

Polymetallic Carbosilane Dendrimers Containing *N,N'*-Iminopyridine Chelating Ligands: Applications in Catalysis

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Abstract. This overview covers the most relevant results obtained by our group in the last few years concerning the synthesis and catalytic applications of metal complexes anchored to the surface of carbosilane dendrimers functionalized with iminopyridine ligands. Nickel dibromide complexes activated with methylaluminoxane (MAO) have been studied for the polymerization of ethylene, whereas cationic palladium(II) derivatives have been applied to the copolymerization of carbon monoxide and *tert*-butylstyrene. In addition, palladium dendrimers have been tested in the Heck reaction between methyl acrylate and iodotoluene. Correlations between the catalyst activities or reaction products (product distributions, polymer molecular weights, etc.) and the dendrimer generation are discussed and tentative explanations for these correlations provided.

INTRODUCTION

Homogeneous catalysis based on transition-metal complexes is characterized by the possibility of precisely controlling the environment of the active metal center through an appropriate choice of ligands.¹ A combination of rational and empirical design of their electronic and steric properties therefore allows, in principle, a fine-tuning of the catalyst properties in terms of activity, selectivity or stability. In contrast to metalloenzymes, where the metal complex is built into a high-molecular-weight protein, the control of the metal environment in classical transition-metal complexes is closely linked to the ligand dimensions. The interest in using dendrimers in homogeneous catalysis resides mainly in the enlargement of the molecular scale, which, in contrast to other supports, is compatible with the retention of a well-defined catalyst structure.^{2–4} The nanometric size

of the macromolecule facilitates catalyst separation,⁵ especially by nanofiltration with membrane techniques.⁶ The term “dendritic effects” is applied to those special features imparted by the dendrimer to the catalytic centers that are not achievable otherwise.^{7,8} Much of the literature published over the last few years on catalysis with dendrimers has therefore been devoted to comparing the catalytic behavior of dendritic catalysts with their non-dendritic counterparts.

In accordance with their central role in homogeneous catalysis, phosphanes are the most ubiquitous ligands to have been used in the preparation of metallodendrimer catalysts, often together with palladium as the metal.⁹ Nitrogen-donating neutral or anionic ligands are important in many catalytic processes and, in the course of

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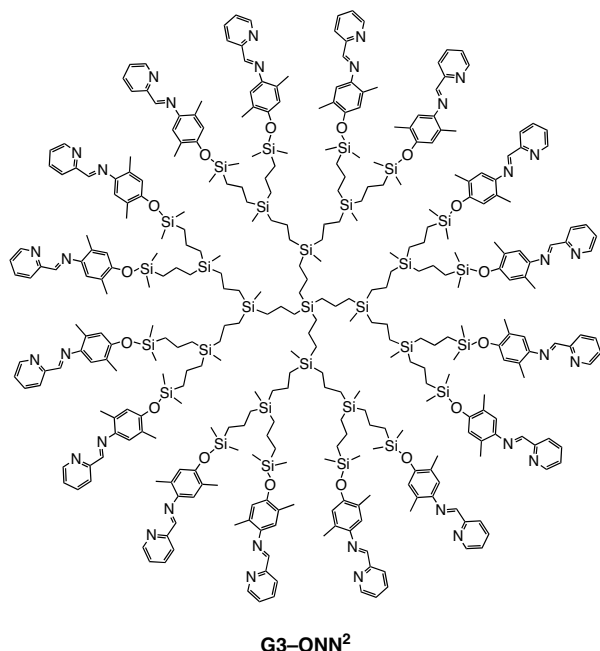


Fig. 1. A carbosilane dendrimer with 16 iminopyridine end groups.

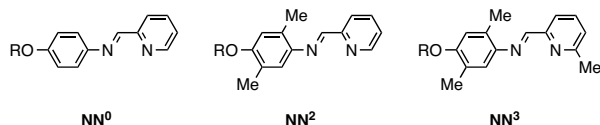


Chart 1. Substitution patterns used on the iminopyridine fragment.

our research, we have often selected this type of donor for the ligation of early and late transition-metal complexes to dendrimers.^{10–13} Herein we give an overview of recent results obtained by our group on the application of dendrimers decorated at their periphery with iminopyridine ligands in catalysis (Fig. 1). We used the three different substitution patterns on the iminopyridine fragments shown in Chart 1, which are labeled as **NN⁰**, **NN²**, and **NN³** throughout the text. A detailed description of the synthesis of these dendrimers, and the polymerization studies carried out with them, can be found elsewhere;^{14–17} therefore we will only highlight some conclusions extracted from this previous work and describe recent results obtained with the same systems on the coupling of olefins with aryl halides (the Heck reaction).

