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New homochiral amino-phosphine ligands: application in asymmetric palladium catalyzed allylic alkylation[1]

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Abstract

A new series of homochiral amino-phosphine ligands was prepared. The use of these ligands in the palladium catalyzed allylic alkylation of 1,3-diphenyl-1-acetoxy-2-propene with sodium malonate gave substitution products with up to 76% e.e. The enantioselectivity was largely dependent on the nitrogen substituent.

1. Introduction

Palladium catalyzed allylic substitution is a mild, versatile method for carbon–carbon and carbon–heteroatom bond formation.[2] Consequently, there is considerable interest in enantioselective allylic substitution reactions, and a number of groups have demonstrated high levels of control with a wide range of homochiral ligands.[3,4] In particular, excellent asymmetric induction has been provided by oxazoline ligands,[3b,e] and Trost's 'deep pocket' and several other C_2 ligands.[4] As part of a general investigation into catalytic asymmetric reactions, we were interested in developing new, inexpensive, and easily prepared ligands for transition metal catalyzed reactions. We wish to report the results of a study on the preparation and applications of a new series of amino-phosphine ligands.

2. Results and discussion

Disubstituted diamines **1** were prepared from the (R,R) cyclohexanediamine-tartrate salt in a three step, one pot reaction in high yields.[5,6] Reaction of the disubstituted diamines **1** with one equivalent of chlorodiphenylphosphine in toluene and triethylamine (Scheme 1) resulted in clean monophosphinylation to give ligands **2b–g**. The remaining free amine group of monophosphines **2c–g** was unreactive towards

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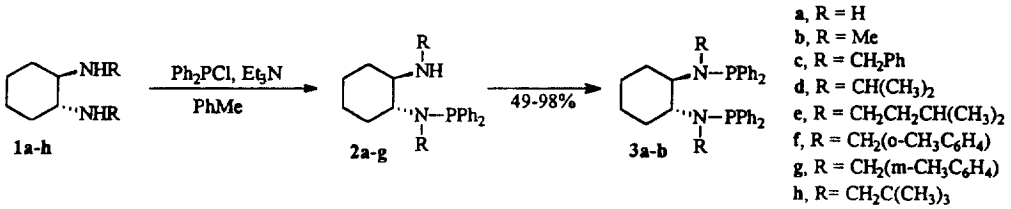
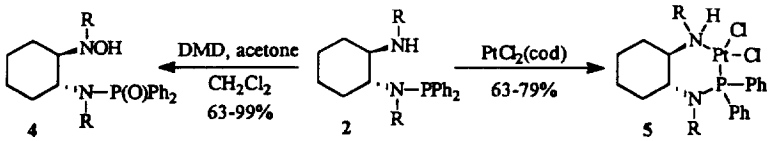
further phosphinylation even upon exposure to a large excess of chlorodiphenylphosphine. In contrast, treatment of the N,N′-dimethyl substituted diamine **1b** and the parent cyclohexane diamine **1a** with excess chlorodiphenylphosphine resulted in bisphosphinylation to give the known[7] ligands **3a** and **3b**, whereas the N,N′-dineopentyl diamine **1h** failed to phosphinylate at all. The amino-phosphine ligands **2** were purified by chromatography over alumina. However, several of the amino-phosphines **2** were sensitive to hydrolysis and were converted to the corresponding oxide **4** by reaction with dimethyl dioxirane (DMD), or the Pt(II) complex **5** by reaction with $[PtCl_2(cod)]$ to give stable, crystalline compounds for characterization (Scheme 2).



Scheme 1.



Scheme 2.

The amino-phosphines **2** exhibited a broad resonance in the room temperature ^{31}P NMR spectrum which sharpened at elevated temperatures. At low temperatures, two sharp resonances were observed. The ratio of the two resonances was dependent upon the N-substituent.[8] The N-benzyl derivative **2c** (Fig. 1) showed a more intense high field signal (δ 73.6 and 37.6, ratio 1:4), whereas the N-methyl derivative **2b** showed the more intense signal at low field (δ 63.5 and 34.5, ratio 4:1).

A more detailed structural investigation was carried out using X-ray crystallography. The amino-phosphine ligand **2c** was recrystallized giving crystals suitable for X-ray structure determination (Fig. 2). The ligand **2c** was reacted with $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ to give the corresponding palladium π-allyl complex (Scheme 3). The chloride was exchanged for PF_6^- and the complex **6** was crystallized to give X-ray quality crystals (Fig. 3).

