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Norbornene Bidentate Ligands: Coordination Chemistry and Enantioselective Catalytic Applications

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N- and P-donor derivatives have been prepared by functionalization of a readily available norbornene precursor. Palladium catalytic systems containing these new ligands were applied in allylic substitution, and yielded high activities and excellent enantioselectivities for the allylic alkylation and amination reactions (*ee* up to 97%). A full coordination analysis of the catalytic precursors including modelling studies was also carried out.

Introduction

The creation of an asymmetric environment around a metallic centre in order to accommodate the partners of an organic transformation allows enantioselectivity induction in catalytic processes.[1,2] A classical approach to get this goal is the use of enantiomerically pure ligands containing donor atoms (mainly nitrogen and phosphorus) with a defined symmetry.[3] The rigidity of the backbone is one of the key aspects to take into account in the design of chiral ligands. Furanose,[4] 9,10-dihydroanthracene[5] or imide[5a] backbones are significant examples that contain donor moieties that lead to excellent asymmetric inductions in several processes. Keeping this idea in mind, we have developed a new family of ligands containing a polycyclic backbone derived from the norbonene carboxylic anhydride. Although similar compounds have been widely used as substrates in ring opening metathesis polymerization (ROMP) reactions,[6] only one study that involves the use of related ligands (derived from bicyclo[2.2.2]-2-octene) in V-catalyzed asymmetric epoxidation of homoallylic alcohols has thus far been reported.[7] We have been interested in N- and P-donor ligands because these derivatives, in particular, give excellent enantioselectivies in allylic substitutions catalyzed by palladium.[8] With regard to the nature of the nitrogen atom, ligands containing both sp^2 (imines) and sp^3 (amines) hybridized nitrogen moieties have been explored;[9] the former (pyridine and related aromatic heterocycles[10] or oxazoline derivatives[11]) is the most largely applied in enantioselective reactions. As is known, P-donor fragments are included in the main part of classical homogeneous catalysis, ligands such as phosphanes and phosphites, but also phosphinites, phosphonites and phosphoramidites.[12] After the successful results obtained with diphosphites derived from (2*R*,4*R*)-pentanediol by Union Carbide in the 1990s,[13] diphosphites derived from different backbones were designed, in particular those with the xylofuranose skeleton described by van Leeuwen.[4a,4b] In the last few years, we have also reported the synthesis of diphosphites derived from rigid backbones, such as ribofuranose and glucofuranose,[4c,14] and also from 9,10-dihydroanthracene,[5c] obtaining excellent selectivities (*ee* > 97%) and activities (TOF > 22000 h^{-1}) for the Pd-catalyzed allylic substitution.[15] These diphosphites have also found remarkable application in styrene hydroformylation (*ee* > 50%).[4,5c,14]

Herein we report the synthesis of new ligands derived from *endo*-norborn-5-ene-2,3-dicarboxylic anhydride (Figure 1) and their application in Pd-catalyzed enantioselective allylic substitution reactions. The coordination chemistry of the new amine and phosphite ligands has been studied both in solution and in the solid state.

Results and Discussion

Synthesis of Ligands

N,*N*- and P,P-donor ligands with a norbornene scaffold were developed (Figure 1). Bis(amines) **3** and **4** were prepared following a two-step synthetic procedure based on our previously reported methodology (Schemes 1 and 2).[16] In the first step, bis(imides) **1** and **2** were prepared by condensation of the anhydride with the appropriate primary bis(amine) in toluene at reflux,[17] by using a Dean–Stark

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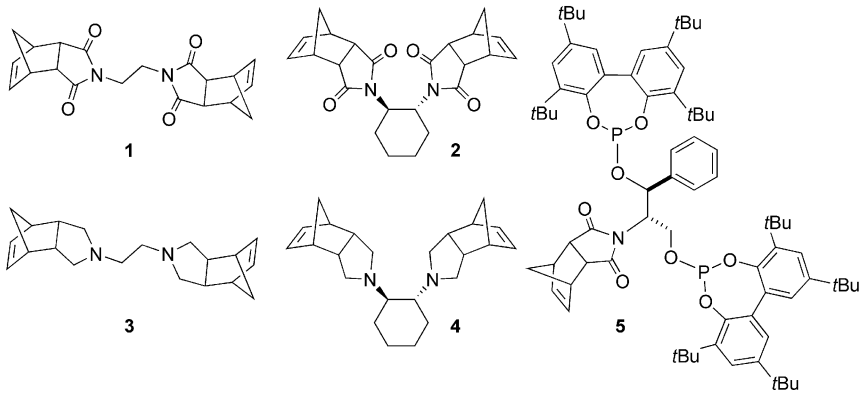
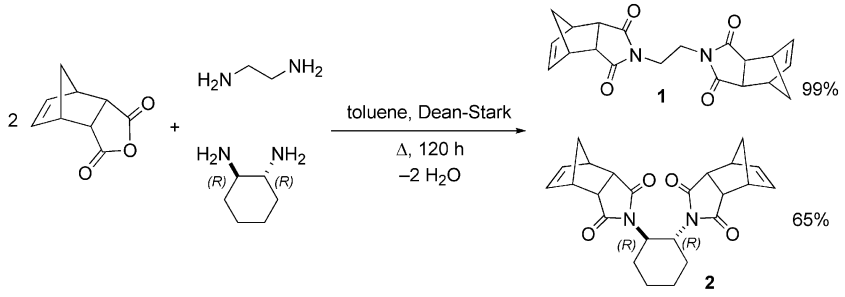
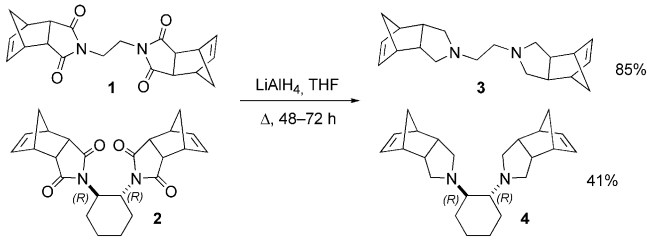


Figure 1. New N- and P-donor ligands containing a norbornene scaffold.



Scheme 1. Synthesis of imides **1** and **2** starting from *endo*-carbic anhydride.

system to eliminate the water formed (Scheme 1). When the more sterically hindered (1*R*,2*R*)-1,2-diphenylethylenediamine was used, a mixture of the mono(imide) and the corresponding amido acid only was recovered.



Scheme 2. Synthesis of bis(amines) **3** and **4** from the corresponding imides.