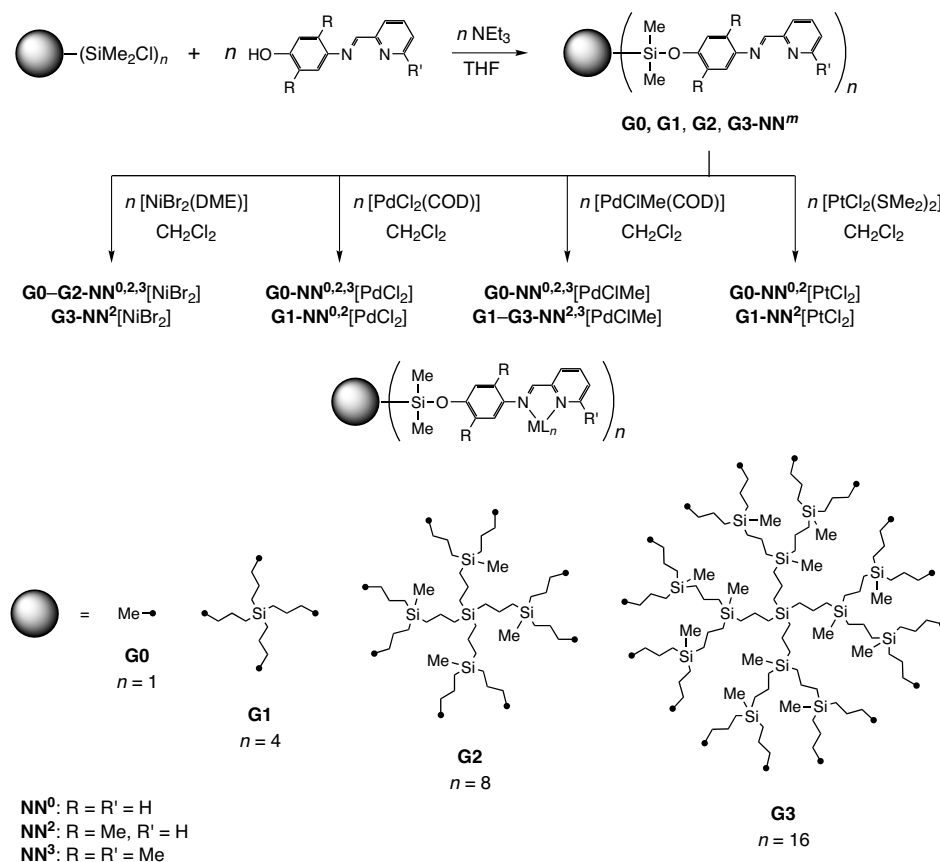
FUNCTIONALIZATION OF CARBOSILANE DENDRIMERS AT THEIR PERIPHERY

Carbosilanes are widely used in catalysis with dendrimers because they combine the chemical inertness of

their interior with the flexible functionalization of their periphery, where silicon–chloride bonds and vinyl or allyl groups alternate during growth of the macromolecule.¹⁸ The dendritic ligands **G1**, **G2**, and **G3-NN^{0,2,3}** were obtained by phenolysis of the terminal silicon–chloride groups with the corresponding hydroxy-functionalized iminopyridine ligand **NN** in the presence of **NEt₃** as a base (Scheme 1).¹² Ligands **G0-NN^{0,2,3}**, which are bonded to a trimethylsilyl group instead of a dendrimer molecule, served as a comparative reference in the catalytic studies.

Coordination of metal complexes to these dendritic ligands was carried out by replacing the more labile ligands of the appropriate metal precursor (Scheme 1). The square-planar palladium(II) and platinum(II) complexes are diamagnetic whereas the nickel(II) complexes are tetrahedral and paramagnetic. Chlorido(methyl)palladium complexes were obtained as a mixture of *cis* or *trans* diastereoisomers, as determined by the relative position of the methyl and imine groups on the square-planar palladium environment. The composition of this mixture was found to depend on the substitution pattern of the iminopyridine ligand but was independent of the dendrimer generation: the *cis* isomer was the major diastereoisomer (ca. 75%) with the unsubstituted ligand **NN⁰** and the only isomer when methyl substituents were present in the ligand.