The P–N bond lengths for ligand **2c** and allyl complex **6** are 1.685(10) Å and 1.681(3) Å. The shortened P–N bond on ligand **2c** (1.685(10) Å) compared to the theoretical single P–N bond length of 1.77 Å is an indication of some 2p(N)→3d(P) π-bond character. The ligand **2c** and allyl complex **6** showed the N atom connected to phosphorus has close to planar geometry ($\sum$N=360°), as indicated by the sum of the three N atom bond angles ($\sum$N=358.3(8)° and $\sum$N=355.5(8)°, respectively). In both the ligand and the complex, the benzyl substituents on the nitrogen tend to position themselves away from the large PPh_2 group, which in turn, has the phenyl rings in a propeller arrangement, and almost perpendicular to each other. The palladium–carbon (allyl group) bonds are also within the expected range. The Pd–C(33) bond is longer (2.221(4) Å) than the Pd–C(35) bond (2.099(4) Å) due to the differing *trans* influence of the phosphine and amine groups.

The application of the amino-phosphine ligands **2** in the palladium-catalyzed asymmetric allylic alkylation of dimethyl malonate with 1,3-diphenyl-2-propenyl acetate **5** was investigated (Scheme 4). Ligand **2c** was used to optimize the reaction conditions. The palladium complex was formed in situ by mixing the ligand **2** with $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$. Addition of 1,3-diphenyl-2-propenyl acetate **7** to the

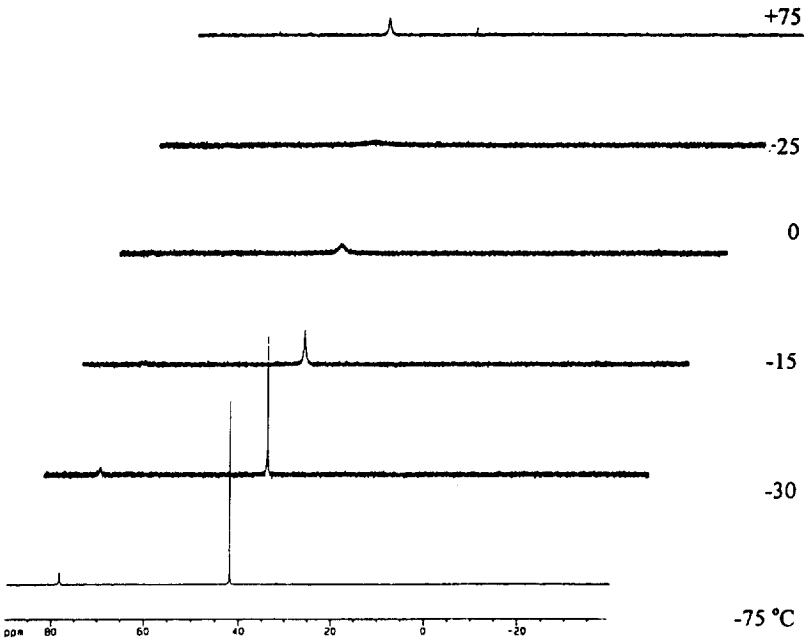


Fig. 1. Variable temperature ^{31}P NMR spectra of amino-phosphine **2c**

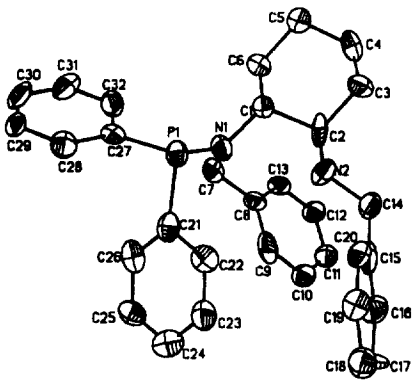
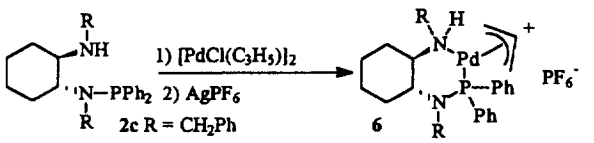


Fig. 2. The molecular structure of amino-phosphine ligand **2c** shown with 50% probability displacement ellipsoids (peripheral H atoms have been omitted for clarity)



Scheme 3.

catalyst solution, followed by sodium dimethyl malonate afforded the allyl substituted product **8** in good yield and with good enantioselectivity (Table 1).

An examination of reaction conditions (entries 2–10) revealed that NaH in THF at room temperature was optimal. The use of alternative bases[10] and solvents, or the addition of a phase-transfer catalyst (entries 4 and 9) afforded similar or slightly lower enantioselectivity. However, in several cases the

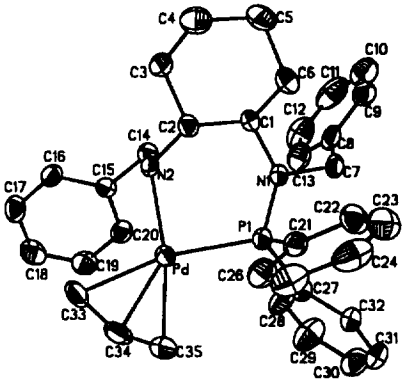
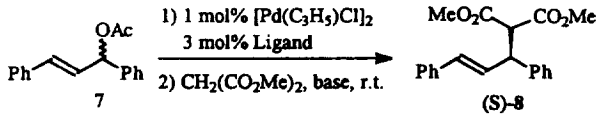


Fig. 3. The molecular structure of π-allyl complex **6** shown with 50% probability displacement ellipsoids (peripheral H atoms have been omitted for clarity)



Scheme 4.

