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Authors: Ana Carmen Albéniz, Jesús Ángel Molina de la Torre, Ignacio Pérez-Ortega, Alvaro Beltrán, Manuel Rodríguez, Mar Díaz-Requejo, and Pedro Pérez

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■ **Supported Trispyrazolylborate ligands**

Trispyrazolylborate Ligands Supported on Vinylic Addition Polynorbornenes and their Copper Derivatives as Recyclable Catalysts

Jesús A. Molina de la Torre,[a] Ignacio Pérez-Ortega,[a] Álvaro Beltrán, [b] Manuel R. Rodríguez,[b] M. Mar Díaz-Requejo,*[b] Pedro J. Pérez*[b] and Ana C. Albéniz*[a]
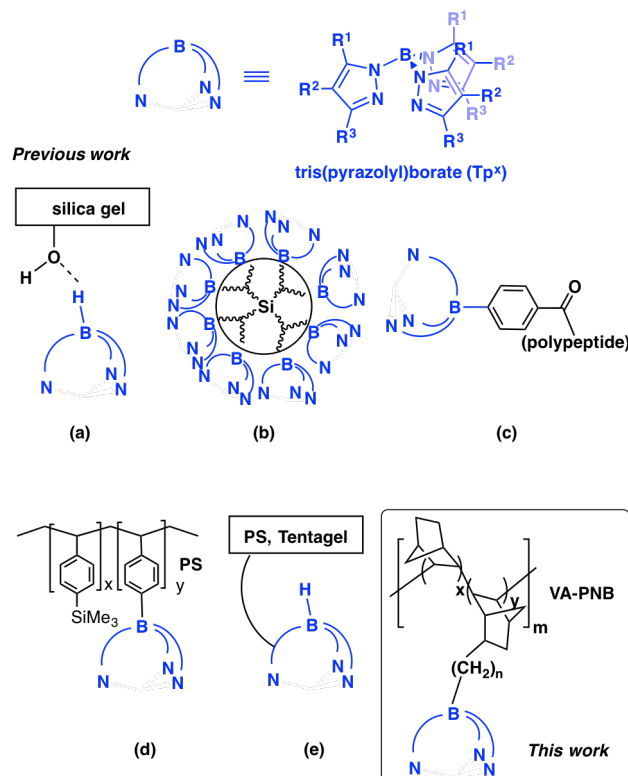
Abstract: Polynorbornenes prepared by vinylic addition polymerization and bearing pendant alkenyl groups serve as skeletons to support trispyrazolylborate ligands (Tp^x) built at those alkenyl sites. Reaction with CuI in acetonitrile leads to VA-PNB-Tp^{x}Cu(NCMe) with a 0.8-1.4 mmol incorporation of Cu per gram of polymer. The presence of tetracoordinated copper(I) ions has been assessed by FTIR studies with the corresponding VA-PNB-Tp^{x}Cu(CO) adducts, that match those for discrete Tp^{x}Cu(CO). The new materials have been employed as heterogeneous catalysts in several carbene and nitrene transfer reactions, showing a behavior similar to the homogeneous counterparts but also being recycled several times maintaining a high degree of activity and selectivity. This is the first example of supported Tp^x ligands onto polymeric supports with catalytic applications.

Introduction

Borate derivatives that attach N-heterocyclic donor groups are probably the most common scorpionate ligands and, among them, trispyrazolylborates (Tp^x) have been extensively used.[1] Being anionic, these tridentate ligands were early identified as analogues of cyclopentadienyl (Cp) groups, a challenged[2] assumption which boosted their extensive use in organometallic chemistry and catalysis.[3] The careful design of these ligands upon variation of the substituents on the pyrazole rings led to an exquisite control of electronic and steric features of each ligand, at variance with the limited tuning for Cp ligands. Along the years, Tp^x-metal complexes have been used in many catalytic transformations,[4] including the more testing functionalization of unreactive C-H bonds.[5] These ligands have also been used to synthesize model complexes that mimic the active site of some metaloenzymes,[6] and to generate materials with interesting magnetic properties.[7]

In the field of catalysis, and in line with one of the main goals of modern synthetic chemistry focused in a high level of sustainability, the recovery of the catalyst and its reuse after each cycle still constitute a major challenge. Moreover, a recyclable catalyst is more efficient as far as cumulative TON is concerned, and it does not generate the extra waste resulting when the catalyst is discarded after each reaction. In the area of trispyrazolylborate-containing metal-based catalysts, very few reports have appeared regarding this issue. Earlier work from our laboratories showed that silica gel interacted with pre-formed trispyrazolylborate copper(I) complexes through weak H-bonding interactions, allowing their use as catalysts in the olefin cyclopropanation reaction for several cycles (Scheme 1a),[8] albeit catalyst leaching was significant probably due to the lack of

[a] Dr. J. A. Molina de la Torre, I. Pérez-Ortega, Prof. Dr. A. C. Albéniz
IU CINQUIMA/Química Inorgánica. Universidad de Valladolid. E-47071 Valladolid. Spain.
E-mail: albeniz@qi.uva.es
[b] Dr. A. Beltrán, M. R. Rodríguez, Prof. Dr. M. M. Díaz-Requejo, Prof. Dr. P. J. Pérez
Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC
CIQSO-Centro de Investigación en Química Sostenible and
Departamento de Química
Universidad de Huelva, 21007-Huelva (Spain)
Fax: (+34)959219942
E-mail: perez@dqcm.uhu.es; mmdiaz@dqcm.uhu.es

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Scheme 1. Supported trispyrazolylborate ligands.

covalent interactions between complex and support. Such bonding was later described by several groups with the trispyrazolylborate ligand bound to carbosilanes (Scheme 1b),[9] polypeptides (Scheme 1c),[10] and other resins,[11] and polymers. For the latter, two different approaches have been used: i) the presence of an aryl group as the fourth substituent of boron, which is part of a polystyrene structure (Scheme 1d), [12,13] and ii) the substitution of one of the pyrazolyl groups by a polymer-bound N-heterocycle (Scheme 1e).[14] None of these supported trispyrazolylborates have been used in catalysis.