Not all the combinations of dendritic ligands and metal complexes were obtained as pure products due to the lack of solubility of some of the final products. The groups located at the dendrimer surface are mainly responsible for the solubility of dendrimers in a given solvent, and this feature has been taken advantage of in many applications of these macromolecules. For instance, catalysts that are more suitable for use in non-conventional solvents or with better recovery properties can be obtained by embedding metal complexes or nanoparticles in the interior of dendrimers fitted with the appropriate end groups.^{19–22} In contrast, when metal complexes of low solubility are anchored to the periphery of dendrimers, a common practical problem is the precipitation of highly insoluble, partially functionalized intermediates that precludes the isolation of pure materials. The increased metal loadings of high-generation dendrimers accentuate this problem, and this explains, for instance, why the **G1-NN²**[PtCl₂] complex, which is insoluble in all common solvents, was the only pure polymetallic compound obtained for platinum. On the other hand, the presence of a methyl group in PdClMe complexes makes them more soluble in ethereal, aromatic, or chlorinated solvents, thereby facilitating the synthesis of higher-generation dendrimers. Modifications of the ligand that anchors the



Scheme 1. Synthesis of metallodendrimers.

complex to the dendrimer are also effective and, in the case of the iminopyridine ligand, the solubility increases with the number of methyl substituents ($\text{NN}^3 > \text{NN}^2 > \text{NN}^0$). In agreement with this solubility order, several G3 dendrimers could be prepared with the substituted $\text{NN}^{2,3}$ ligands, but none could be isolated pure with the non-substituted NN^0 ligand.

ETHYLENE OLIGOMERIZATION/

POLYMERIZATION WITH NICKEL DENDRIMERS

Dendrimers have rarely been used in the polymerization of ethylene or α -olefins with transition-metal complexes,²³⁻²⁷ most probably due to the lack of a stimulus for catalyst recovery, one of the major objectives of dendrimer catalysis. However, dendrimers can enhance, not only the performance of catalysts,^{13,24} but also modify the characteristics of the polymers, as we have shown in our early studies with group 4 metallocenes.²⁸ Nickel(II) and other late transition-metal catalysts are attractive when compared to group 4 polymerization catalysts because of their better tolerance to water or oxygen impurities and to monomers with heteroatom

functionalities.²⁹ The tendency of late transition-metal catalysts to produce mainly dimers or oligomers due to competing hydride elimination was finally overcome by Brookhart and coworkers, who designed ligands that are able to afford high molecular weight polymers.³⁰ The products obtained with this type of catalyst are therefore very sensitive to the metal environment and the reaction conditions, and range from small oligomers to high-molecular-weight polymers and have both linear and hyperbranched microstructures. This prompted us to explore the effect of the dendritic structure on the products obtained from ethylene using the nickel(II) iminopyridine dendrimers **G_n-NN^m[NiBr₂]**.^{14,15,31}

The polymerizations were run in toluene at 20 °C under 2 bar of ethylene pressure, and the nickel precursors were activated by methylaluminoxane. The same amount of catalyst based on nickel centers was used in all the experiments. All the catalysts gave a mixture of a toluene-soluble fraction of oligomers together with solid polyethylene. The oligomers were basically composed of linear 1- or 2-alkenes, whereas the degree of branching was much higher for the polymer fraction.

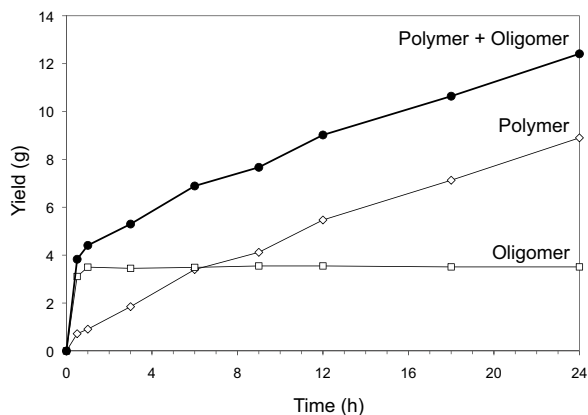


Fig. 2. Variation of yield of polymer and oligomer fractions and total yield with time.