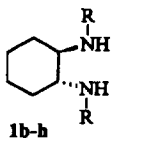
Table 1
Palladium catalyzed enantioselective allylic alkylation using amino-phosphines **2c**

Entry	Base	Solvent	Time(h)	Yield(%)[a]	% E.e[b]	Config.[c]
1	**NaH**	**THF**	**15**	**79**	**62**	**(-)S**
2[d]	NaH	THF	15	41	56	(-)S
3[e]	NaH	THF	18	79	50	(-)S
4	NaH/ nBu_4NBr[f]	THF	16	65	58	(-)S
5	Cs_2CO_3	THF	7days	44	64	(-)S
6	**KH**	**THF**	**15**	**41**	**56**	**(-)S**
7	KH/ nBu_4NBr	THF	36	75	55	(-)S
8	**BSA/cat. KOAc**	**CH_2Cl_2**	**40**	**82**	**63**	**(-)S**
9	**NaH**	**CH_2Cl_2**	**15**	**73**	**61**	**(-)S**
10	**KH**	**CH_2Cl_2**	**12**	**43**	**63**	**(-)S**

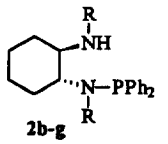
a) Yield of analytically pure product after column chromatography (silica, 3:1 hexanes/EtOAc). b) Enantiomeric excesses were determined by HPLC with a chiral stationary phase (Regis (S,S)-Whelk 0-1 column; 9:1 hexane/EtOH; flow 1.0 mL/min.). c) Absolute configuration was determined by comparison with literature values, see ref 9. d) Ligand conc. = 7.5 mol%, ratio Pd/L = 1:3. e) $Pd(OAc)_2$, ratio Pd/L = 1:3. f) 3 eq. nBu_4NBr.

chemical yields were lower and longer reaction times were required. In addition, changing the palladium source (entry 3) or ligand concentration (entry 2) had little effect.

Using the optimized reaction conditions, the phosphines **2c–2f** were examined to search for substituent effects (Table 2). Control experiments using the precursor diamines **1** showed a significant reduction in enantioselectivity and change in the configuration of the new chiral center, indicating that the phosphine ligand probably remained intact throughout the reaction. Moreover, the diamine **1h** (entry 11) failed to give any product.



1b-h



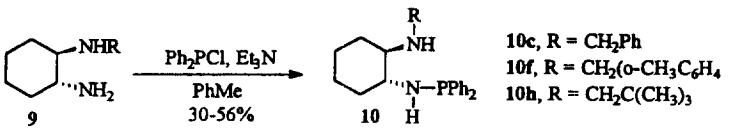
2b-g

a, R = H
b, R = Me
c, R = CH_2Ph
d, R = $CH(CH_3)_2$
e, R = $CH_2CH_2CH(CH_3)_2$
f, R = $CH_2(o\text{-}CH_3C_6H_4)$
g, R = $CH_2(m\text{-}CH_3C_6H_4)$
h, R= $CH_2C(CH_3)_3$

Table 2
Allylic alkylation using ligands **2c–2f**

Entry	Ligand	Yield (%)	% E.e.	Confign.
1	2b	78	44	(-)S
2	2c	79	62	(-)S
3	2d	75	66	(-)S
4	2e	58	43	(-)S
5	2f	70	72	(-)S
6	2g	60	59	(-)S
7	1c	91	29	(+)R
8	1d	65	29	(+)R
9	1f	51	64	(+)R
10	1g	69	21	(+)R
11	1h	No rxn	—	—

The smaller or more flexible N-substituents such as in **2b** and **2e**, respectively, gave lower enantioselectivities. However, the more sterically demanding groups such as the isopropyl and *o*-tolyl derivatives (entries 3 and 5, respectively) together with the benzyl group of **2c** gave the best enantioselectivities, thus suggesting a strong correlation between the nitrogen substituent and the level of induction in the alkylation reaction. To further examine the influence of the nitrogen substituent, amino-phosphines **10** (Scheme 5) were prepared which lack an alkyl group on the phosphinamine nitrogen.



9 10

10c, R = CH_2Ph
10f, R = $CH_2(o\text{-}CH_3C_6H_4$
10h, R = $CH_2C(CH_3)_3$

Scheme 5.

Using the optimized reaction conditions, the phosphines **10** were examined (Table 3). The allyl malonate **8** was formed with enantiomeric excesses that were similar (**10h**) or marginally higher (**10c**) than for the corresponding N,N′-disubstituted ligands **2**. These results suggest that for these aminophosphine ligands bearing large substituent groups, the absence of a substituent on the nitrogen connected to the phosphorus atom does not significantly affect the stereochemical outcome and enantiomeric excess of the alkylation reaction.