With the idea of providing a strong linkage between the Tp^x moiety and the support, we have explored the possibility of anchoring trispyrazolylborate metal complexes to the polymeric structure of polynorbornenes. Herein we report the synthesis of vinylic addition polynorbornenes (VA-PNBs) with pendant trispyrazolylborate ligands (Scheme 1) as well as their corresponding copper complexes. Catalytic experiments have shown that the catalytic properties of such complexes are similar to those previously reported in the homogeneous phase, with the benefit of the easy catalyst separation and recycling.

Results and discussion

Synthesis of the Tp-functionalized VA-polynorbornenes

The synthetic route developed to prepare the polymer-containing Tp^x ligands involves the post-polymerization functionalization of vinylic addition polynorbornenes with pendant alkenyl groups (Scheme 2). Polymeric starting materials 1a,b were prepared by copolymerization of norbornene and an alkenyl norbornene, using [Ni(C$_6$F$_5$)$_2$(SbPh$_3$)$_2$] as the catalysts, as previously described.[15,16] There are few examples of group 10 metal-based catalysts in the polymerization of alkenyl norbornenes.[17] In contrast to some early transition metal catalysts,[18] there is a clear preference for the insertion of the

endocyclic double bond when using Ni or Pd complexes,[19] a feature of relevance in our case toward preservation of the terminal alkene group for further functionalization.

Commercial 5-vinyl-2-norbornene (mixture of isomers *endo:exo* = 79:21) was employed in the synthesis of 1a, whereas 5-(but-1-en-4-yl)-2-norbornene (*endo: exo* = 80:20), prepared by the Diels-Alder reaction of cyclopentadiene and 1,5-hexadiene,[20] was used in the preparation of 1b. In both cases, the polymers were obtained as white solids with moderate yields and molecular weights in the range 35-45 x 10^3 Da and polydispersities of ca. 2. The ^{1}H NMR spectra of the polymers assess the presence of the terminal double bond and the disappearance of the endocyclic norbornene double bond. Integration of the alkene vs the aliphatic resonances allows determining the composition of the copolymer (x/y ratio) and therefore the degree of functionalization of the material (see Experimental Section). Using an equimolar amount of monomers in the feed, the copolymers obtained display a higher ratio in the more reactive norbornene (x/y >1), as it has been observed before for other NB/NB-X copolymerizations.[16b] *Endo* and *exo* arrangements of the alkenyl substituent in the bicycle are visible in the ^{13}C NMR spectra of polymers 1a, in a ratio that does not reproduce the diastereoisomeric ratio in the starting alkenyl norbornene monomer (see Figure S2 in the supporting information). This is expected since the minor *exo* isomer polymerizes faster than the *endo* one, leading to a more similar distribution of both isomers in the VA-PNB.[16a,b, 21] Nonetheless, the presence of both arrangements has no further influence in the post-polymerization functionalization reactions leading to the supported Tp^x.

The regioselective hydroboration of the terminal double bonds of 1 with commercial BHBr$_2$·SMe$_2$ leads to the polymeric alkyldibromoborane, which was not isolated but reacted in situ with an excess of the corresponding pyrazole (Scheme 2).[22] This process most probably produces RBpz$^x_3$H species by substitution of both bromides and coordination of an additional pyrazole.[1] Slightly stronger reaction conditions (refluxing CH$_2$Cl$_2$ instead of room temperature) and longer reaction times were used for the bulkier 3,5-dimethyl-4-bromo pyrazole or 3-mesityl pyrazole. The subsequent addition of three equivalents of the strong base Li(N^{i}Pr$_2$) (LDA) induces the neutralization of the acid produced in the reaction and provides the alkali counterion. The polymer becomes insoluble upon functionalization and can be easily isolated by filtration and repeated washing with acetonitrile. Being insoluble, polymers 2-4 were characterized by solid state NMR; all of them showed characteristic signals of the pyrazole moieties in the ^{13}C CP-MAS spectrum as well as the typical ^{11}B resonance for tetracoordinated borates about 0-2 ppm. It is known that vinylic addition polynorbornenes undergo conformational changes upon heating or postfunctionalization that increase their insolubility, and they are attributed to mutual rotation of the bicyclic units of the rigid polymer chain to their thermodynamically stable form.[23] This has a practical advantage for a recyclable support, and has been observed before in other postfunctionalization processes.[16,24,25] Also when water is added to the polymeric dibromoborane in Scheme 2 to form the polymeric boronic acid.[22] A specific cross linking process by formation of pyrazabole units, where two pyrazole rings are bridging two different boron atoms, could be possible but it is disfavored by the use of an excess of pyrazole in the synthesis of polymers 2-4.[26]
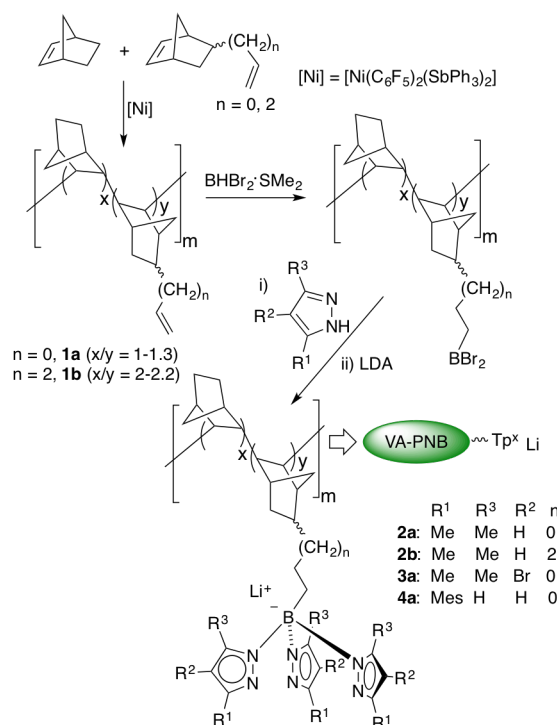
Scheme 2. Synthetic route to obtain the VA-PNB supported trispyrazolylborates.