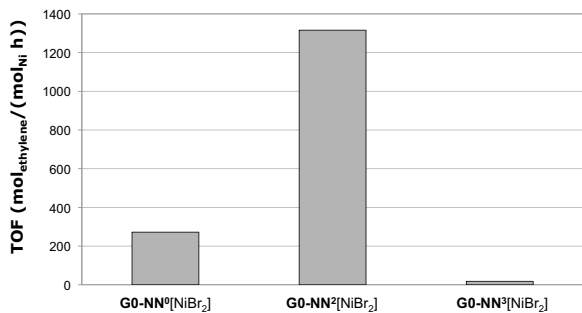


Fig. 3. Turnover frequencies of mononuclear catalyst (polymer + oligomer fractions).

This disparity is important because it suggests some kind of difference in the nature of the active species or in the conditions under which the oligomer and polymer fractions are generated. In addition, the oligomers were mainly produced in the first half hour of reaction, whereas the polymeric fraction was steadily produced for at least 24 h (Fig. 2). On the other hand, the effect of the methyl substituents on the catalytic behavior follows the trend $NN^2 > NN^0 > NN^3$, with the NN^3 catalysts having negligible activity (Fig. 3). The steric influence of substituents in the *ortho* ring positions therefore produces opposing results: the methyl group on the rigid pyridine ring blocks the equatorial coordination sites and hampers olefin coordination,³¹ whereas that on the *ortho* aryl ring protects the axial coordination sites and enhances the catalytic behavior.

Several trends emerged from the comparison of the performance of the catalysts and the nature of the products with regard to the generation of the dendrimers. The first trend is connected with the relative formation of oligomers and polymers, with oligomer formation clearly being favored by higher-generation dendrimers

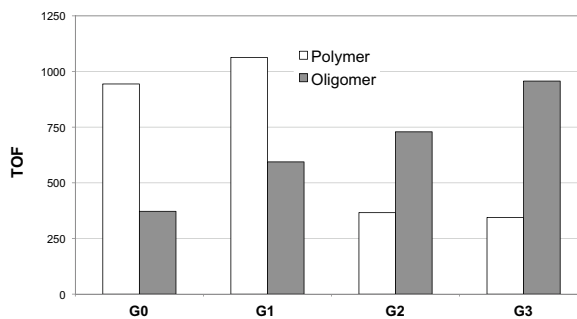


Fig. 4. Turnover frequencies for the formation of oligomers and polymers by G_n - NN^2 [NiBr₂] catalysts.

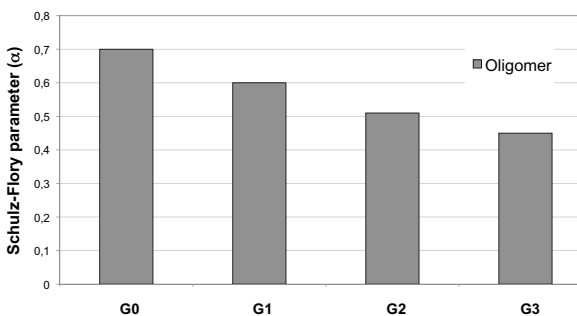


Fig. 5. Schulz-Flory parameter (α) for the oligomers obtained with the G_n - NN^2 [NiBr₂] catalysts.

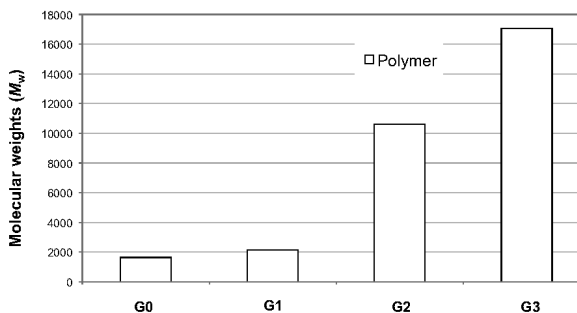


Fig. 6. Weight-average molecular weights (M_w) for the polymers obtained with the G_n - NN^2 [NiBr₂] catalysts.

(Fig. 4). At the same time, the oligomer chains formed by these high-generation dendrimers were found to be shorter than those produced by monometallic or low-generation complexes. The composition of the oligomer fractions followed a typical Schulz-Flory distribution, which is characterized by a constant, α (Fig. 5).³² Thus, an oligomer distribution with a small α value (e.g., 0.5) consists mainly of dimers and lower oligomers, while the bulk of an oligomer distribution with a high α (e.g., 0.8) will consist of higher oligomers. In contrast to the behavior observed for the oligomers, the polymers produced by larger dendrimers had higher molecular weights (Fig. 6) and, in addition, a lower ratio of branches (Fig. 7), particularly longer branches (C_6 or higher).