Table 3
Allylic alkylation using ligands **10**

Entry	Ligand	Base	Solvent	Yield(%)	%ee	Config
1	10c	NaH	THF	70	76	(-)S
2	10f	NaH	THF	56	26	(-)S
3	10h	NaH	THF	72	68	(-)S

We are currently investigating the factors which contribute to the stereoselection using NMR spectroscopy and X-ray crystallography,[9,11] and attempting to optimize the enantioselectivity through changes in the nitrogen substituent and ligand design.

3. Experimental

Unless otherwise indicated, all reactions were performed under an inert (argon) atmosphere using standard Schlenk techniques. Solutions were degassed through freeze–pump–thaw cycles and all solvents were dried before use. Toluene, CH_2Cl_2 and EtOAc were distilled from CaH_2, THF and Et_2O were distilled from sodium-benzophenone ketyl, methanol was distilled from Mg and hexanes were distilled from Na. Triethylamine was distilled twice from KOH. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in C_6D_6, $CDCl_3$ or CD_2Cl_2 solution on a Varian Unity Plus 300 MHz or Varian XL-300 spectrometer at 300, 75 and 121 MHz, respectively. The ^1H chemical shifts are reported in ppm relative to TMS, and the ^{31}P chemical shifts are reported in ppm relative to external H_3PO_4. Infrared spectra were recorded on a Perkin–Elmer 1600 series FTIR. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Optical rotations were determined on an Rudolph Research Autopol III polarimeter. Column chromatography of ligands and platinum complexes was performed on neutral alumina (Fisher Scientific, Brockman Activity I, 80–200 mesh).

3.1. General procedure for amino-phosphine ligands (2) and their oxide derivatives (4)

To a stirred solution of (R,R)-N,N′-dialkyl-1,2-cyclohexanediamine (3.6 mmol) in toluene (10 mL) was added Et_3N (4.7 mmol) dropwise. The reaction mixture was cooled to 10°C, and Ph_2PCl (4.0 mmol) was added slowly. After the addition was complete, the resulting yellow solution was stirred for 3 to 5 hours and monitored by TLC (alumina, hexanes:EtOAc=2:1). The reaction mixture was vacuum filtered through anhydrous $MgSO_4$ in a glove box, to remove the by-product triethylamine hydrochloride salt. The solvent was evaporated *in vacuo* to give the crude product, which was purified by column chromatography (neutral Al_2O_3, hexane:EtOAc=3:1). Isolated yields and data analysis for each ligand are given below.

3.2. N,N′-Dimethyl-N-(diphenylphosphinyl)-(1R,2R)-cyclohexanediamine (2b)

The crude product was obtained as a yellow solid (60%). The mixture was further purified by short alumina column chromatography. (Al_2O_3, hexane:EtOAc=3:1), followed by immediate complex formation. ^{31}P NMR (C_7D_8) (90°C) δ 55.40 ppm; (25°C) δ 55.60 ppm (brd); (−65°C) δ 63.46 and 34.48 ppm (4:1 ratio, respectively). [$PtCl_2$(cod)] (0.40 mmol) was added to a solution of the phosphine (0.40 mmol) in CH_2Cl_2 (5 mL). The resulting solution was concentrated *in vacuo* to give dichloro(N,N′-dimethyl-N-(diphenylphosphinyl)-(1R,2R)-cyclohexanediamine)-platinum (**5b**) as a yellow solid which was recrystallized twice from THF/hexanes to give yellow crystalline plates (0.025 g, 63%). Mp: 272.6–273.9°C; $[\alpha]_D$ −12.3 (c=0.35, $CHCl_3$); IR (KBr) 3423, 2937, 1732, 1655, 1438, 1294, 1149, 629 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.94–7.78 (m, 4H), 7.54–7.40 (m, 10H), 4.69 (s, 1 N*H*, J_{HPt}=48.0 Hz), 3.63 (m, 1H), 3.01 (d, 3H, J_{PtH}=39.6 Hz, J_{PH}=6.3 Hz), 2.42 (d, 3H, $^3J_{PH}$=9.6 Hz), 2.11–2.00 (m, 3H), 1.88–1.84 (m, 2H), 1.65–1.50 (m, 3H), 1.34–1.25 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 134.36 (d, J_{CP}=11.6 Hz), 133.41 (d, J_{CP}=11.1 Hz), 132.15–131.06 (m), 129.13–128.16 (m), 67.40, 63.85, 56.20, 47.11, 31.51,

31.13, 29.91, 29.61, 25.31, 25.07; ^{31}P NMR ($CDCl_3$) δ 41.56 ppm, (J_{PPt}=4215.6 Hz). Anal. calcd for $[C_{20}H_{27}N_2P]PtCl_2 \cdot 0.5H_2O$: C, 39.94; H, 4.69; N, 4.66. Found: C, 39.96; H, 4.45; N, 4.21.