The bis(amines) **3** and **4** were obtained by standard reduction of the carbonyl groups with $LiAlH_4$, from the isolated bis(imides) (Scheme 2).[18]

An X-ray diffraction study carried out on monocrystals of compound **1** reveals a centrosymmetric structure that presents a quasi-planar five-membered heterocycle. The short N1–C2 and N1–C3 bond lengths (ca. 1.39 Å) relative to the N1–C1 distance (1.45 Å) points to an electronic delocalization between the nitrogen and the close carbonyl groups (Figure 2).

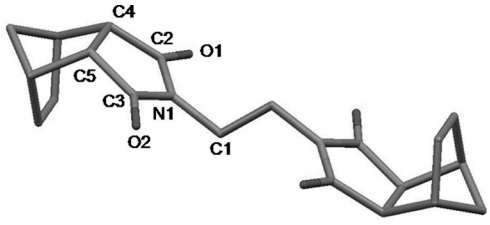
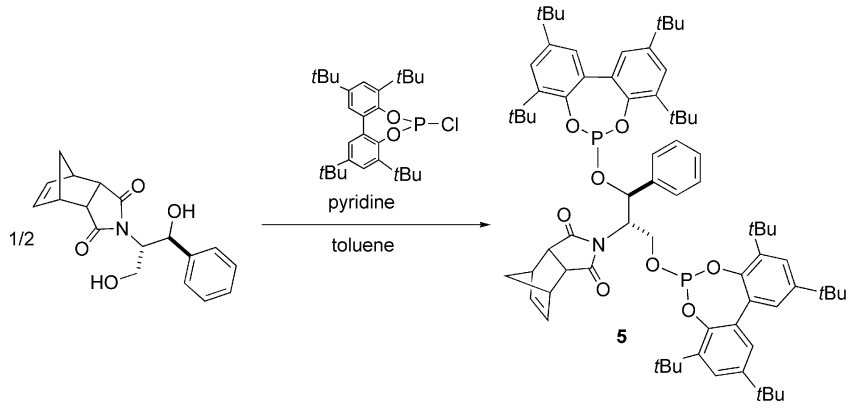


Figure 2. View of the molecular structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: N1–C1 = 1.455; N1–C2 = 1.390; N1–C3 = 1.385; O1–C2 = 1.208; O2–C3 = 1.214. Selected torsion angles [°]: O1–C2–N1–C3 = 179.3; N1–C2–C4–C5 = 2.7.

For **2**, the VT ^{1}H NMR study in solution (323–223 K) evidences the presence of two isomers below room temperature in a ratio of 4:3 (Figure S1 in the Supporting Information), presumably resulting from the rotation around the C*–N bond; this result is in agreement with the modelling study carried out (Figure 3). This rotation is more sterically hindered for the corresponding bis(amine) **4** than for the corresponding imide **2**, mainly because of the pyramidalization of the nitrogen atom after reduction of the carbonyl groups (Figure 3). Actually, the ^{1}H NMR spectra of **4** shows only the presence of one species in the temperature range studied (298–223 K) (Figure S2 in the Supporting Information).



Scheme 3. Synthesis of the chiral diphosphite **5** from the corresponding diol.

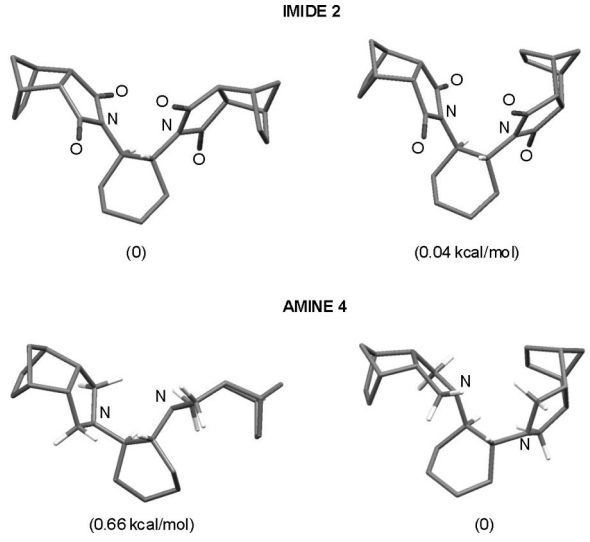


Figure 3. Modelled structures (by PM3 methodology) of both isomers of compounds **2** and **4** (their relative formation enthalpies are in parentheses). Only selected hydrogen atoms are shown.

A bidentate P-donor ligand was also synthesized by functionalization of the alcohol groups integrated in an optically pure imide–norbornene precursor.[16] Thus, diphosphite **5** was isolated following our previously reported methodology (Scheme 3).[5c] The diol was treated with the appropriate phosphorochloridite (prepared in situ by standard procedures[19]) to give **5** in a good yield (71%).

This ligand shows two isomers in solution in a ratio of 3:1 (for the ^{1}H and ^{31}P spectra, see Figure S3 in the Supporting Information). In order to understand the origin of these conformers, a modelling study (PM3 semiempirical level) was carried out. These isomers probably arise because of the relative position of both substituents on the C stereocentres (Figure 4). No interconversion was observed in solution, which is in agreement with the important difference in their relative calculated enthalpies (ΔE = 3.9 kcal/mol) and with the calculated rotation barrier around the corresponding C–N bond (ca. 3 kcal/mol).

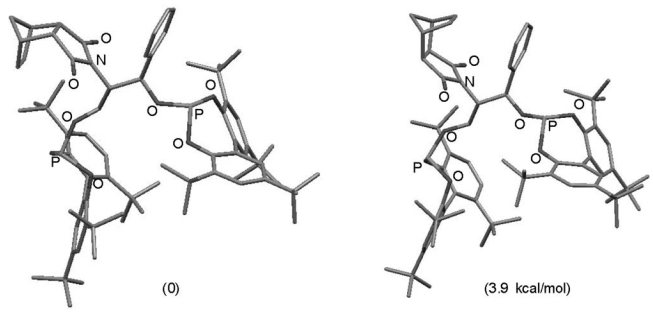
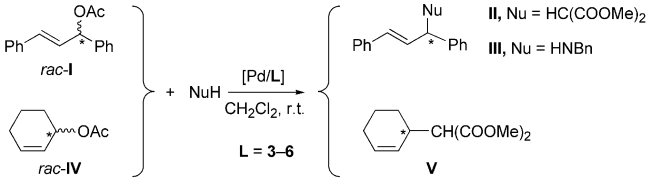


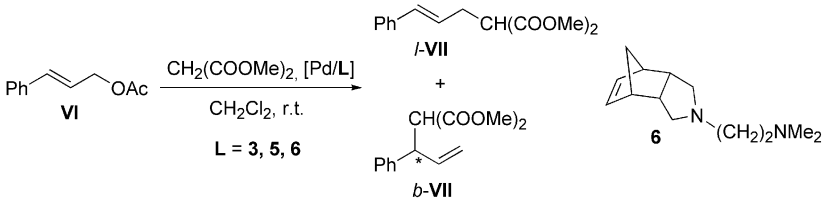
Figure 4. Modelled structures (by PM3 methodology) of both isomers of ligand **5** (their relative formation enthalpies are in parentheses). Hydrogen atoms are omitted for clarity.