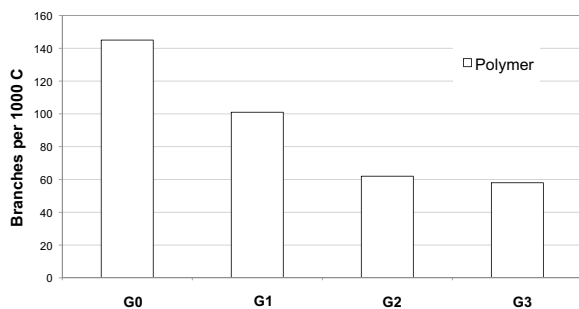
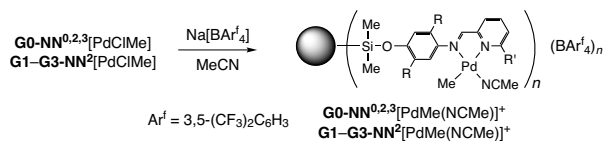


Fig. 7. Number of branches per 1000 carbon atoms for the polymers obtained with the G_n - NN^2 [NiBr₂] catalysts.

We interpreted these results as being partly due to the steric interaction between the dendritic structure and the growing polymer chains. Thus, the steric pressure caused by larger dendrimers might enhance chain transfer at the expense of chain propagation, thereby favoring the formation of a larger number of shorter oligomeric chains. Moreover, it is also reasonable to propose that the so-called “chain walking” process³³ is sterically disfavored for larger dendrimers, which therefore lead to less branched polymers. The opposite trends observed in the relationship between average chain molecular size and generation number obliged us to assume, in addition, the existence of different active species for the production of oligomers and polymers. The fact that the polymerization of ethylene is a highly exothermic reaction might, however, give an alternative explanation for this opposite trend. Maximal head generation occurs within the first half hour of reaction in our polymerizations, when the catalyst activity is maximal and mainly oligomers are formed (see Fig. 2). We can reasonably argue that the preferred formation of shorter chains (oligomers) during the early stages of the reaction might be due to the strong exothermicity of the reaction. When the reaction reaches a steady state, however, chain propagation predominates and longer polymeric chains are formed. The formation of shorter oligomeric chains for higher-generation dendrimers could then be an effect of the high concentration of active centers in the small surface of these macromolecules, which means that high local temperatures can be reached if the heat dispersion is not efficient enough. In conclusion, the dependence of product distribution and dendrimer generation can be attributed to either chemical or physical cooperative effects.

COPOLYMERIZATION OF CO AND *tert*-BUTYLSTYRENE WITH PALLADIUM DENDRIMERS
Cationic palladium(II) complexes containing chelating diphosphine ligands such as propane-1,3-diylbis(di-



Scheme 2.

phenylphosphane) (dppp) have made the commercial production of aliphatic polyketones economically attractive.³⁴ These copolymers are characterized by their chemoregularity, in the sense that their propagation occurs by perfect alternation of olefin and carbon monoxide co-monomers. Such chelating diphosphine ligands are, however, of no use for making copolymers based on styrene and CO, although bidentate nitrogen-donating chelates give good results.³⁵ The CO/*tert*-butylstyrene copolymers are regioregular and their stereoregularity can be modified by the choice of the ligand to give syndiotactic or isotactic microstructures. The cationic palladium(II) G_n - NN^m [PdMe(NCMe)]⁺ complexes shown in Scheme 2 afford mainly syndiotactic polyketones (60–70% based on the *uuu* triad proportion) in the copolymerization of *tert*-butylstyrene and carbon monoxide, although this and other parameters of the catalytic reaction, along with the nature of the polymer, are dependent on the substitution pattern of the iminopyridine ligand and the dendrimer generation of the catalyst.¹⁶ In parallel with the observations made for the nickel polymerization catalysts, the NN^3 complexes are completely inactive; therefore, we will limit our discussion to the most productive NN^2 complexes and dendrimers.