3.3. *N,N′-Dibenzyl-N-(diphenylphosphinyl)-(1R,2R)-cyclohexanediamine (2c)*

The crude product was obtained as a yellow solid (98%), then was dissolved in toluene and passed through a short alumina column, to remove some of the impurities. After removing the solvent *in vacuo*, the resulting solid was recrystallized, by slow diffusion of diethyl ether into a benzene solution to give the ligand **2c** as colorless crystalline blocks. Mp 85–85.6°C; ^{31}P NMR (C_7D_8) (90.0°C) δ 44.18 ppm; (25.0°C) δ 46 ppm (brd); (−60.0°C) δ 37.63 and 73.61 ppm (8:2 ratio, respectively); ^{1}H NMR (C_7D_8, 90.0°C) δ 7.67 (m, 4H), 7.33 (m, 8H), 7.10 (m, 2H), 6.96 (m, 1H), 4.44 (dd, 1H, J_{HH}=14.4 Hz, $^3J_{HP}$=2.4 Hz), 4.23 (dd, 1H, J_{HH}=14.4 Hz, $^3J_{HP}$=2.1 Hz), 3.89 (d, 1H, J_{HH}=12.9 Hz), 3.58 (d, 1H, J_{HH}=13.2 Hz), 3.20 (m, 1H), 3.04 (m, 1H), 2.17 (m, 2H), 1.88 (m, 3H), 1.34 (m, 3H). The crude amino-phosphine **2c** (0.55 g, 83 mmol) was oxidized with anhydrous dimethyldioxirane (25 mL, 0.077 M in acetone) in methylene chloride (8 mL). Reaction progress was monitored by TLC (hexane:EtOAc=3:1) and disappearance of DMD using potassium iodide/starch paper. After 10 min, the reaction was complete and the resulting solution was concentrated *in vacuo* to give a white solid (0.54 g, 93%). Column chromatography (Al_2O_3, hexane:EtOAc=2:1) followed by recrystallization from C_6H_6/hexanes afforded pure N,N′-dibenzyl-N-(diphenylphosphinous)-N′-hydroxy-(1R,2R)-cyclohexanediamine (**4c**) as white crystals (0.43 g, 80%). Mp 185–185.6°C; $[\alpha]_D$ −61.0 (c=0.69, C_6H_6); IR (KBr) 3290, 3030, 2950, 2905, 1495, 1438, 1175, 1120, 921, 870, 725, 695, 555 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.71 (s, 1H), 8.03 (m, 2H), 7.87 (m, 2H), 7.60 (m, 4H), 7.43 (m, 3H), 7.36 (m, 2H), 7.15 (m, 4H), 6.99 (m, 3H), 4.19 (d, 1H, J_{HH}=13.2 Hz), 4.14 (d, 2H, $^3J_{HP}$=9.9 Hz), 3.68 (d, 1H, J_{HH}=13.2 Hz), 3.56 (dddd, 1H, J_{HH}=12.0, 10.2, 3.6 Hz, $^3J_{HP}$=11.7 Hz), 2.49 (ddd or app. dt, 1H, J_{HH}=10.5, 10.5, 3.3 Hz), 2.03 (d, 1H, J_{HH}=12.9 Hz), 1.81 (d, 1H, J_{HH}=12.3 Hz), 1.67 (m, 2H), 1.25 (m, 1H), 0.99 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 140.55 ($^3J_{CP}$=7.0 Hz), 139.49, 133.53 (d, $^1J_{CP}$=131.5 Hz), 132.93 (d, $^3J_{CP}$=9.0 Hz), 132.76 (d, $^3J_{CP}$=9.5 Hz), 132.49 (d, $^1J_{CP}$=126.9 Hz), 132.12 (d, $^2J_{CP}$=2.9 Hz), 131.96 (d, $^2J_{CP}$=2.9 Hz), 129.51, 128.79, 128.63, 128.59, 128.39, 128.31, 128.20, 127.18 and 126.99 (m, aromatic CH's), 64.92, 59.52, 57.69 (d, $^2J_{CP}$=1.7 Hz), 47.29 (d, $^2J_{CP}$=4.5 Hz), 33.65 (d, $^3J_{CP}$=5.1 Hz), 26.32, 25.07, 22.09; ^{31}P NMR (C_6D_6) δ 34.1 ppm. Anal. calcd for $C_{32}H_{35}N_2PO_2$: C, 75.27; H, 6.91; N, 5.49. Found: C, 75.14; H, 6.92; N 5.44.