	R^1	R^3	R^2	n
2a	Me	Me	H	0
2b	Me	Me	H	2
3a	Me	Me	Br	0
4a	Mes	H	H	0

n = 0, 1a (x/y = 1-1.3)
n = 2, 1b (x/y = 2-2.2)

In contrast with the more common M(HBpz$_3$) derivatives, the synthesis of alkyl or aryl-substituted Tp^x, i. e. M(RBpz$^x_3$), is less straightforward. There are several precedents in the literature on the preparation of M(RBpz$_3$) from RBBr$_2$.[27] In none of those reports the dibromoborane was synthesized through an alkene hydroboration step. This is a convenient way to access the RBBr$_2$ intermediate and, in our case, allows us to have a pendant trispyrazolylborate fragment attached to the polymer backbone by a more flexible alkyl tether rather than the aryl linkage used in the few examples of polymer-containing Tp^x reported so far (Scheme 1).

Synthesis of the VA-PNB-Tp^x copper complexes.

The formation of the supported Tp^{x}Cu complexes can be readily accomplished by addition of a solution of CuI in acetonitrile to a suspension of polymers 2-4 in the same solvent (Scheme 3). The metal loading of the polymers was determined by ICP-MS analysis of the copper content, found within the 40-90 mg Cu per gram of polymer interval, ensuring enough amount for its further use in catalysis. The copper incorporation in the polymer is quite efficient when compared to the maximum amount that can be loaded, according to the initial functionalization of the specific polymer 1 used; it ranges from 68% in the case of the bulkier ligand in 4a to 90-100% for polymers 2 (see the Experimental Section for details). However, quantification of copper in the solid does not guarantee that it is coordinated by the N-donors of the ligand, a feature that is crucial for its catalytic behavior. The lower resolution of the solid state ^{13}C CP-MAS NMR spectra of these polymers does not allow to evaluate small chemical shift differences in the Tp^x fragment that arise from coordination to the metal, as it is the case in solution chemistry. Thus, a different approach was taken based on the generation of carbonyl adducts VA-PNB-Tp^{x}Cu(CO) upon bubbling carbon monoxide through a suspension of the polymers (Scheme 3).

Table 1. ν(CO) absorptions (cm^{-1}) for the VA-PNB supported copper complexes and their discrete analogues.

Entry	Tp^x	VA-PNB-Tp^{x}Cu(CO)		Tp^{x}Cu(CO)
1	Tp*, R^1 = R^3 = Me; R^2 = H	2a-Cu(CO),	2052	2056
2	Tp*,^{Br}, R^1 = R^3 = Me; R^2 = Br	3a-Cu(CO),	2066	2073
3	Tp^{Ms}, R^1 = Mes R^2 = R^3 = H	4a-Cu(CO),	2089	2079

Catalytic behavior of the polymer-containing copper materials 2a-Cu and 3a-Cu.

We have previously used VA-PNB-based polymers as support in catalysis bearing other donor ligands such as N-heterocyclic carbenes.[16c, 29] We also have supported organotin reagents and used them in palladium catalyzed Stille couplings,[16a,24] and radical reactions,[30] with good recyclability and the additional advantage of leaving a very low tin contamination in the products. From this work we have learnt that the polymer chain is robust enough to be used in catalysis and it is resistant for example to high temperature or radical processes, conditions that could compromise the performance of other type of polymeric supports.

Given the well-known capabilities of discrete Tp^{x}Cu(L) complexes to induce the catalytic transfer of carbene and nitrene units,[4] we have evaluated two of the new VA-PNB-Tp^{x}Cu(NCMe) materials, analogous to the homogeneous catalytic systems, in the well-known styrene cyclopropanation and aziridination, and cyclohexane amination (Scheme 4 and Table 2). We have chosen 2a-Cu and 3a-Cu as representative examples since both of them are known to promote reactions A-C, at variance of 4a, with limited activity in nitrene transfer. Additionally, since the catalytic performance in due to the Tp^{x}Cu core, 2a-Cu and 2b-Cu are identical from that point of view and the synthesis of 2a-Cu hast he additional advantage of using a commercial monomer in the preparation of the precursor 1a.

Scheme 3. Formation of the VA-PNB supported TpxCu(L) (L = NCMe, CO) complexes.

FTIR studies on those materials showed the ν(CO) band in close proximity to those observed for the well-defined mononuclear complexes,[4b, 28] assessing the presence of tetracoordinated Tp^{x}Cu(CO) moieties as well as the corresponding Tp^{x}Cu(NCMe) in the parent Cu-containing polymers (Figure 1 and Table 1).
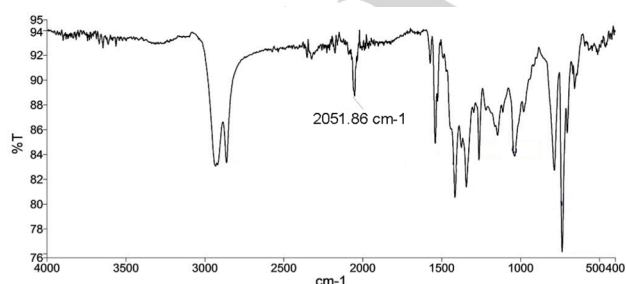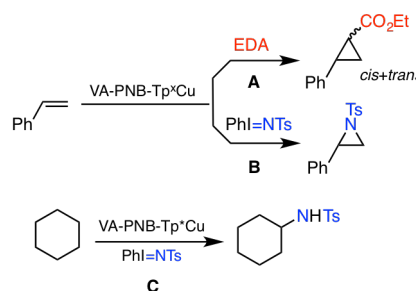

Scheme 4. Catalytic experiments carried out with VA-PNB-Tp^{x}Cu(NCMe).