Enantioselective Catalytic Reactions

The allylic alkylation of racemic substrate *rac*-**I** with dimethyl malonate under basic conditions (BSA/KOAc) was performed, which involved in situ catalyst formation by reaction of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and the corresponding ligand (**3**–**6**, Scheme 4). Unlike other catalytic systems containing nonchiral bis(amines), **3** and **6** gave good conversions after 2 h (Entries 1 and 2, Table 1); the catalyst containing the bulkier and more rigid chiral bis(amine) **4** was inactive (Entry 3, Table 1). In contrast, Pd/**5** gave nearly total conversion of the substrate after 30 min of reaction (Entries 4 and 5, Table 1), with an excellent asymmetric induction [*ee* = 97% (*S*) for **II**]. This system was also very active in allylic amination with benzylamine as the nucleophile; 80% conversion of *rac*-**I** was observed in 1 h with an *ee* of 95% (*R*) for **III** (Entries 6 and 7, Table 1). However, the allylic



Scheme 4. Allylic substitution catalyzed by palladium systems containing ligands **3**–**6**.



Scheme 5. Regioselective allylic alkylation catalyzed by palladium systems containing ligands **3**, **5** and **6**.

alkylation of the less hindered cyclohexenyl allylic acetate *rac*-**IV** catalyzed by Pd/**5** led to a low asymmetric induction, *ee* up to 17% (*S*) (Entries 8 and 9, Table 1).

Table 1. Palladium-catalyzed allylic substitution with ligands **3**–**6**.[a]

Entry	L	Substrate	NuH[b]	Time [h]	Conv. [%][c]	*ee* [%][d]	*l*/*b* ratio[c]
1	**3**	*rac*-**I**	DMM	2	64	–	–
2	**6**	*rac*-**I**	DMM	2	100	–	–
3[e]	**4**	*rac*-**I**	DMM	4	0	–	–
4	**5**	*rac*-**I**	DMM	0.25	76	97(*S*)	–
5	**5**	*rac*-**I**	DMM	0.5	95	97(*S*)	–
6	**5**	*rac*-**I**	$BnNH_2$	0.25	35	95(*R*)	–
7	**5**	*rac*-**I**	$BnNH_2$	1	80	95(*R*)	–
8	**5**	*rac*-**IV**	DMM	0.5	34	9(*S*)	–
9	**5**	*rac*-**IV**	DMM	2	99	17(*S*)	–
10	**5**	**VI**	DMM	0.5	96	–	7:1
11	**3**	**VI**	DMM	1	92	–	>9:1
12	**6**	**VI**	DMM	1	98	–	>9:1

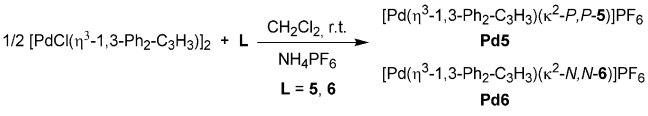
[a] Catalytic conditions for alkylation: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/L/substrate/DMM/BSA = 1:2.5:100:300:300, CH_2Cl_2, room temperature.; for amination: $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/L/substrate/$BnNH_2$ = 1:2.5:100:300, CH_2Cl_2, room temperature. [b] NuH = dimethylmalonate (DMM) using BSA and a catalytic amount of KOAc as a base; NuH = benzylamine ($BnNH_2$). [c] Determined by ^1H NMR spectroscopy. [d] Determined by HPLC for **II** and **III** and by GC for **V**. The absolute configuration of the substituted product determined by optical rotation is given in parentheses: for **II** and **III**, see ref.[25]; for **V**, see ref.[26] [e] When Pd/**4** = 1:2.5, 7% conversion was obtained after 4 h of reaction.

In order to evaluate the regio- and enantioselectivity, we studied the reactivity of the Pd/**5** catalytic system in the allylic alkylation of cinnamyl acetate (Scheme 5). Unfortunately, this catalytic system principally favoured the formation of the linear regioisomer (*l*/*b* = 7:1, Entry 10, Table 1). The use of the achiral bis(amine) ligands **3** and **6**[16] improves this regioselectivity and exclusively gives the linear isomer (Entries 11 and 12, Table 1). No reactivity differences were observed when preformed complex Pd**6** (see below) was used as a catalytic precursor.

Bis(amine) ligands **3**, **4** and **6** were also used in the Ru-catalyzed asymmetric hydrogen transfer reaction of acetophenone by using 2-propanol in the presence of potassium *tert*-butoxide as the hydrogen source. Ru/bis(amine) systems were moderately active, but unfortunately Ru/**4** did not induce enantioselectivity (see Supporting Information for catalytic results and experimental details).

Coordination Chemistry

We have carried out a coordination chemistry study involving the ligands which were active and/or enantioselective in the catalytic processes studied (Scheme 6). Therefore we prepared the palladium allylic complexes Pd**5** and Pd**6** containing the chiral diphosphite **5**, which led to excellent enantioselectivies in the alkylation and amination reactions, and the bis(amine) **6**, which gave the highest activity in the allylic alkylation of substrate *rac*-**I** and a high regioselectivity towards the linear isomer in the alkylation of cinnamyl acetate The complexes were fully characterized by conventional techniques (see Experimental Section). The results of the elemental analysis and the mass spectrometry and IR spectroscopy studies are in agreement with the formation of ionic complexes with the formula $[Pd(\eta^3\text{-}1,3\text{-}Ph_2\text{–}C_3H_3)(\kappa^2\text{-}X,X\text{-}\mathbf{L})]PF_6$ (where X = P or N and L = **5** or **6**, respectively), proposed in Scheme 6.



Scheme 6. Synthesis of **Pd5** and **Pd6** complexes.