3.4. cis-*Dichloro(N,N′-dibenzyl-N-(diphenylphosphinyl)-(1R,2R)-cyclohexanediamine)-platinum (5c)*

$[PtCl_2(cod)]$ (0.40 mmol) was added to a solution of the phosphine (0.40 mmol) in methylene chloride (5 mL). The resulting solution was purified by a short silica column, concentrated *in vacuo* to give a yellow solid, then recrystallized (2×) from THF/hexanes to give *cis*-dichloro(N,N′-dibenzyl-N-(diphenylphosphinyl)-(1R,2R)-cyclohexanediamine)-platinum (**5c**) as yellow crystalline blocks (0.33 g, 79%). Mp: 230–231°C; $[\alpha]_D$ −18.4 (c=0.50, C_2Cl_2); IR (KBr) 3200, 2933, 1775, 1435, 1105, 1025. 750 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 8.15 (m, 2H), 7.80 (m, 2H), 7.63–7.47 (m, 8H), 7.36 (m, 2H), 7.27 (m, 2H), 7.19 (m, 2H), 6.95 (m, 2H), 5.55 (s, 1H, J_{HPt}=68 Hz), 5.14 (d, 1H, J_{HH}=12.3 Hz), 4.23 (dd, 1H, J_{HH}=11.2, J_{HP}=11.3 Hz), 4.02 (dd, 1H, J_{HH}=11.2, J_{HP}=5.9 Hz), 3.84 (m, 1H), 3.71 (dd, 1H, J_{HH}=12.6, J_{HP}=11.4 Hz), 2.66 (m, 1H), 2.20 (m, 2H), 1.78–1.65 (m, 1H), 1.58–1.46 (m, 2H), 1.29–1.21 (m, 2H), 1.10–1.02 (m, 1H), 0.92–0.73 (m, 1H), ^{13}C NMR (CD_2Cl_2) δ 140.11 (d, $^3J_{CP}$=3.1 Hz), 135.85 (d, $^3J_{CP}$=12.6 Hz), 135.43 (brd), 133.15 (d, $^2J_{CP}$=2.7 Hz), 131.69 (d, $^2J_{CP}$=2.8 Hz), 129.57, 129.48, 129.24, 129.06, 128.45, 128.30, 127.79, 69.49 (d, $^3J_{CP}$=13.0 Hz), 62.70 (brd d, $^2J_{CP}$=9.3 Hz), 57.84 (brd d, $^2J_{CP}$=6.8 Hz), 47.57

(brd), 33.07, 30.58 (d, $^3J_{CP}$=6.9 Hz), 25.64, 24.81; ^{31}P NMR (CD_2Cl_2) δ 41.56 ppm, (J_{PPt}=4215.6 Hz). Anal. calcd for $[C_{32}H_{35}N_2P]PtCl_2 \cdot H_2O$: C, 50.40; H, 4.89; N, 3.67. Found: C, 50.69; H, 4.66; N, 3.32.

3.5. *N,N′-Di-(2-propyl)-N-(diphenylphosphinyl)-(1R,2R)-cyclohexanediamine (2d)*

The crude product was obtained as a yellow solid (99%) which was purified by column chromatography (Al_2O_3, hexane:EtOAc=3:1, 70% yield). Mp 89.8–91.0°C; $[\alpha]_D$ +17.8 (c=0.90, C_6H_6); IR (KBr) 3324, 3048, 2925, 2855, 1460, 1436, 1362, 1160, 1093, 1040, 1010, 846, 747, 699, 514 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.53 (m, 4H), 7.43–7.32 (m, 6H), 3.67 (m, 1H), 3.09 (m, 1H), 2.92 (m, 2H), 2.18–1.85 (m, 3H), 1.82–1.66 (m, 3H), 1.40–1.07 (m, 2H), 1.25 (d, 3H, J_{HH}=6.3 Hz), 1.03 (d, 3H, J_{HH}=6.3 Hz), 0.79 (d, 3H, J_{HH}=6.3 Hz), 0.64 (d, 3H, J_{HH}=6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 139.80 (d, $^1J_{CP}$=7.3 Hz), 133.68 (d, $^3J_{CP}$=22.0 Hz), 131.16 (d, $^3J_{CP}$=20.7 Hz), 128.34, 127.77 (d, $^2J_{CP}$=7.0 Hz), 127.53, 58.26 (d, $^3J_{CP}$=23.4 Hz), 56.69 (d, $^2J_{CP}$=11.1 Hz), 50.85 (d, $^2J_{CP}$=10.7 Hz), 45.13, 36.59 (d, $^3J_{CP}$=14.9 Hz), 32.47, 26.12, 24.62, 24.44, 23.10, 21.71, 21.22; ^{31}P NMR ($CDCl_3$) δ 40.77 ppm. Anal. calcd for $C_{24}H_{35}N_2P$: C, 75.36; H, 9.22; N, 7.32. Found: C, 75.10; H, 9.14; N 7.19.