Under standard conditions, 2a-Cu induced 90-99% yields in these three experiments, whereas the bromide-containing 3a-Cu behaved similarly for the cyclopropanation reaction but the nitrene transfer to styrene was less effective (50%), precluding its use for the amination reaction. This lower yield corresponds to the formation of TsNH$_2$ as byproduct, due to the presence of adventitious water. This collateral reaction is more favored with more active catalysts toward PhI=NTs decomposition, as it is the case of 3a-Cu. Usually the addition of molecular sieves precludes this drawback, but the heterogeneous nature of this system does not allow this strategy.

Since these results are in line with those previously reported in the homogenous phase,[31] the potential recycling of the

Figure 1. IR spectrum of 2a-Cu(CO) showing the characteristic ν(CO) band.

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Table 2. Catalytic activity VA-PNB-Tp^{x}Cu complexes toward the styrene cyclopropanation[a], aziridination reactions[b] and amination of cyclohexane.[c] See Scheme 4 for reaction notation.

Entry	Rxn	Catalyst	Yield(%)	cis:trans
1	A	VA-PNB-Tp*,^{Br}Cu(L)[d] **3a-Cu**	85[a]	48:52
2	A	VA-PNB-Tp*Cu(L)[e] **2a-Cu**	90[a](81)	45:55
3	B	VA-PNB-Tp*,^{Br}Cu(L) **3a-Cu**	50[b]	
4	B	VA-PNB-Tp*Cu(L) **2a-Cu**	99[b](89)	
5	C	VA-PNB-Tp*Cu(L) **2a-Cu**	90[c]	

[a] [M]/[EDA]/[styrene] = 1:5:50, at room temperature; Yields and selectivity (cis:trans) were determined by GC (diethyl fumarate and maleate accounted until 100% of EDA). Isolated yields are given in brackets. [b] [M]/[PhINTs]/[styrene] = 1:5:25, at room temperature; Yields were determined by ^{1}H NMR (TsNH$_2$ accounted until 100% of PhINTs). Isolated yields are given in brackets. [c] [M]/[PhINTs] = 1:25 in 5 mL of cyclohexane at t = 60 ºC. Yields were determined by ^{1}H NMR (TsNH$_2$ accounted until 100% of PhINTs). [d] mg Cu/g polymer = 64.96; L = NCMe. [e] mg Cu/g polymer = 90.42; L = NCMe.

heterogeneous materials was investigated with the three reactions. Figure 2 shows the variation of the yields for the styrene cyclopropanation reaction using **2a-Cu** as the catalyst, showing an excellent degree of recovery and reuse with no effect on those values up to five times. It is also worth mentioning that the cis:trans diastereoselectivity was maintained along those cycles. For the nitrene transfer reaction, also with **2a-Cu**, recycling was performed three times (Figure 2), with a slight decrease of activity of ca. 10% after each cycle in both the styrene aziridination and cyclohexane amination. This can be the result of partial degradation of the catalytic site due to the oxidant nature of the nitrene source, PhI=NTs.
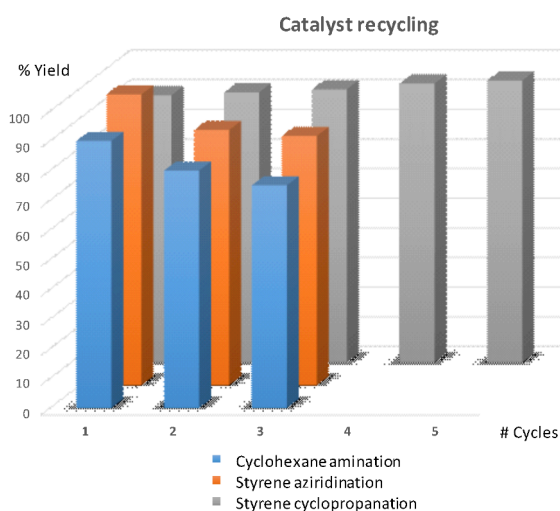

Figure 2. Recycling of **2a-Cu** in the heterogeneous styrene cyclopropanation and aziridination reaction and cyclohexane amination.

Conclusions

Trispyrazolylborate ligands have been attached to polymeric materials derived from vinylic addition polynorbornenes, in a new strategy that can be employed in the preparation of supported Tp^x-metal complexes VA-PNB-Tp^{x}Cu(NCMe). FTIR studies have shown that the coordination environment around the metal center is identical to that in discrete Tp^{x}Cu(NCMe). As a proof of such feature, carbene and nitrene transfer reactions catalyzed by the new heterogeneous materials have been carried out showing a similar behavior than those found under homogeneous conditions. Moreover, the solids can be separated by simple filtration and reuse with a high degree of activity being maintained along the cycles.

Experimental Section

General. The compounds [Ni(C$_6$F$_5$)$_2$(SbPh$_3$)$_2$],[32] 5-(but-1-en-4-yl)-2-norbornene,[20] 3,5-dimethyl,4-bromopyrazole,[33] and 3-(2,4,6-trimethylphenyl)pyrazole[34] were prepared according to the literature procedures. 5-Vinyl-2-norbornene (mixture of exo and endo isomers), 3,5-dimethylpyrazol and BHBr$_2$·SMe$_2$, were purchased from Sigma-Aldrich or Acros. EDA, styrene and reagents for catalytic experiments were purchased from Sigma-Aldrich and used without previous purification. PhINTS was prepared according to the literature procedure.[35]