^1H and ^{31}P spectra at variable temperatures were recorded for Pd**5**. The ^{31}P NMR spectrum at room temperature shows broad signals in the region ca. 125–135 ppm. At lower temperatures, two groups of signals can be distinguished (ca. 134 and 124 ppm); each of these groups exhibit several signals, probably resulting from the presence of several isomers (Figure 5). At 233 K, a ^{31}P-^{31}P COSY experiment was recorded in order to observe the correlations between both groups of signals, but, unfortunately, no signals were observed. The ^1H NMR spectra show a complicated pattern, and it is difficult to assign the different signals to the different isomers involved in solution (Figure S4 in the Supporting Information). These observations evidence the formation of several isomers in solution, which arise from the ligand conformers (see above) and the allyl isomers.

With regard to Pd**6**, the ^1H and ^{13}C NMR spectra at room temperature proves the presence of two isomers in solution in a ratio of ca. 7:1 (Figure S5 in the Supporting Information). The complex shows three sources of plausible isomerism. One of them is the relative position of the bicycle moiety of the bis(amine) in relation to the phenyl group of the allyl ligand (isomers A and B or C and D in Scheme 7). Another arrangement that can lead to different isomers is the relative position of the central allylic carbon atom in relation to the PdNN′ coordination plane (isomers A and C or B and D in Scheme 7); A and C, and B and D

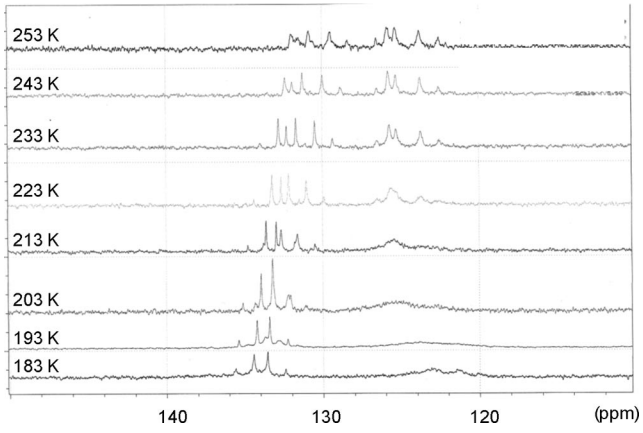
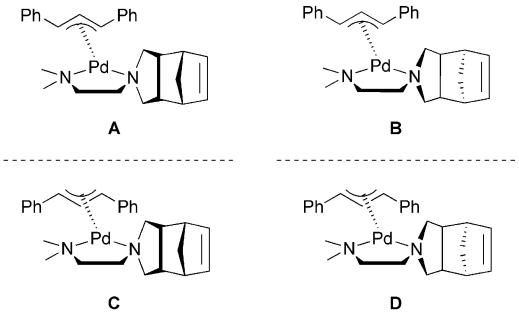


Figure 5. VT ^{31}P NMR spectra (150–110 ppm region, 161 MHz, CD_2Cl_2) for Pd**5**. At –145.5 ppm, a septet assigned to the hexafluorophosphate anion is observed.

represent two couples of enantiomers. The third arrangement comes from the relative *syn* or *anti* position of the phenyl groups in the allyl fragment; taking into account that the *syn* arrangement corresponds to the most stable conformation and that the 2D NOESY NMR spectrum does not exhibit exchange signals between the two isomers observed in solution, we can propose that the π–σ–π interconversion did not take place and consequently only *syn*/*syn* isomers are observed.

Therefore the two isomers observed by NMR spectroscopy must arise as a result of the relative position of the bicycle. The X-ray diffraction analysis of monocrystals obtained by slow evaporation of a chloroform solution shows a structural disorder with 88.7% occupancy for the isomer A and 11.3% for B (Figure 6). Both molecules show a slightly distorted square-planar arrangement around the palladium atom (dihedral angle between N1PdN2 and C20Pd1C22 is ca. 11°, Figure 6). The five-membered metallacycle adopts a half-chair conformation.



Scheme 7. Possible isomers of Pd**6** (only the cation is shown) depending on the relative position of the bicycle group of the bis(amine) and the allyl ligands.

We were also interested in the study of the coordination of the symmetrical bis(amines) **3** and **4** with ruthenium. Actually, Ru**3** was obtained in a good yield (63%) from the Ru dimer $[RuCl_2(p\text{-cymene})]_2$ in the presence of **3**. However, attempts to isolate the corresponding complex containing the chiral bis(amine) **4** were unsuccessful, probably because of the steric hindrance around the metal centre upon coordination (see Supporting Information for characterization and experimental details).

Conclusions

In summary, new N-donor (**3** and **4**) and P-donor (**5**) ligands containing a norbornene backbone were synthesized, and their catalytic applications in Pd-catalyzed allylic substitution reactions were examined. For the more active and selective systems, a coordination chemistry study was carried out both in the solid state and in solution by means of NMR spectroscopy. A full discussion about the different isomers observed in solution was considered including modelling approaches. The chiral diphosphite **5** gave excellent asymmetric induction in allylic alkylation (97% *ee*) and amination (95% *ee*). With respect to the bidentate *N*,*N*-do-

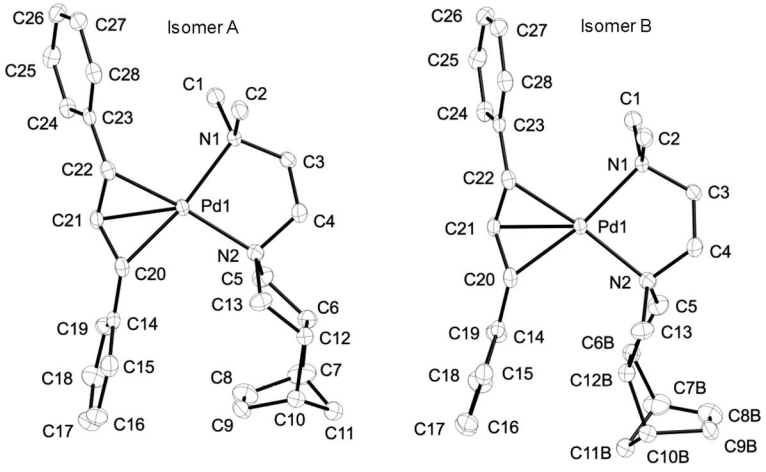


Figure 6. ORTEP diagrams of Pd**6** corresponding to the isomers A and B. Their enantiomers and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Pd1–C20 = 2.171; Pd1–C22 = 2.174; Pd1–C21 = 2.134; Pd1–N1 = 2.160; Pd1–N2 = 2.148. Selected bond angles [°]: C20–Pd1–C22 = 67.65; N1–Pd1–N2 = 84.09; C20–C21–C22 = 118.3.

nor ligands **3** and **6**, the palladium systems were active in allylic alkylation. The palladium systems were highly regioselective towards the linear isomer (*l*/*b* > 9:1) in the allylic alkylation of cinnamyl acetate. However, the chiral bis(amine) **4** was not active in allylic alkylation, probably because of its steric hindrance to give metallacycle. A preliminary study involving the Ru systems did not induce enantioselectivity in the hydrogen transfer of acetophenone.