Much effort has been dedicated to determining the conformation of dendrimers both experimentally and theoretically.^{12,36} Conformational studies are relevant to catalysis because the accessibility of the active centers located at the periphery in solution could be severely restricted by a significant backfolding of the dendritic chain ends. Because conformations in solution are, in part, determined by the solvent–dendrimer interactions, the adaptation of the dendritic conformation to a given solvent has been proposed to explain alterations in the catalytic behavior.^{19,37} An example of the changes that could be ascribed to solvent-dependent conformational effects is shown in Fig. 8, where it can be seen that the yields of copolymers are larger in neat *tert*-butylstyrene as solvent than in CH₂Cl₂. More relevant, however, is the fact that $G1$ – $G3$ - NN^2 [PdMe(NCMe)]⁺ dendrimers are less productive in CH₂Cl₂ than the corresponding monometallic derivative **G0**, whereas the opposite trend is observed in neat *tert*-butylstyrene. The productivity depends on the balance between the intrinsic activity of

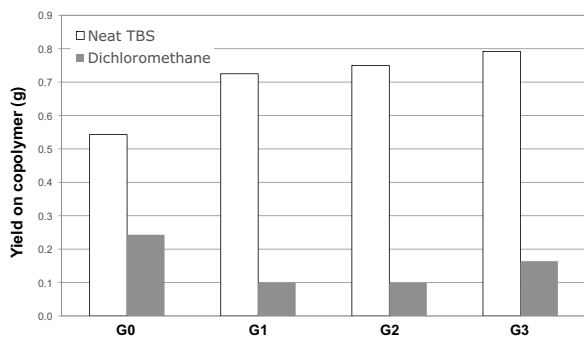


Fig. 8. Productivities for G_n - NN^m [PdCl(NCMe)]⁺ in dichloromethane and in neat *tert*-butylstyrene. Conditions: 1.4 mL of *tert*-butylstyrene in 5 mL of dichloromethane or 2.5 mL of neat *tert*-butylstyrene and catalyst (12.5 μ mol, based on Pd) stirred for 24 h at 20 °C under 1 atm of CO pressure.

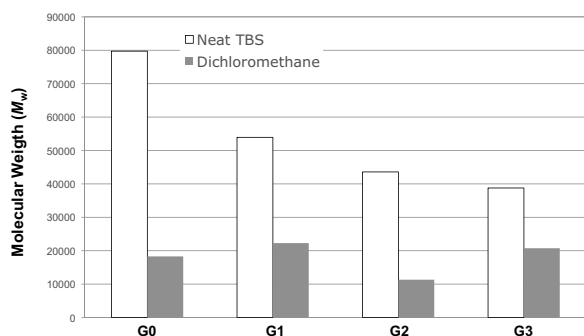


Fig. 9. Molecular weights of copolymers obtained with G_n - NN^m [PdCl(NCMe)]⁺.

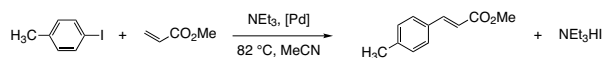
the catalysts, i.e., the rate of the propagation steps, and the rate of catalyst degradation,³⁸ both of which could be affected by solvent-dependent conformational changes in the dendrimers. However, we observed that the dendrimer has no apparent effect on the lifetime of the active species, which means that the differences observed in different solvents are more likely caused by differences in the rate of the propagation steps.

Decreasing molecular weights were observed in neat *tert*-butylstyrene for the higher generations (Fig. 9). As discussed previously, this result might be produced by the steric pressure that bulkier dendrimers cause on the growing chains, although this argument alone does not explain the absence of a correlation between molecular weights and dendrimer generation for the copolymers obtained in dichloromethane. It is worth mentioning that precipitation of black Pd⁰ is particularly notable in CH₂Cl₂, whereas in neat *tert*-butylstyrene the initial color of the solutions (yellow-orange) remains very intense, which is a sign of catalyst stability.

C-C COUPLING HECK REACTION BETWEEN METHYL ACRYLATE AND IODOTOLUENE

The Heck–Mizoroki reaction³⁹ between alkenes and aryl halides is one of the best-studied carbon–carbon coupling reactions and is an indispensable method in organic synthesis.⁴⁰ Core-¹⁹ or peripherally-functionalized^{7,22b,41,42} palladium dendrimers, as well as composite materials obtained by anchoring the latter to inorganic or organic supports,^{43,44} have been applied as catalysts for Heck reactions. We decided to study the coupling of methyl acrylate and iodotoluene, as both are activated substrates in this reaction (Scheme 3).