Solvents such as THF and CH$_2$Cl$_2$ were dried using a Solvent Purification System (SPS); acetonitrile was dried over CaH$_2$, distilled and deoxygenated prior to use. NMR spectra were recorded at 293 K using Bruker AV-400 and Agilent MR-500 instruments. Chemical shifts (δ) are reported in ppm and referenced to SiMe$_4$ (^{1}H, ^{13}C). The solid state NMR spectra were recorded at room temperature under magic angle spinning (MAS) in a Bruker AV-400 spectrometer using a Bruker BL-4 probe with 4 mm diameter zirconia rotors spinning at 10 kHz. ^{13}C CP MAS NMR spectra were measured at 100.61 MHz and recorded with proton decoupling (tppm), with 90º pulse length of 4.5 µs and a contact time of 3 ms. Chemical shifts were calibrated indirectly through the glycine CO signal recorded at 176.0 ppm relative to SiMe$_4$. ^{11}B MAS NMR spectra were recorded at 128.38 MHz with proton decoupling, with a 90º pulse length of 7.5 µs. ^{11}B NMR chemical shifts are in ppm and were calibrated using powdered NaBH$_4$, which has a chemical shift of -42.06 ppm relative to the primary standard, liquid BF$_3$·O(C$_2$H$_5$)$_2$ (where δ(^{11}B) = 0.00 ppm).[36] IR spectra were recorded on neat samples using a Perkin-Elmer FT/IR SPECTRUM FRONTIER spectrophotometer with CsI + ATR diamond accessory in the range 200-4000 cm^{-1}. The catalytic reactions were monitored by GC analyses performed on Agilent Technologies model 6890N gas chromatography instrument with a FID detector using 30 m x 0.25 mm HP-5 capillary column.

Size exclusion chromatography (SEC) was carried out using a Waters SEC system on a three-column bed (Styragel 7.8x300 mm columns: 50-10^5, 5x10^3-5x10^5 and 2x10^3-4x10^6 Da) and a Waters 410 differential refractometer. SEC samples were run in CHCl$_3$ at 313 K and calibrated to polystyrene standards. The copper content of the polymers was determined by ICP–MS, using Agilent 7500i equipment; the samples were dissolved in HNO$_3$ (65%) using an ETHOS SEL Milestone microwave oven. Each analysis is the average of two independent determinations for each sample. The maximum amount of copper in the polymers was calculated taking into account the initial functionalization of the starting polymer **1** (x/y ratio) and assuming a quantitative transformation in the reactions shown in Scheme 2.

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Synthesis of polymer VA-PNB-NBCH=CH₂ (1a). In a 250 mL two-necked round-bottom flask, under nitrogen atmosphere, 5-vinyl-2-norbornene (4.373 g, 36.39 mmol) and norbornene (6.31 M in CH₂Cl₂, 5.77 mL, 36.39 mmol) were dissolved in CH₂Cl₂ (110 mL). In another Schlenk flask [Ni(C₆F₅)₂(SbPh₃)₂] (0.8 g, 0.73 mmol) and SbPh₃ (0.10 g, 0.3 mmol) were dissolved in CH₂Cl₂ (20 mL). This solution was added to the mixture of monomers dropwise and allowed to react at 25 ºC for 24 hours. After this time the dark solution was poured onto MeOH (250 mL) resulting in the appearance of a grey powder. The solid was filtered and re-dissolved in CH₂Cl₂ (100 mL). Activated carbon was added and the mixture was filtered through diatomaceous earth affording a colorless solution, which was poured onto MeOH (250 mL) and stirred for 3 hours. The polymer was filtered, washed with MeOH (3 x 15 mL) and air-dried. A white solid was obtained (3.930 g, 50% yield). The integration of the alkene resonances in the ^{1}H NMR spectrum vs the aliphatic region gave a composition x/y = 1.17 (x/y = {(a-3b)/10}/{b/3} where a = total integral value of the aliphatic region, b = total integral value of the alkene region and the numeric coefficients take into account the number of protons in norbornene and 5-vinyl-2-norbornene). M_w (Daltons) = 43741. M_w /M_n = 2.32. IR (neat, cm^{-1}) v = 1635m (C=C st), 992m (C=C-H δ oop), 906s (C=C-H δ oop). ^{1}H NMR (400.15 MHz, δ, CDCl₃): 6.1-5.6 (br, 1H, H^{8}), 5.2-4.6 (br, 2H, H^{9}), 2.8-0.2 (br, 19H). ^{13}C NMR (100.61 MHz, δ, CDCl₃): 145-143 (br, 1C, C^{8} exo), 143-140 (br, 1C, C^{8} endo), 116-113 (br, 1C, C^{9} endo), 113-111 (br, 1C, C^{9} exo), 55-45 (br, 4C, C^{2}, C$^{2'}$, C^{3}, C$^{3'}$), 44-39 (br, 4C, C^{1}, C$^{1'}$, C^{4}, C$^{4'}$), 41-39 (br, 1C, C^{5}), 38-34 (br, 2C, C^{7}, C$^{7'}$), 34-28 (br, 3C, C$^{5'}$, C^{6}, C$^{6'}$).
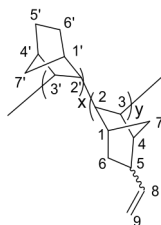

This polymer can also be prepared in a larger scale starting from a seven-fold amount of monomers to obtain about 25 g of polymer (43% yield): White solid, x/y = 1.25, M_w (Daltons) = 45663. M_w /M_n = 2.34.