Experimental Section

General Remarks: Compounds were prepared under a purified nitrogen atmosphere by using standard Schlenk and vacuum-line techniques. Organic solvents were purified by standard procedures and distilled under nitrogen. Unless stated otherwise, all reactants and reagents were purchased commercially and used without further purification. Syntheses of the Pd^{II} dimer,[20] substrates *rac*-**I**[21] and *rac*-**IV**,[22] *endo*-*N*-[(1*S*,2*S*)-1,3-dihydroxy-1-phenylprop-2-yl]bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide and ligand **6**[16] are described elsewhere. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian Mercury 400 and Bruker Advance 500 spectrometers equipped with a CryoFlowProbe. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$ for ^1H and ^{13}C and 85% H_3PO_4 for ^{31}P), and coupling constants are given in Hz. IR spectra were carried out on pellets of dispersed samples of the corresponding compounds in KBr and were obtained on a FTIR Nicolet Nexus 5700 spectrometer. MS spectra were recorded with a Hewlett–Packard 5989A instrument with an electron energy of 70 eV (EI), with a ThermoFinnigan TRACE DSQ mass spectrometer with an electron energy of 70 eV, and ammonia as reactant gas (CI), or with a LC/MSD-TOF mass spectrometer (HR-ES). Elemental analyses were carried out at the Servei d′Anàlisi Elemental of the Universitat de Barcelona or the Servei d′Anàlisi Química of the Universitat Rovira i Virgili, in both cases by using an Eager 1108 instrument. Optical rotations were measured on a Perkin–Elmer 241MC polarimeter at room temperature. GC routine analyses were carried out by using an Agilent 6890N chromatograph (30 m × 0.32 mm HP5 column), while enantioselectivities in product **V** were also analyzed by GC on a Hewlett–Packard 5890 chromatograph (30 m × 0.25 mm capillary Chiraldex B-DM column), both of them with a FID detector. Enantiomeric excesses in products **II** and **III** were determined by HPLC by using a Waters 717 Plus autosampler chromatograph with a Waters 996 multidiode array detector fitted with a Chiralcel OD-H chiral column [eluent: hexane/2-propanol (95:5)] for **II** or a Alliance 2695 chromatograph with PDA-UV detector fitted with a Chiralcel OJ-H column [eluent: hexane/2-propanol (95:5)] for **III**. Modelling studies were performed with the SPARTAN′06 software.[27]

Synthesis of Ligands

Bis(*endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide)s 1 and 2: *endo*-Norborn-5-ene-2,3-dicarboxylic anhydride (2.00 g, 12.18 mmol) was dissolved in toluene (50 cm^3) under vigorous stirring. The corresponding diamine (6.13 mmol) was then slowly added, which lead to a white suspension. The mixture was heated at reflux and stirred for 120 h with continuous extraction of water (by means of a Dean–Stark apparatus). After cooling to room temperature, the solution formed was concentrated under reduced pressure to render a yellowish solid, which was subsequently dissolved in CH_2Cl_2 (30 cm^3) and consecutively washed with 1 M H_2SO_4 (3 × 20 cm^3) and water (3 × 20 cm^3). The aqueous phases were extracted with 10 cm^3 of CH_2Cl_2. The combined organic extracts were dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated to dryness under reduced pressure, to give the corresponding bis(imide). **Bis(imide) 1:** White solid. Yield: 2.13 g (99%). White crystals suitable for the structural resolution by X-ray diffraction were grown by slow evaporation of a solution of this product in water. IR (KBr pellet): $\tilde{\nu}$ = 2997, 2956, 1703 (CO), 1395, 1339, 1162, 1127, 1029, 874, 843, 781, 720, 613 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.51 (d, J = 8.8 Hz, 2 H, 2 × C*H*H′bridge), 1.71 (dt, J = 1.6 and 8.8 Hz, 2 H, 2 × CH*H*′bridge), 3.23 (dd, J = 1.6 and 3.2 Hz, 4 H, 4 × CH_{olefin}C*H*CH_2bridge), 3.34 (*m*, 4 H, 4 × C*H*CON), 3.47 (*s*, 4 H, 2 × CONC*H*$_2$), 6.05 (*t*, J = 1.8 Hz, 4 H, 4 × C*H*$_{olefin}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.5 (2 × CON*C*H$_2$), 44.8 (4 × CH_{olefin}*C*HCH_2bridge), 46.1 (4 × *C*HCON), 52.4 (2 × *C*H$_2$bridge), 134.6 (4 × *C*H$_{olefin}$), 177.8 (4 × *C*O) ppm. MS (EI): calcd. for $C_{20}H_{20}N_2O_4$ $[M]^+$ 352.1; found 352.0. $C_{20}H_{20}N_2O_4$ (352.1): calcd. C 68.2, H 5.7, N 8.0; found C 67.7, H 5.8, N 7.9. **Bis(imide) 2:** White solid obtained after crystallization of the original brown oil in hexane/CH_2Cl_2 (5:1). Yield: 1.62 g (65%). $[\alpha]_D^{25}$ = –13.1 (*c* 1.0, $CHCl_3$). IR (KBr pellet): $\tilde{\nu}$ = 2990, 2941, 2871, 1702 (CO), 1376, 1337, 1257, 1187, 1124, 1044, 845, 752, 725, 662, 626 cm^{-1}. ^1H NMR (40 MHz, $CDCl_3$): Isomer A (66%): δ = 1.32 (bs t, 2 × CONCHC*H*H′, J = 10.2 Hz, 2 H), 1.44–1.50 (bs, s, 2 × CONCHCH$_2$C*H*H′, 2 H), 1.47 (d, J = 8.4 Hz, 2 H, 2 × C*H*H′bridge), 1.64–1.74 (bs, s, 2 × CONCHCH*H*′, 2 H), 1.68 (d, J = 8.4 Hz, 2 H, 2 × CH*H*′bridge), 2.06 (br. s, 2 H, 2 × CONCHCH$_2$CH*H*′), 3.10 (bs, s, 4 H, 4 × C*H*CON), 3.34 (bs, s, 4 H, 4 × CH_{olefin}C*H*CH_2bridge), 4.61 (bs, s, 2 H, 2 × CONC*H*CH$_2$), 6.04 (bs, s, 4 H, 4 × C*H*$_{olefin}$). Isomer B (34%): 1.32 (bs, t, 2 × CONCHC*H*H′, J = 10.2 Hz, 2 H), 1.47 (d, J = 8.4 Hz, 2 H, 2 × C*H*H′bridge), 1.61 (bs, s, 2 H, 2 × CONCHCH$_2$C*H*H′), 1.64–1.74 (bs, s, 2 H, 2 × CONCHCH*H*′), 1.68 (d, J = 8.4 Hz, 2 H, 2 × CH*H*′bridge), 1.86 (bs, s, 2 H, 2 × CONCHCH$_2$CH*H*′), 3.10 (bs, s, 2 H, 2 × C*H*CON), 3.16 (bs, s, 2 H, 2 × C*H*′CON), 3.34 (bs, s, 4 H, 4 × CH_{olefin}C*H*CH_2bridge), 4.80 (bs, s, 2 H, 2 × CONC*H*CH$_2$), 5.89 (bs, s, 2 H, 2 × C*H*$_{olefin}$), 6.04 (bs, s, 2 H, 2 × C*H*′$_{olefin}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.7 (2 × CONCH*C*H$_2$), 28.9 (bs, 2 × CONCHCH$_2$*C*H$_2$), 45.1 (2 × CH_{olefin}*C*HCH_2bridge), 45.3 (2 × CH_{olefin}*C*′HCH_2bridge), 45.4 (2 × *C*HCON), 45.5 (2 × *C*′HCON), 49.8–50.1 (bs, 2 × CON*C*HCH$_2$), 52.0–52.4 (bs, 2 × *C*H$_2$bridge), 133.7–135.1 (bs, 4 × C*H*$_{olefin}$), 176.8–177.5 (4 × *C*O) ppm. MS (CI, NH_3): calcd. for $[M + H]^+$ 407.2; found 407.6. $C_{24}H_{26}N_2O_4{\cdot}H_2O$: calcd. C 67.9, H 6.7, N 6.6; found C 68.2, H 6.6, N, 6.5.