The reactions were carried out at reflux, with triethylamine as a base to remove the hydrogen iodide formed, and monitored periodically by gas chromatography. The formation of variable amounts of palladium black was observed in all cases. Final conversions after 24 h of reaction exceeded 90% for all the palladium catalysts tested. However, the conversion values at intermediate periods were clearly different in the case of catalytic precursors having different substitution patterns at the iminopyridine ligand or supported on dendrimers of different generation. The NN⁰ and NN² ligands, for instance, afforded the most active catalysts and, in contrast with the observations described in previous sections, catalysts derived from the NN³ ligand were also quite active (Fig. 10). The palladium precursor was essentially irrelevant, as shown in Fig. 11, where several mononuclear PdCl₂, PdClMe, and PdMe(NCMe)⁺ complexes are compared. In contrast, the monometallic



Scheme 3.

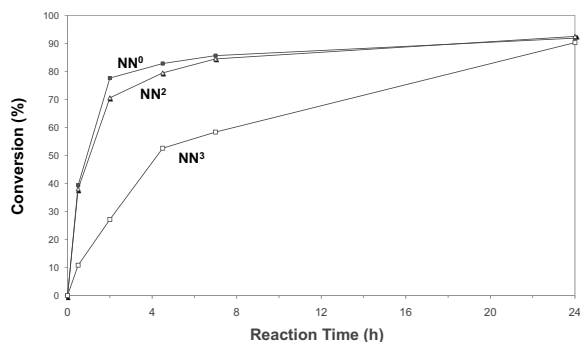


Fig. 10. The effect of the iminopyridine ligand of complexes G_0 - NN^m [PdCl₂] on the conversion of iodotoluene and methyl acrylate into the *trans* coupling product at different reaction times. Conditions: *para*-iodotoluene (0.50 mmol), methyl acrylate (0.50 mmol), triethylamine (0.50 mmol), and the palladium catalyst (1 mol % based on Pd) in acetonitrile (5 mL) at 82 °C.

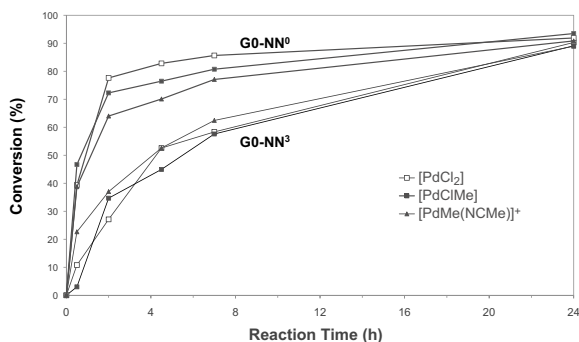


Fig. 11. Reaction profile for different mononuclear palladium precursors.

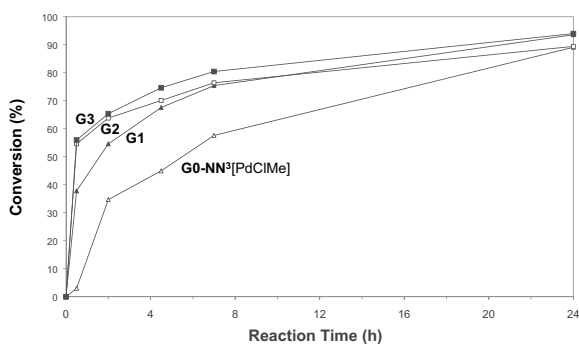
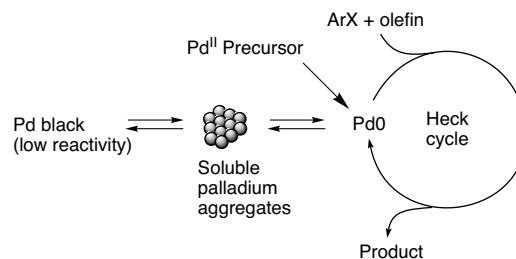


Fig. 12. The effect of dendrimer generation on the conversion profile for complexes G_n - NN^3 [PdClMe].

or dendritic nature of the catalytic precursor seems to be one of the most important factors affecting the reaction profile (Fig. 12). The larger initial activities observed for dendrimers are in agreement with the results reported by Mapolie and coworker in a related study on the Heck reaction using non-substituted iminopyridine ligands and polypropyleneimine (PPI) dendrimers.⁴²