3.6. *N,N′-Di-(3-methylbutyl)-N-(diphenylphosphinyl)-(1R,2R)-cyclohexanediamine (2e)*

The crude product was obtained as a yellow oil, which was further purified by chromatography (Al_2O_3, hexane:EtOAc=3:1 , 86% yield). ^{31}P NMR ($CDCl_3$) (65.0°C) δ 46.05 ppm; (25°C) δ 41.2 ppm (brd); (−55.0°C) δ 38.75 and 73.46 ppm (11:1 ratio, respectively); ^{1}H NMR ($CDCl_3$, 65.0°C) δ 7.51 (m, 9H), 7.21 (m, 1H), 3.15 (m, 1H), 2.94 (m, 2H), 2.79 (m, 2H), 2.45 (m, 1H), 2.21 (d, 1H, J_{HH}=13.2 Hz), 2.16 (d, 1H, J_{HH}=13.2 Hz), 1.83 (m, 4H), 1.65 (ddd, 1H, J_{HH}=13.2, 6.6 Hz, $^3J_{HP}$=19.8 Hz), 1.40 (m, 3H), 1.26–0.94 (m, 4H), 0.90 (d, 3H, J_{HH}=6.6 Hz), 0.89 (d, 3H, J_{HH}=6.6 Hz), 0.72 (t, 6H, J_{HH}=6.6 Hz). The crude amino-phosphine (0.10 g, 0.24 mmol) was oxidized with DMD (7.8 mL, 0.0663 M in acetone) in methylene chloride (10 mL). After 10 min, the reaction was complete and the resulting solution was concentrated *in vacuo* to give a white solid. Column chromatography (Al_2O_3, hexane:EtOAc=2:1) afforded pure N,N′-di-(3-methylbutyl)-N-(diphenylphosphinous)-N′-hydroxy-(1R,2R)-cyclohexanediamine (**4e**) as white crystals (0.10 g, 99%). Mp 101.2–102.0°C; $[\alpha]_D$ −95.7 (c =0.70, $CHCl_3$); IR (KBr) 3252, 2950, 1438, 1179, 1121, 699, 543 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.34 (s, 1H), 7.92–7.78 (m, 4H), 7.56–7.38 (m, 6H), 3.48 (dddd, 1H, J_{HH}=10.5, 10.5, 3.0 Hz, $^3J_{HP}$=10.5 Hz), 3.00 (ddd, 1H, J_{HH}=12.6, 8.1, 4.8 Hz), 2.89 (ddd, 2H, J_{HH}=10.5, 6.6. Hz, $^3J_{HP}$=17.1 Hz), 2.59 (ddd or app. dt, 1H, J_{HH}=10.8, 10.8, 3.3 Hz), 2.53 (ddd, 1H, J_{HH}=12.3, 7.8, 7.8 Hz), 1.97–1.73 (m, 4H), 1.67–1.49 (m, 6H), 1.31 (ddd, 2H, J_{HH}=10.5, 6.6, 6.6 Hz), 1.16–1.04 (m, 2H), 0.97 (d, 3H, J_{HH}=6.6 Hz), 0.92 (d, 3H, J_{HH}=6.6 Hz), 0.61 (d, 3H, J_{HH}=6.6 Hz), 0.56 (d, 3H, J_{HH}=6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 133.97 ($^1J_{CP}$=130.9 Hz), 133.11 ($^1J_{CP}$=125.9 Hz), 132.85 (dd, $^3J_{CP}$=10.0, 9.1 Hz), 131.86 (d, $^2J_{CP}$=2.5 Hz), 128.65, 128.49, 128.32, 128.15, 66.71, 57.14 (d, $^2J_{CP}$=2.5 Hz), 53.80, 42.09 (d, $^2J_{CP}$=5.1 Hz), 41.40 (d, $^3J_{CP}$=2.6 Hz), 37.48, 33.60 (d, $^3J_{CP}$=4.5 Hz), 26.77, 26.33, 26.18, 25.43, 23.34, 22.75, 22.54, 22.25, 21.99; ^{31}P NMR ($CDCl_3$) δ 35.97 ppm. Anal. calcd for $C_{28}H_{43}N_2PO_2$: C, 71.46; H, 9.21; N, 5.95. Found: C, 71.21; H, 9.10; N 5.82.

3.7. *N,N′-Di-(2-methylbenzyl)-N-(diphenylphosphinyl)-(1R,2R)-cyclohexanediamine (2f)*

The crude product was obtained as a yellow oil (99%) and was purified by column chromatography (Al_2O_3, hexane:EtOAc=3:1, 49% yield). ^{31}P NMR ($CDCl_3$) (55.0°C) δ 47.96 ppm; (25°C) δ 47.32 ppm (brd); (−60.0°C) δ 42.94 and 76.80 ppm (12:1 ratio, respectively); ^{1}H NMR ($CDCl_3$, 55.0°C) δ 8.01 (m, 2H), 7.52 (m, 7H), 7.00 (m, 1H), 6.92 (m, 1H), 4.27 (m, 1H), 3.93 (d, 1H, J_{HH}=13.2 Hz), 3.84 (m, 1H),

