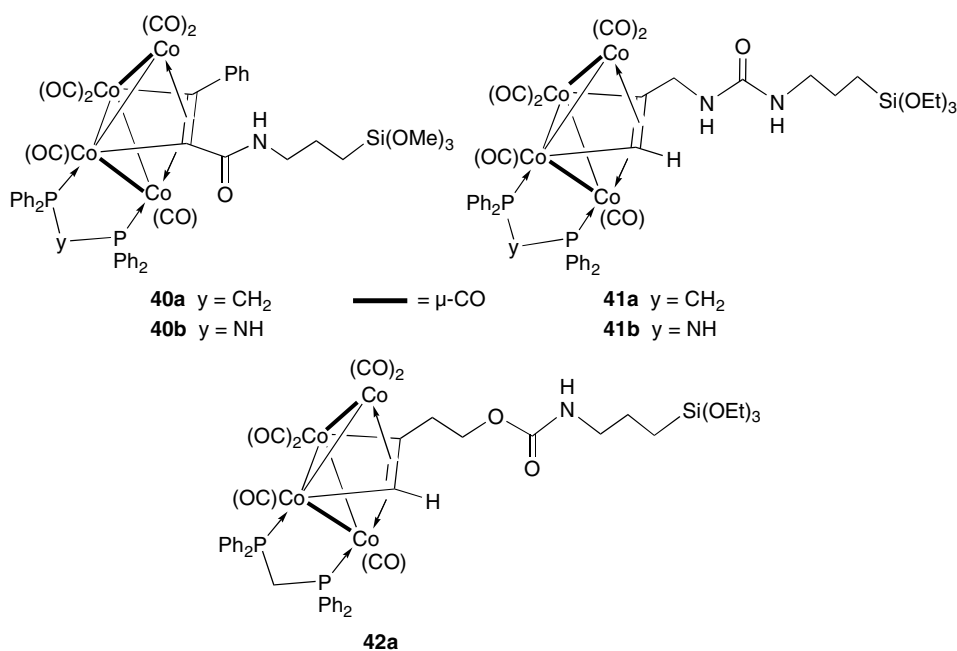
We have also functionalized an ordered mesoporous silica of the type SBA-15 [64], which is a MCM-41 type material with larger pores (about 90 Å) and walls, with $(\text{Ph}_2\text{P})_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$. The molecular cluster to be tethered [Scheme 7, (A)] was again $[\text{Co}_4(\text{CO})_{10}(\mu\text{-dppa})]$ (**39**) and subsequent thermal treatment of the organometallic hybrid mesoporous silica led to pure nanocrystalline Co_2P particles that were more regular in spatial repartition, size and shape than when a silica xerogel, obtained by the sol–gel process, was used [65]. The preparation of transition-metal phosphides is generally not easy and requires direct combination of elements at high temperature [66], reaction of toxic phosphide with metal or metal hydride [67] or metal organic chemical vapour deposition techniques [61c]. New approaches for the synthesis of Co_2P nanocrystals have been recently developed. Xie et al. [68] have prepared nanocrystalline Co_2P , Ni_2P and Cu_3P by a direct solvothermal reaction of metal halides with yellow phosphorus, at 80–140 °C, with ethylenediamine as solvent. They obtained plate-like



Scheme 8. Anchoring of the dppa-stabilized Co_4 cluster **39** onto functionalized alumina membranes [62].

Co_2P particles of about 500 Å diameter, with a wide size distribution. Lukehart et al. [61c,69] have obtained nanoclusters of metal phosphide confined into silica xerogels, such as Fe_2P , RuP , Pd_5P_2 , PtP_2 , Ni_2P and Co_2P , by covalent incorporation into a xerogel of metal complexes containing a bifunctional ligand with an alkoxy silane function and one or more phosphine groups, followed by a thermal treatment under H_2 . Metal phosphides

stabilization of the cluster against fragmentation is highly desirable and was achieved with the short-bite diphosphine ligands $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, $\text{Ph}_2\text{PNHPPH}_2$ and $(\text{Ph}_2\text{P})_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ [74b]. As hoped, we could show that combining the beneficial basicity of phosphine donors and the bridging ability of these diphosphine ligands leads to functional alkyne-substituted clusters, **40–42**, more stable than when starting from $[\text{Co}_4(\text{CO})_{12}]$.