Bis(*endo*-4-azatricyclo[5.2.1.0^{2,6}]dec-8-enes) 3 and 4: A solution of the corresponding bis(imide) (2.84 mmol) in THF (75 cm^3) was cooled to 0 °C, and lithium tetrahydridoaluminate (2.15 g, 56.75 mmol) was then slowly added. The resulting grey suspension was heated at reflux for 48–72 h and then cooled to 0 °C. Ethyl ether (30 cm^3) and a saturated aqueous solution of Na_2SO_4 were poured into the reaction mixture. The aqueous solution was added very slowly and stopped when effervescence was no longer observed. The white gel thus obtained was filtered through Celite, and the resulting colourless solution was washed several times with a mixture CH_2Cl_2/MeOH (9:1). The organic layer was washed with water (3 × 30 cm^3), dried with anhydrous Na_2SO_4 and filtered, and the solvent evaporated under reduced pressure to give the corresponding product. **Bis(amine) 3:** White solid. Yield: 717 mg (85%). IR (KBr pellet): $\tilde{\nu}$ = 3059, 2965, 2930, 2865, 2804, 1475, 1336, 1252, 1137, 903, 872, 815, 796, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ

= 1.55 (d, J = 8.0 Hz, 2 H, 2 × C*H*H′bridge), 1.67 (d, J = 8.0 Hz, 2 H, 2 × CH*H*′bridge), 1.78–1.81 (m, 4 H, 4 × CHC*H*H′N), 2.40 (s, 4 H, 2 × $CHCH_2NCH_2$), 2.76 (bs, s, 4 H, 4 × $CH_{olefin}CHCH_2$-bridge), 2.83–2.90 (m, 4 H, 4 × CHCH*H*′N), 2.89 (bs, s, 4 H, 4 × $CHCH_2N$), 6.09 (bs, s, 4 H, 4 × CH_{olefin}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.7 (4 × $CH_{olefin}CHCH_2$bridge), 46.7 (4 × *C*HCH_2N), 54.0 (2 × *C*H_2bridge), 55.1 (4 × $CHCH_2NCH_2$), 57.3 (4 × $CHCH_2N$), 137.5 (4 × *C*H_{olefin}) ppm. MS [HR-ES(+)]: calcd. for $[M + H]^+$ 297.2331; found 297.2337. **Bis(amine) 4:** White solid obtained after crystallization of the original brown paste by slow evaporation of a solution of the product in 40 cm^3 hexane. Yield: 408 mg (41%). $[a]_D^{25}$ = +10.5 (*c* 0.2, $CHCl_3$). IR (KBr pellet): $\tilde{\nu}$ = 2964, 2934, 2788, 1456, 1439, 1383, 1343, 1260, 1091, 1014, 802, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23 (bs, d, 2 × NCHC*H*H′, J = 4.4 Hz, 2 H), 1.28 (bs, d, J = 14.8 Hz, 2 H, 2 × NCHCH$_2$C*H*H′), 1.43–1.46 (*bs*, *s*, 2 H, 2 × NCHCH*H*′), 1.44 (d, J = 7.6 Hz, 2 H, 2 × C*H*H′bridge), 1.54 (d, J = 7.6 Hz, 2 H, 2 × CH*H*′bridge), 1.64 (bs, s, 2 H, 2 × $NCHCH_2CHH'$), 2.02 (bs, s, 2 H, 2 × $NCHCH_2$), 2.10 (bs, s, 4 H, 4 × CHC*H*H′N), 2.53 (bs, s, 4 H, 4 × $CH_{olefin}CHCH_2$bridge), 2.78 (s, 8 H, 4 × *C*HCH_2N and 4 × CHCH*H*′N), 6.11 (bs, s, 4 H, 4 × C*H*$_{olefin}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0 (2 × $NCHCH_2$), 24.8 (2 × $NCHCH_2CH_2$), 45.7 (2 × $CH_{olefin}CHCH_2$bridge), 45.7 (2 × $CH_{olefin}C'HCH_2$bridge), 45.9 (4 × *C*HCH_2N), 53.0 (4 × $CHCH_2N$), 54.5 (2 × *C*H_2bridge), 62.9 (2 × $NCHCH_2$), 136.6 (4 × *C*H_{olefin}) ppm. MS [HR-ES(+)]: calcd. for $[M + H]^+$ 351.2800; found 351.2804.