Polymer VA-PNB-NBCH₂CH₂CH=CH₂ (**1b**) was prepared in the same way but using 5-(but-1-en-4-yl)-2-norbornene instead of 5-vinyl-2-norbornene: White solid, 32% yield x/y = 2.12, M_w (Daltons) = 34261. M_w /M_n = 1.77. ^{1}H NMR (400.15 MHz, δ, CDCl₃): 5.9-5.7 (br, 1H, H^{8}), 5.1-4.8 (br, 2H, H^{9}), 2.7-0.2 (br, 23H). ^{13}C NMR (100.61 MHz, δ, CDCl₃): 139 (s, 1C, C^{8}), 114 (s, 1C, C^{9}), 55-45 (br, 4C, C^{2}, C$^{2'}$, C^{3}, C$^{3'}$), 44-39 (br, 4C, C^{1}, C$^{1'}$, C^{4}, C$^{4'}$), 41-39 (br, 1C, C^{5}), 38-34 (br, 2C, C^{7}, C$^{7'}$), 34-28 (br, 3C, C$^{5'}$, C^{6}, C$^{6'}$), 33, 32 (CH₂-CH₂). IR (neat, cm^{-1}) v = 1639m (C=C st), 991m (C=C-H δ oop), 908s (C=C-H δ oop).
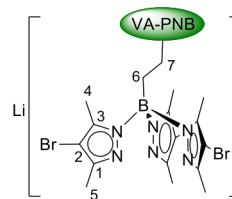
Synthesis of polymer VA-PNB-NBCH₂CH₂B(pz^{Me2})₃Li (2a). Polymer VA-PNB-NBCH=CH₂ (x/y = 1.25, 5 g, 21.02 mmol of –CH=CH₂) was dissolved in CH₂Cl₂ (350 mL) under nitrogen.[37] Dibromoborane-dimethyl sulfide adduct (1.0 M solution in CH₂Cl₂, 21 mL, 21 mmol) was added dropwise and the mixture was stirred for 5 hours at reflux. The reaction was then cooled to room temperature and 3,5-dimethylpyrazole (8.083 g, 81.08 mmol) was added. After stirring for 16 hours at room temperature the reaction was cooled to -78 ºC. A freshly prepared solution of lithium diisopropylamide (63.06

mmol), by mixing Li^{n}Bu (1.6 M solution in hexanes, 39.4 mL, 63.04 mmol) and NH^{i}Pr₂ (9 mL, 63.03 mmol) in THF (50 mL) at -78 ºC, was added dropwise. The mixture was stirred overnight while the suspension slowly warmed to room temperature. Volatiles were then removed under vacuum and the residue was thoroughly washed with CH₃CN (6 x 50 mL). The solid was filtered under a nitrogen atmosphere, washed with CH₃CN (6 x 30 mL) and dried under vacuum. The product was obtained as an orange solid (10.62 g, 93% yield). ^{13}C CP-MAS NMR (100.61 MHz): 155-140 (br, C^{1}, C^{3}), 113-102 (br, C^{2}), 72-20 (br, C^{6}, C^{7}, polyNB), 20-10 (br, C^{4}, C^{5}). ^{11}B MAS NMR (128.38 MHz): 0.9 (br). IR (neat, cm^{-1}): 1541s, 1415s, 1344s, 1165m, 1034m, 781s.
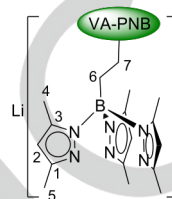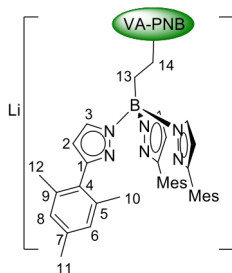

Synthesis of polymer VA-PNB-NB(CH₂)₄B(pz^{Me2})₃Li (2b). The same procedure described for VA-PNB-NBCH₂CH₂B(pz^{Me2})₃Li was used in this case, but using polymer VA-PNB-NBCH₂CH₂CH=CH₂ (x/y = 2.12, 2.87 mmol of –CH=CH₂ /g). Yield 95%. ^{13}C CP-MAS NMR (100.61 MHz): 155-145 (br, C^{1}, C^{3}), 112-105 (br, C^{2}), 65-20 (br, C^{6}, C^{7}, C^{8}, C^{9}, polyNB), 19-10 (br, C^{4}, C^{5}). ^{11}B MAS NMR (128.38 MHz): -0.5 (br). IR (neat, cm^{-1}): 1539s, 1416s, 1344s, 1166m, 1034s, 774s, 646m, 452m.

Synthesis of polymer VA-PNB-NBCH₂CH₂B(pz^{BrMe2})₃Li (3a). Polymer VA-PNB-NBCH=CH₂ (x/y = 1.25, 5 g, 21.02 mmol of –CH=CH₂) was dissolved in CH₂Cl₂ (350 mL) under nitrogen. Dibromoborane-dimethyl sulfide adduct (1.0 M solution in CH₂Cl₂, 21 mL, 21 mmol) was added dropwise and the mixture was stirred for 5 hours at reflux. The reaction was then cooled to room temperature and 3,5-dimethyl, 4-bromopyrazole (18.4 g, 105.1 mmol) was added. After stirring for 48 hours at reflux the yellowish reaction mixture was cooled to -78 ºC. A freshly prepared solution of lithium diisopropylamide (63.04 mmol), by mixing Li^{n}Bu (1.6 M solution in hexanes, 39.4 mL, 63.04 mmol) and NH^{i}Pr₂ (9 mL, 63.2 mmol) in THF (50 mL) at -78 ºC, was added dropwise. The mixture was stirred overnight while the suspension slowly warmed to room temperature. Volatiles were then removed under vacuum and the residue was thoroughly washed with CH₃CN (6 x 50 mL). The solid was filtered under a nitrogen atmosphere, washed with CH₃CN (6 x 30 mL) and dried under vacuum. The product was obtained as a light brown solid (15.69 g, 96% yield). ^{13}C CP-MAS NMR (100.61 MHz): 153-142 (br, C^{1}, C^{3}), 101-94 (br, C^{2}), 70-18 (br, C^{6}, C^{7}, polyNB), 18-9 (br, C^{4}, C^{5}). ^{11}B MAS NMR (128.38 MHz): 2.1 (br). IR (neat, cm^{-1}): 1526m, 1416s, 1339s, 1160s, 1082s, 1036m, 836m, 760m, 508m.