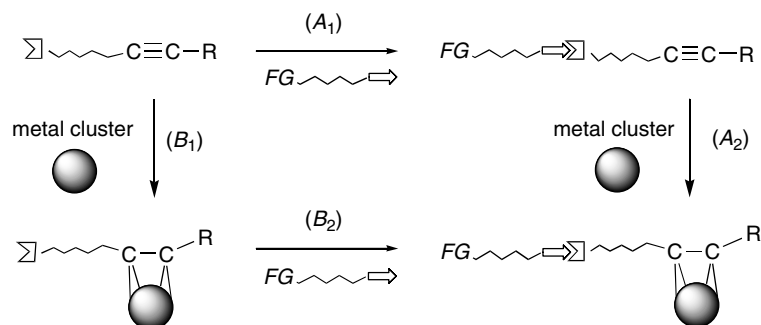
are very interesting as semiconductors or phosphorescent, magnetic or electronic materials [70] and Co_2P has applications in catalytic hydrodenitration [71].

In the previous example, a covalent linkage has been established between the ligand and the matrix but dative bonds connect the ligand to the cluster. Generating covalent bonds between the ligand and the cluster represents an attractive extension for improved stability. We have used the sol-gel process [72] to incorporate mono- and bimetallic species into an inorganic matrix by condensation of alkoxy silyl-substituted metal alkyl complexes, which contain a strong $\text{M}-\text{C}$ σ -bond, with $\text{Si}(\text{OEt})_4$ (TEOS) [73]. In the search for other ligands that would form strong, covalent bonds with the metal cluster and could be amenable to condensation with an inorganic matrix or its precursor (e.g. TEOS), we prepared the new functional alkynes of variable chain length $\text{PhC}\equiv\text{CC}(\text{O})\text{NH}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$, $\text{HC}\equiv\text{CCH}_2\text{NHC}(\text{O})\text{NH}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ and $\text{HC}\equiv\text{C}(\text{CH}_2)_2\text{OC}(\text{O})\text{NH}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ because interaction of their carbon-carbon triple bond with two or more metal centres should lead to the formation of strong, covalent metal-carbon σ bonds [74]. Whereas reactions of $[\text{Co}_4(\text{CO})_{12}]$ with alkynes are known to afford butterfly clusters, prior

We have explored two strategies to covalently link a metal cluster to a functional alkyne: either by the reaction of the cluster with the desired functional alkyne [Scheme 9, route (A_2)] or by the functionalization of an organic backbone already linked to the metal cluster [Scheme 9, route (B_2)] [74a].

These two methods may or may not be used indiscriminately and comparative studies of their respective advantages/disadvantages should be particularly instructive. In all cases, the chemo- and regioselectivity of the reactions represent central issues to be investigated. It appeared to us that, to the best of our knowledge, strategy ($B_1 + B_2$) had not been previously applied to cluster chemistry. These two approaches were compared using the mixed-metal cluster $[\text{NET}_4][\text{RuCo}_3(\text{CO})_{12}]$ as precursor [74a]. This cluster offers additional advantages over the isoelectronic cluster $[\text{Co}_4(\text{CO})_{12}]$ as it allows a study of the metalselectivity of the reaction between the cluster and the alkyne and provides an access to mixed-metal nanomaterials.

Furthermore, using alkynes with $-\text{SH}$ or $-\text{SR}$ end groups (Scheme 9) will allow deposition of cluster assemblies on gold surfaces. These aspects are the subject of ongoing work.



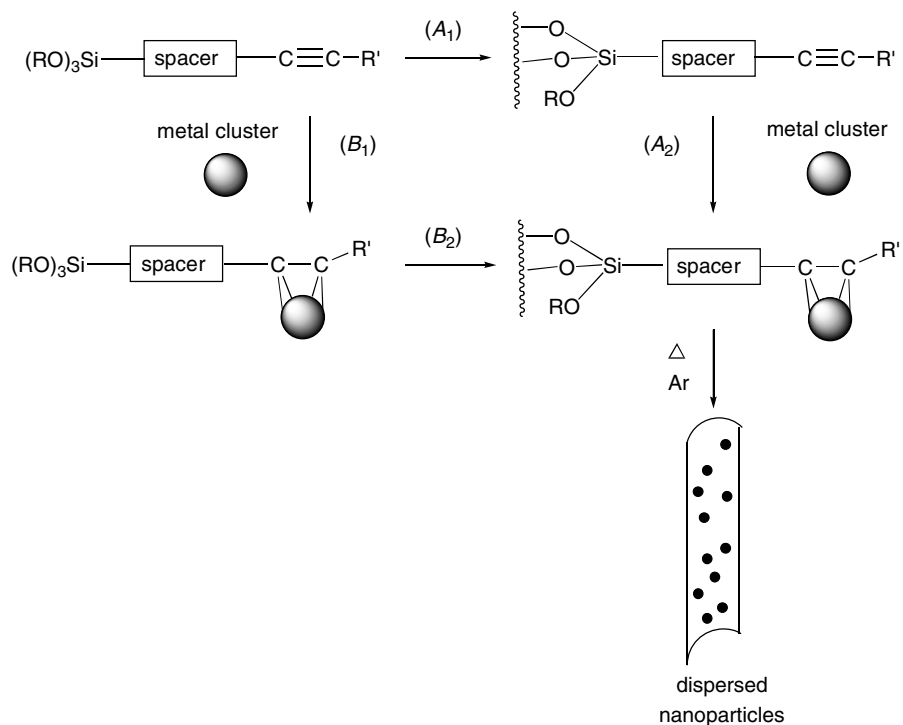
Scheme 9. Complementary strategies for the incorporation of functional alkynes into metal clusters. $FG = -Si(OR)_3$ or $-SR$ [74a].