***endo*-*N*-[(1*S*,2*S*)-1,3-Bis(3,3′,5,5′-tetrakis(*tert*-butyl)biphenyl-2,2′-diylphosphito)-1-phenylprop-2-yl]bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (5):** A solution of *endo*-*N*-[(1*S*,2*S*)-1,3-dihydroxy-1-phenylprop-2-yl]bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (313 mg, 1.00 mmol), previously azeotropically dried with toluene (3 × 1 cm^3), in dry and degassed toluene (10 cm^3) and cooled to 0 °C, was slowly added to a solution of phosphorochloridite (2.10 mmol), synthesized in situ by standard procedures,[4a,19b] in dry and degassed pyridine (1.5 cm^3). The resulting mixture was stirred overnight allowing the temperature to rise to room temperature. The pyridinium salts were then removed upon filtration, and the solution was concentrated to dryness under reduced pressure. The white foam thus obtained was purified by flash column chromatography under nitrogen by using toluene as the eluent to give the desired product as a white solid. Yield: 832 mg (71%). IR (KBr pellet): $\tilde{\nu}$ = 3445, 2961, 1708, 1456, 1436, 1396, 1360, 1227, 1091, 994, 878, 802, 782, 699 cm^{-1}. ^{31}P NMR (162 MHz, $CDCl_3$): Isomer A (74%): δ = 134.4, 146.9 ppm; Isomer B (26%): δ = 132.8, 146.7 ppm. ^1H NMR (40 MHz, $CDCl_3$): Isomer A (74%): δ = 1.42–1.56 [m, 74 H, 8 × C(CH_3)$_3$ and CH_2bridge], 3.23 (bs, s, 2 H, 2 × $CH_{olefin}CHCH_2$bridge), 3.27 (bs, s, 2 H, 2 × C*H*CON), 3.44 (bs, s, 1 H, CONCHC*H*H′), 4.13 (bs, s, 1 H, CONCHCH*H*′), 4.58 (dt, J = 4.4 and 10.4 Hz, 1 H, CONC*H*), 5.47 (pt, J = 9.8 Hz, 1 H, CONCHC*H*Ph), 5.95 (bs, s, 1 H, C*H*$_{olefin}$), 6.00 (bs, s, 1 H, C*H*′$_{olefin}$), 7.16–7.54 (m, 13 H, H Ar) ppm. ^{13}C NMR (10 MHz, $CDCl_3$): Isomer A (74%): δ = 31.1 [C(*C*H_3)$_3$], 31.4 [C(*C*H_3)$_3$], 31.7 [3 × C(*C*H_3)$_3$], 31.8 [2 × C(*C*H_3)$_3$], 31.9 [C(*C*H_3)$_3$], 34.7 [2 × *C*(CH$_3$)$_3$], 34.8 [2 × *C*(CH$_3$)$_3$], 35.4 [2 × *C*(CH$_3$)$_3$], 35.5 [2 × *C*(CH$_3$)$_3$], 44.6 ($CH_{olefin}CHCH_2$bridge), 44.7 ($CH_{olefin}C'HCH_2$-bridge), 45.2 (*C*HCON), 45.3 (*C*′HCON), 51.7 (*C*H_2bridge), 57.0 (CON*C*H), 59.6 (CONCH*C*H_2), 72.0 (CONCH*C*HPh), 124.1–146.5 (C Ar) ppm. MS [HR-ES(+)]: calcd. for $[M + Na]^+$ 1212.6587; found 1212.6584; calcd. for $[M + K]^+$ 1228.6326; found 1228.6325. $C_{74}H_{97}NO_8P_2$ (1228.6): calcd. C 74.7, H 8.2, N 1.2; found C 74.5, H 8.3, N 1.3.

Synthesis of Complexes

[*endo*-*N*-[(1*S*,2*S*)-1,3-Bis(3,3′,5,5′-tetrakis(*tert*-butyl)biphenyl-2,2′-diylphosphito)-1-phenylprop-2-yl]bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide](η^3-1,3-diphenylallyl)palladium(II) Hexafluorophosphate (Pd5): Di-μ-chlorobis[(η^3-1,3-diphenylallyl)palladium(II)] (22 mg, 33.3 × 10^{-3} mmol) and ligand **5** (76 mg, 63.4 × 10^{-3} mmol) were combined in CH_2Cl_2 (20 cm^3), and the resulting yellow solution was stirred at room temperature for 6 h. Ammonium hexafluorophosphate (33 mg, 0.20 mmol) was then added, and the mixture was stirred at room temperature for a further 18 h. The brownish suspension obtained was then filtered through Celite to eliminate Pd^0 and gave a yellow solution. The solvent was then evaporated under reduced pressure, and the yellow foam obtained was recrystallized from a hexane/CH_2Cl_2 mixture (3:1) at 4 °C. The solid formed was separated upon filtration and washed with freshly distilled hexane. The product was thus obtained in the form of yellow crystals. Yield: 47 mg (45%). IR (KBr pellet): $\tilde{\nu}$ = 3445, 2961, 2871, 1715, 1456, 1393, 1224, 1200, 1121, 1077, 1048, 885, 842 (PF_6^-), 619, 556 cm^{-1}. MS [HR-ES(+)]: calcd. for $[M]^+$ 1488.6735; found 1488.6745. $C_{89}H_{110}F_6NO_8P_3Pd$ (1633.7): calcd. C 65.4, H 6.8, N 0.9; found C 64.4, H 6.9, N 0.9.