In contrast to the copolymerization reactions described in the previous section, the first step of the Heck reaction involves the reduction of the Pd^{II} precursors to form the Pd^0 active species, which are involved in the Pd^0/Pd^{II} catalytic cycle.⁴⁵ These molecular Pd^0 species tend to decompose to give soluble metal nanoparticles and colloids or precipitates of inactive palladium black, therefore the true nature of the active catalysts—molecular or not—has been the subject of intense debate. Several experimental studies have suggested that Pd aggregates might merely be a reservoir of palladium atoms from which catalytically active Pd complexes are formed by oxidative addition of the aryl halide on the nanoparticle surface (Scheme 4).⁴⁶

The exact mechanism and species involved depend on the temperature, aryl halide, and other reaction conditions, but it is important to note that the impact of ligands and other additives on the observed kinetics can



Scheme 4. A general picture of the nature of the palladium species present in Heck reactions

occur not only due to direct effects on the Heck cycle but also due to changes in the concentration of active Pd^0 complexes in solution. We suggest, as a preliminary model to explain our results in this reaction, that iminopyridine ligands are not coordinated to the palladium(0) active centers during the catalytic process. The influence of these ligands on the reaction kinetics should therefore be attributed to differences in the rate of generation of the Pd^0 active species from the Pd^{II} precursors or, more likely, on the equilibria involving the Pd aggregates. We also propose that iminopyridine ligands play a role in stabilizing these metal nanoparticles by coordinating to their surface. The enhancement of the reaction kinetics produced by dendrimers can then be rationalized as a result of two different steric effects. First, dendrimers are more efficient than simple ligands in sterically protecting the nanoparticle against aggregation and precipitation. Second, the amount of iminopyridine ligands coordinated to the nanoparticle surface is smaller in the case of dendrimers due to steric congestion, which leads to a surface that is less coordinatively saturated and more susceptible to the leaching of palladium atoms by oxidative addition of aryl iodide. Similar arguments have been employed to explain dendrimer effects in Pd-catalyzed reactions employing nanoparticles stabilized by dendritic ligands (the so-called nanoparticle-cored dendrimers).⁴⁷ In the type of protection we are discussing here, the dendrimer envelops the nanoparticle surface.⁴⁸ Dendrimer-encapsulated nanoparticles, which have been developed mainly by Crooks and coworkers,⁴⁹ are completely different because the metal particle is supposedly encapsulated inside the dendritic molecule. Thus, the dendrimers used in Crooks' strategy should only contain internal coordinating groups (PPI or PAMAM dendrimers are usually used) and should be large enough to completely encapsulate the nanoparticle.⁴⁹ Most reports describing dendritic effects with molecular metallodendrimers in the Heck and other related Pd-catalyzed coupling reactions have used PPI or other dendrimers with internal coordinating groups.

However, the ability of these dendrimers to stabilize Pd nanoparticles has rarely been discussed.

CONCLUSIONS

Carbosilane dendrimers containing peripheral iminopyridine groups represent a new set of versatile dendritic ligands that have been used for the preparation of new metallodendrimers. We have overviewed the most relevant results obtained in the use of nickel or palladium complexes in polymerization, copolymerization, and Heck reactions, and have shown that even an inert dendritic structure such as that of carbosilanes influences all the processes discussed here to a greater or lesser extent. We have found a considerable number of trends when correlating catalyst activities or reaction outputs (product distributions, polymer molecular weights, etc.) and generation number, and tentative explanations for these correlations have been provided as illustrative examples of the types of influence that dendrimers can have in the catalyst reactivity, even though full and definitive rationalizations are difficult in most cases.

EXPERIMENTAL

General Procedure for the Heck Reaction

para-Iodotoluene (0.50 mmol), methyl acrylate (0.50 mmol), triethylamine (0.50 mmol), and the palladium catalyst (5.0 μ mol, 1 mol % based on Pd) were dissolved under argon atmosphere in acetonitrile (5 mL, distilled under argon) in a vial fitted with a septum. The solution was then heated at 82 °C in an oil bath with continuous magnetic stirring. Samples (1 μ L) were periodically withdrawn by syringe and analyzed by GC using a Chrompack CP 9001 fitted with a capillary column of melted silica HP-INNOWax (15 m length, 0.25 mm i.d., 0.25 μ m film thickness).

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