4.2. Formation of bimetallic particles by the sol-gel method

We have seen above how well-defined molecular clusters can be obtained which contain a covalent linkage between the metals and the functional ligand. The alkoxyethyl function of the latter can be subsequently condensed with the surface OH groups of the matrix to generate the covalent tethering. This corresponds to the strategy $(B_1) + (B_2)$ depicted in Scheme 10. An alternative approach is also conceivable: first attach the $-Si(OR)_3$ end of the ligand to the inorganic matrix [Scheme 10, (A_1)] and then react its alkyne function with the molecular cluster [Scheme 10, (A_2)]. The strategies depicted in Schemes 7 and 10 should be rather general

and since they are not necessarily interchangeable, they should be helpful in providing different potential access to new functional materials.

In preliminary experiments, the trialkoxysilyl alkyne $HC\equiv C(CH_2)_2OC(O)NH(CH_2)_3Si(OEt)_3$ was used to prepare a xerogel according to Scheme 10 (A_1) . It was shown to remain highly porous, $657\text{ m}^2/\text{g}$, with a mean pore diameter of 11 nm. Anchoring of $[RuCo_3(CO)_{12}]^-$ was achieved by reaction of the cluster in THF with the functionalized xerogel [Scheme 10 (A_2)]. Thermal decomposition was followed in situ in a magnetic thermal-balance [60] and resulted in the formation of spherical particles of 2.2–5.5 nm in diameter (TEM). X-ray diffraction showed the presence of a hexagonal phase of a $RuCo_3$ alloy and these particles display ferromagnetic



Scheme 10. Complementary strategies based on functional alkyne ligands for the covalent grafting of metal clusters, followed by thermal treatment to generate nanoparticles.

behaviour [75]. Further studies are in progress to explore the scope of this sol–gel method applied to mixed-metal clusters for the preparation of bimetallic nanoparticles.

5. Conclusion

Organometallic chemistry remains a fast expanding field of research which concerns all the elements of the Periodic Table. In this account and at the invitation of the editors of this anniversary issue, we wished to illustrate recent developments by selecting examples from our own research activities. We should remember that in addition to the huge diversity of structures and applications available with mononuclear complexes, where new classes of ligands offer fascinating opportunities, like the recently discovered quinoneimine-type $6\pi+6\pi$ potentially antiaromatic zwitterions and related systems [76], the metal–ligand interplay is even more complex in dinuclear complexes and clusters. But this complexity provides opportunities for the study of interactions not available in mononuclear chemistry. As a result of increasingly systematic and rational synthetic approaches, the diversity of single source molecular precursors to new materials by OM-CVD techniques has increased dramatically over the years [61c,78]. Furthermore, any study on bridging ligands (their structure, reactivity, electronic relay between metal centres, etc.) is by definition not possible with mononuclear systems. This innovation may be illustrated by the discovery of the bridging behaviour of alkoxysilyl ligands which opens considerable perspectives not only in molecular synthetic chemistry but also in homogeneous catalysis and material sciences [77], and by the recently delivered proof that the ubiquitous phosphine [79] and silyl ligands [80], which are related by the isolobal analogy [81], can also behave as bridging ligands, a situation that was predicted back in 1989 in the former case [82]. The potential of cluster complexes to mediate unique bond forming/breaking reactions [83] or of heterobimetallic complexes to display reactivity patterns that are unknown for their homometallic analogs, as recently observed in the dimerization of methylacrylate promoted by a Ni–Mo complex [84] is also noteworthy. The diversity provided by synthetic chemistry remains a fascinating challenge and new bonding situations continue to be discovered [85], in particular in cluster chemistry which offers unique opportunities for aesthetically pleasing mixed-metal, often dynamic molecules (Mn_4Pd_4 helices, Fe_2HgCu molecular torsion pendulum) [86], very large clusters [56,87], giant single-molecule magnets [88] and extended structures [89], including systems that move towards bimetallic wires [90].

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