Synthesis of polymer VA-PNB-NBCH₂CH₂B(pz^{Mes})₃Li (4a). Polymer VA-PNB-NBCH=CH₂ (x/y = 1.15, 0.3 g, 1.31 mmol of –

CH=CH$_2$) was dissolved in CH$_2$Cl$_2$ (30 mL) under nitrogen. Dibromoborane-dimethyl sulfide adducts (1.0 M solution in CH$_2$Cl$_2$, 1.3 mL, 1.3 mmol) was added dropwise and the mixture was stirred for 5 hours at reflux. The reaction was then cooled to room temperature and 3-(2,4,6-trimethylphenyl)-pyrazole (0.976 g, 5.24 mmol) was added. After stirring for 40 hours at reflux the yellowish reaction mixture was cooled to -78 ºC. A freshly prepared solution of lithium diisopropylamide (3.93 mmol), by mixing Li^{n}Bu (1.6 M solution in hexanes, 2.46 mL, 3.93 mmol) and NH^{i}Pr$_2$ (0.56 mL, 3.93 mmol) in THF (7 mL) at -78 ºC, was added dropwise. The mixture was stirred for 30 min at -78 ºC and 90 min at room temperature. Volatiles were then removed under vacuum and the residue was triturated with CH$_3$CN (20 mL). The solid was filtered under a nitrogen atmosphere, washed with CH$_3$CN (5 x 10 mL) and dried under vacuum. The product was obtained as a light brown solid (0.7025 g, 67% yield). ^{13}C CP-MAS NMR (100.61 MHz): 154-148 (br, C^1), 145-136 (br, C^3, C^5, C^7, C^9), 136-132 (br, C^4), 132-124 (br, C^6, C^8), 112-100 (br, C^2), 65-25 (br, C^{13}, C^{14}, polyNB), 25-17 (br, C^{10}, C^{11}, C^{12}). ^{11}B MAS NMR (128.38 MHz): 3 (br). IR (neat, cm^{-1}): 1449s, 1100s, 849s, 770s, 441m.

Synthesis of polymer VA-PNB-NBCH$_2$CH$_2$B(pz^{Me2})$_3$Cu(NCMe) (2a-Cu). To VA-PNB-NB(CH$_2$)$_2$B(pz^{Me2})$_3$Li (10.2 g, 18.9 mmol) suspended in CH$_3$CN (40 mL) was added a solution of CuI (3.6 g, 18.9 mmol) in CH$_3$CN (120 mL). The mixture was stirred at room temperature for 3 hours. The solid was filtered under a nitrogen atmosphere, washed with CH$_3$CN (6 x 50 mL) and dried in vacuo (11.7 g, 97% yield). ICP-MS Cu: 90.485 mg Cu/g polymer; calculated maximum amount (for the initial functionalization of **1a** x/y = 1.25 and complete transformation in previous steps): 99.359 mg Cu/g polymer. ^{13}C CP-MAS NMR (100.61 MHz): 153-141 (br, C^1, C^3), 114-100 (br, C^2), 60-19 (br, C^6, C^7, polyNB), 19-9 (br, C^4, C^5), 3 (NC*Me*).[38] ^{11}B MAS NMR (128.38 MHz): -1.5 (br). All the polymers with the -Cu(NCMe) fragment were synthesized following the same procedure.

VA-PNB-NBCH$_2$CH$_2$B(pz^{Mes})$_3$Cu(NCMe) (4a-Cu). 97% yield. ICP-MS Cu: 48.032 mg Cu/g polymer; calculated maximum amount (for the initial functionalization of **1a** x/y = 1.15): 70.545 mg Cu/g polymer. ^{13}C CP-MAS NMR (100.61 MHz): 157-153 (br, C^1), 146-136 (br, C^3, C^4, C^5, C^7, C^9), 134-126 (br, C^6, C^8), 117 (br, NC*Me*), 110-106 (br, C^2), 65-25 (br, C^{13}, C^{14}, polyNB), 25-18 (br, C^{10}, C^{11}, C^{12}), 3.2 (NC*Me*). ^{11}B MAS NMR (128.38 MHz): -2.6 (br).

VA-PNB-NBCH$_2$CH$_2$B(pz^{BrMe2})$_3$Cu(NCMe) (3a-Cu). 96% yield. ICP-MS Cu: 65.007 mg Cu/g; calculated maximum amount (for the initial functionalization of **1a** x/y = 1.25): 72.521 mg Cu/g polymer. ^{13}C CP-MAS NMR (100.61 MHz): 153-141 (br, C^1, C^3), 101-95 (br, C^2), 60-20 (br, C^6, C^7, polyNB), 19-8 (br, C^4, C^5), 2.9 (NC*Me*). ^{11}B MAS NMR (128.38 MHz): -1.1 (br).

VA-PNB-NBCH$_2$CH$_2$CH$_2$CH$_2$B(pz^{Me2})$_3$Cu(NCMe) (2b-Cu). 95% yield. ICP-MS Cu: 85.083 mg Cu/g; calculated maximum amount (for the initial functionalization of **1b** x/y = 2.12): 84.766 mg Cu/g polymer. ^{13}C CP-MAS NMR (100.61 MHz): 154-144 (br, C^1, C^3), 119 (br,

NC*Me*), 112-106 (br, C^2), 63-20 (br, C^6, C^7, C^8, C^9, polyNB), 19-9 (br, C^4, C^5), 2.9 (NC*Me*).

Synthesis of polymer VA-PNB-NBCH$_2$CH$_2$B(pz^{Me2})$_3$Cu(CO). A small amount of polymer VA-PNB-NBCH$_2$CH$_2$B(pz^{Me2})$_3$Cu(NCMe) and CH$_2$Cl$_2$ (5 mL) were placed in a Schlenk tube. CO was bubbled through the suspension for 2 hours at room temperature. The polymer was filtered and dried with a small flow of CO. IR (Neat): v = 2051 cm^{-1} (CO).