[*endo*-*N*-(2-(*N*′,*N*′-Dimethylamino)ethyl)-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene](η^3-1,3-diphenylallyl)palladium(II) Hexafluorophosphate (Pd6): Di-μ-chlorobis[(η^3-1,3-diphenylallyl)palladium(II)] (122 mg, 0.18 mmol) and ligand **6** (75 mg, 0.36 mmol) were combined in CH_2Cl_2 (20 cm^3), and the resulting yellow solution was stirred at room temperature for 2 h. Ammonium hexafluorophosphate (178 mg, 1.09 mmol) was then added, and the mixture was stirred at room temperature for a further 22 h. The orange solution obtained was then washed with deoxygenated water (6 × 10 cm^3) under nitrogen atmosphere, and the aqueous phases were extracted with freshly distilled CH_2Cl_2 (10 cm^3). After the combined organic extracts were dried with anhydrous Na_2SO_4 and filtered, the solvent was evaporated under reduced pressure. The resulting yellow foam obtained was treated with distilled ethyl ether (3 × 5 cm^3), and the solvent was evaporated under vacuum, which led to a pale yellow solid product. Yield: 112 mg (47%). Yellow crystals suitable for the structural resolution by X-ray diffraction were grown by slow evaporation of a solution of this product in $CHCl_3$. IR (KBr pellet): $\tilde{\nu}$ = 3429, 2967, 2927, 1649, 1493, 1459, 1260, 1097, 1024, 835 (PF_6^-), 696, 666, 556 cm^{-1}. ^1H NMR (40 MHz, $CDCl_3$): Isomer A (88%): δ = 1.49 (d, J = 8.8 Hz, 1 H, C*H*H′bridge), 1.52 (dd, J = 8.8 and 11.6 Hz, 1 H, CHC*H*H′N), 1.60 (dt, J = 1.8 and 8.0 Hz, 1 H, CH*H*′bridge), 1.72 (s, 3 H, NCH_3), 2.13 (dd, J = 9.6 and 12.4 Hz, 1 H, CHC*H*H′N), 2.51 [bs, s, 5 H, $CH_{olefin}CHCH_2$bridge, C*H*H′N(CH$_3$)$_2$ and NC*H*′$_3$], 2.57–2.63 [m, 3 H, $CH_{olefin}CH'CH_2$-bridge, NC*H*H′CH_2 and CH*H*′N(CH$_3$)$_2$], 2.69–2.87 (m, 4 H, 2 × *C*HCH_2N, CHCH*H*′N and NCH*H*′CH_2), 3.40 (dd, J = 1.5, 7.1 and 12.3 Hz, 1 H, CHCH*H*′N), 4.59 (d, J = 11.6 Hz, 1 H, H$_{anti}$), 4.64 (d, J = 12.0 Hz, 1 H, H′$_{anti}$), 5.00 (dd, J = 3.2 and 5.6 Hz, 1 H, C*H*$_{olefin}$), 5.40 (dd, J = 2.8 and 5.6 Hz, 1 H, C*H*′$_{olefin}$), 6.16 (t, J = 11.6 Hz, 1 H, H$_{central}$), 7.35–7.59 (m, 10 H, H Ar) ppm. ^{13}C NMR (10 MHz, $CDCl_3$): Isomer A (88%): δ = 43.2 ($CH_{olefin}CHCH_2$bridge), 43.9 ($CH_{olefin}C'HCH_2$bridge), 44.3 (*C*HCH_2N), 45.2 (*C*′HCH_2N), 48.7 (NCH_3), 49.2 (N*C*′H_3), 55.3 (*C*H_2bridge), 57.0 (NCH_2CH_2), 58.2 (CH*C*H_2N), 61.0 (CH*C*′H_2N), 61.6 (NCH_2CH_2), 77.0 (C$_{terminal}$), 77.9 (C′$_{terminal}$), 109.7 (C$_{central}$), 128.4–130.2 (C Ar), 135.4 (*C*H$_{olefin}$), 136.0 (*C*′H$_{olefin}$), 136.9 (CH-*C* Ar), 138.0 (CH-*C*′ Ar) ppm. MS [HR-ES(+)]: calcd. for $[M]^+$ 505.1829; found 505.1852.

Palladium-Catalyzed Allylic Substitution Reactions: Di-μ-chlorobis[(η^3-allyl)palladium(II)] (3.7 mg, 0.01 mmol) and the corre-

sponding ligand (0.025 mmol) were dissolved in CH_2Cl_2 (1 cm^3), and the resulting yellow solution was stirred at room temperature for 0.5 (ligand **5**) or 2 h (ligands **3**, **4** and **6**). The corresponding allylic acetate (1.00 mmol, 252 mg of *rac*-**I**, 140 mg of *rac*-**IV** or 157 mg of **VI**), the nucleophile (3.00 mmol, 396 mg dimethyl malonate {DMM} or 107 mg benzylamine), *N*,*O*-bis(trimethylsilyl)-acetamide, BSA (610 mg, 3.00 mmol), each dissolved in CH_2Cl_2 (1 cm^3) and a catalytic amount of potassium acetate were then consecutively added. When benzylamine was used as the nucleophile no extra base (BSA/KOAc) was added. The reaction mixture was stirred at room temperature, and the reaction was monitored by TLC (SiO_2; hexane/ethyl acetate, 3:1). Ethyl ether (10 cm^3) was added to stop the reaction, and the yellow suspension was filtered through Celite and washed with a 10% aqueous solution of NH_4Cl (3×10 cm^3) and water (3×10 cm^3). The organic layer was dried with anhydrous Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure to give a yellow oil.

X-ray Crystallographic Study: The crystalline structure of compound **1** was determined by using a Bruker AXS CCD 1000 X-ray diffractometer operating at 173 K and that of complex Pd**6** by using a Bruker APEX-II CCD diffractometer at 100 K, with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å). Both structures were solved by direct methods with the SHELXS-97 computer program[23] for crystal structure determination and refined by full-matrix least-squares method on F^2, with the SHELXL-97 computer program.[24] Hydrogen atoms were included in calculated positions and refined in riding mode. Selected data for **1**: $C_{20}H_{20}N_2O_4$, M = 352.38, monoclinic, space group $P2_1/c$, a = 10.7757(14) Å, b = 8.4143(11) Å, c = 9.5586(19) Å, β = 103.631(2)°, V = 842.27(19) $Å^3$, Z = 2, crystal size $0.1 \times 0.4 \times 0.4$ mm, 4804 reflections collected (1714 independent, R_{int} = 0.0310), GOF = 1.021, R_1 [$I > 2\sigma(I)$] = 0.0448 and wR_2 = 0.0914, R_1[all data] = 0.0721 and wR_2 = 0.1025, largest diff. peak and hole: 0.177 and –0.169 e $Å^{-3}$. Selected data for Pd**6**: $C_{29}H_{36}Cl_3F_6N_2PPd$, M = 770.32, monoclinic, space group $P21/c$, a = 9.5990(3) Å, b = 33.4444(10) Å, c = 10.8901(4) Å, β = 114.589(2)°, V = 3179.04(18) $Å^3$, Z = 4, crystal size $0.12 \times 0.12 \times 0.11$ mm, 70251 reflections collected (7593 independent, R_{int} = 0.034), GOF = 1.311, R_1 [$I > 2\sigma(I)$] = 0.0456 and wR_2 = 0.1017, R_1 [all data] = 0.0564 and wR_2 = 0.1059, largest diff. peak and hole: 2.699 and –0.989 e $Å^{-3}$. CCDC-739813 (for **1**) and CCDC-739814 (for Pd**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): The results of the coordination chemistry and the catalytic reactivity of the ruthenium systems containing norbornene ligands are presented. NMR spectra of compounds **5** and Pd**6** and variable-temperature NMR spectra of compounds **2**, **4** and Pd**5** are also given.

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