All the polymers with the -Cu(CO) fragment were synthesized following the same procedure.
VA-PNB-NBCH$_2$CH$_2$B(pz^{Mes})$_3$Cu(CO): IR (Neat): v = 2087 cm^{-1} (CO)
VA-PNB-NBCH$_2$CH$_2$B(pz^{BrMe2})$_3$Cu(CO): IR (Neat): v = 2066 cm^{-1} (CO).
VA-PNB-NBCH$_2$CH$_2$CH$_2$CH$_2$B(pz^{Me2})$_3$Cu(CO): IR (Neat): v = 2052 cm^{-1} (CO).

Catalytic cyclopropanation reaction. Dry and deoxygenated CH$_2$Cl$_2$ (5 mL) was added to a Schlenk flask containing VA-PNB-Tp^{x}Cu(NCMe) (70 mg, ca. 0.1 mmol of Cu in **2a-Cu** or **3a-Cu**) and 5 mmol of styrene (50 equiv). A solution of EDA (0.5 mmol) in CH$_2$Cl$_2$ (5 mL) was slowly added for 12 h with the aid of a syringe pump, at room temperature. The mixture was then filtered, the solid washed with CH$_2$Cl$_2$ (2 x 5 mL), dried under vacuum and loaded again with solvent and reactants. The filtrate from the reaction mixture was analyzed by GC, identifying exclusively the product derived from styrene cyclopropanation and some diethyl fumarate and maleate from the formal dimerization of the CHCO$_2$Et units from EDA. The filtrate was taken to dryness and the residue was dissolved in CDCl$_3$. The ^{1}H NMR spectrum verified the results of the GC studies.

In a representative experiment to evaluate isolated yields (Table 2, entry 2), the filtrate was taken to dryness and the oily residue dissolved in 1 mL of CH$_2$Cl$_2$ and purified by silica gel column chromatography with a ethyl acetate-hexane mixture (1:20), leading to 81% isolated yield. This procedure is analogous to the one used with non-supported catalysts and the isolated yields are also similar (usually 10-15% lower than the crude yield).[31a]

Catalytic aziridination reaction. Dry and deoxygenated CH$_2$Cl$_2$ (5 mL) was added to a Schlenk flask containing VA-PNB-Tp^{x}Cu(NCMe) (70 mg, ca. 0.1 mmol of Cu in **2a-Cu** or **3a-Cu**). Styrene (2.5 mmol, 25 equiv.) and PhINTs were introduced in one portion (0.5 mmol), and the mixture was stirred for 12 h at room temperature. The mixture was then filtered, the solid washed with CH$_2$Cl$_2$ (2 x 5 mL), dried under vacuum and loaded again with solvent and reactants. Volatiles from the filtrated were removed under vacuum, the resulting aziridine and TsNH$_2$ (from the reaction of PhINTs with adventitious water) were identified by ^{1}H NMR spectroscopy of the reaction crude in CDCl$_3$. This crude can be purified through silica gel column chromatography using ethyl acetate: hexane (10:1) as the eluent. As a representative example, in the aziridination experiment shown in Table 2, entry 4, the aziridine was obtained in 89% yield. The purification procedure is analogous to the one used with non-supported catalysts and difference between the crude and isolated yields is also similar.[31c]

Catalytic amination of cyclohexane. Dry and deoxygenated cyclohexane (5 mL) was added to an ampule containing VA-PNB-Tp^{x}Cu(NCMe) (70 mg, ca. 0.1 mmol of Cu in **2a-Cu** or **3a-Cu**) and PhINTs (0.5 mmol). The mixture was stirred for 12 h at 60 ºC. After this, the mixture was filtered, the solid washed with CH$_2$Cl$_2$ (2 x 5 mL), dried under vacuum and loaded again with solvent and reactants. Volatiles from the filtrated were removed under vacuum, and the N-cyclohexyl-4-methylbenzenesulfonamide and TsNH$_2$ (from the

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reaction of PhINTs with adventitious water) were identified by ^{1}H NMR spectroscopy of the reaction crude in $CDCl_3$.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Trispyrazolylborates • Polynorbornenes • Supported catalysts • Copper catalyst • Carbene transfer • Nitrene transfer

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[37]   The alkene content of the polymer **1a** (z = mmol CH=CH$_2$/g) and the polymer composition given as a ratio of monomers incorporated (x/y = NB/NB-CH=CH$_2$) are related by the equation: z = 1000/(94.16(x/y)+120.194), where 94.16 and 120.194 are the molecular weights of norbornene and 5-vinyl-2-norbornene respectively

[38]   Acetonitrile is visible in the spectrum but, due to the expected small chemical shift difference, it is not possible to tell if it is coordinated to the metal or it is free solvent embedded in the polymer.
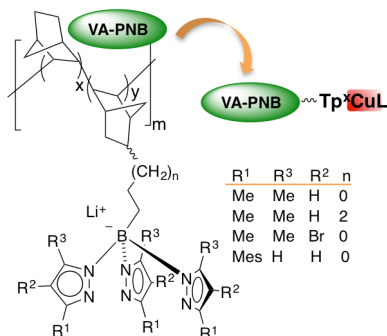
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R¹	R³	R²	n
Me	Me	H	0
Me	Me	H	2
Me	Me	Br	0
Mes	H	H	0

(Table values:)

R^1	R^3	R^2	n
Me	Me	H	0
Me	Me	H	2
Me	Me	Br	0
Mes	H	H	0

Trispyrazolylborate ligands covalently bonded to vinylic addition polynorbornene form copper(I) complexes with catalytic properties toward carbene and nitrene transfer reactions identical to the homogeneous counterparts, but allowing readily catalyst separation and recycling.

Supported trispyrazolylborate ligands

Jesús A. Molina de la Torre, Ignacio Pérez-Ortega, Álvaro Beltrán, Manuel R. Rodríguez, M. Mar Díaz-Requejo,* Pedro J. Pérez*and Ana C. Albéniz*

■■ – ■■
Trispyrazolylborate Ligands Supported on Vinylic Addition Polynorbornenes and their Copper Derivatives as Recyclable Catalysts

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