3.67 (d, 1H, J_{HH}=13.2 Hz), 3.48 (d, 1H, J_{HH}=13.2 Hz), 3.11 (m, 1H), 2.78 (m, 1H), 2.37 (m, 8H), 1.76 (m, 4H), 1.28 (m, 5H); ^{1}H NMR ($CDCl_3$, 25.0°C, 91% purity) δ 7.54 (m, 2H), 7.42 (m, 4H), 7.24 (m, 6H), 7.02 (m, 2H), 6.92 (m, 1H), 6.77 (d, 1H, J_{HH}=7.8 Hz), 4.19 (s, 2H), 3.84 (dd, 1H, J_{HH}=13.5 Hz, $^3J_{HP}$=10.8 Hz), 3.48 (dd, 1H, J_{HH}=13.5 and 4.5 Hz), 3.11 (m, 1H), 2.76 (dddd, 1H, J_{HH}=11.7, 11.7, 3.9 Hz, $^3J_{HP}$=11.7 Hz), 2.35 (m, 1H), 2.23 (s, 3H), 2.14 (s, 3H), 1.86 (m, 4H), 1.32 (m, 3H). The crude amino-phosphine (0.10 g, 0.197 mmol) was oxidized with DMD (6.5 mL, 0.0663 M in acetone) in methylene chloride (8 mL). After 20 min, the reaction was complete and the resulting solution was concentrated *in vacuo*. Column chromatography (Al_2O_3, hexane:EtOAc=2:1) afforded pure N,N′-di-(2-methylbenzyl)-N-(diphenylphosphinous)-N′-hydroxy-(1R,2R)-cyclohexanediamine (**4f**) as an off-white solid (0.087 g, 90%). Mp 174.6–175.6°C; $[\alpha]_D$ −78.6 (c=0.29, $CHCl_3$); IR (KBr) 3428 (brd), 2938, 2853, 1734, 1650, 1438, 1172, 1119, 1026, 747, 727, 698, 546 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.18 (s, 1H), 8.16 (m, 2H), 7.77 (m, 2H), 7.56 (m, 5H), 7.33 (m, 5H), 7.07 (m, 2H), 6.83 (d, 1H, $^1J_{HH}$=7.2 Hz), 4.26 (d, 1H, $^1J_{HH}$=13.2 Hz), 4.06 (dd, 1H, $^1J_{HH}$=17.7 Hz, $^3J_{HP}$=13.5 Hz), 3.89 (d, 1H, $^1J_{HH}$=13.2 Hz), 3.71 (dd, 1H, J_{HH}=17.7 Hz, $^3J_{HP}$=11.4 Hz), 3.47 (dddd, 1H, J_{HH}=11.7, 11.7, 3.0 Hz, $^3J_{HP}$=11.7 Hz), 2.67 (m, 1H), 2.60 (s, 3H), 2.22 (m, 1H), 1.93 (m, 1H), 1.70 (m, 1H), 1.64 (s, 3H), 1.57 (m, 2H), 1.19 (m, 1H), 0.98 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 138.85 (d, $^3J_{CP}$=5.0 Hz), 138.06, 136.72, 135.08, 133.33 (d, $^1J_{CP}$=135.4 Hz), 133.09 (d, $^3J_{CP}$=8.5 Hz), 132.46 (d, $^3J_{CP}$=9.5 Hz), 132.15 (d, $^2J_{CP}$=3.0 Hz), 131.68 (d, $^2J_{CP}$=3.0 Hz), 131.54 (d, $^1J_{CP}$=124.9 Hz), 130.43, 129.94 (d, $^4J_{CP}$=4.5 Hz), 128.84, 128.67, 128.08, 127.92, 127.71, 127.27, 126.46, 125.96, 125.38, 63.45, 58.89 (d, $^3J_{CP}$=1.5 Hz), 57.49, 43.25 (d, $^2J_{CP}$=3.5 Hz), 34.37 (d, $^3J_{CP}$=6.6 Hz), 26.32, 25.03, 21.82, 19.43, 19.14; ^{31}P NMR ($CDCl_3$) δ 35.28 ppm. Anal. calcd for $C_{34}H_{39}N_2PO_2$: C, 75.81; H, 7.30; N, 5.20. Found: C, 75.60; H, 7.38; N 5.14.

3.8. *N,N′-Di-(3-methylbenzyl)-N-(diphenylphosphinyl)-(1R,2R)-cyclohexanediamine (2g)*

The crude product was obtained as a yellow oil (79%) and was purified by column chromatography (Al_2O_3, hexane:EtOAc=3:1, 50% yield). ^{31}P NMR (C_7D_8, 95.0°C) δ 44.60 ppm; (24.4°C) δ 41.69 ppm (brd); (−85.0°C) δ 37.46 and 73.19 ppm (4:1 ratio, respectively); ^{1}H NMR (C_7D_8, 95.0°C) δ 7.63 (m, 1H), 7.14 (m, 3H), 6.80 (m, 11H), 6.41 (m, 2H), 6.17 (brd s, 1H), 3.92 (d, 1H, J_{HH}=14.4 Hz), 3.71 (d, 1H, J_{HH}=15.0 Hz), 3.39 (d, 1H, J_{HH}=12.9 Hz), 3.09 (d, 1H, J_{HH}=12.3 Hz), 2.75 (m, 1H), 2.55 (m, 1H), 1.83 (s, 3H), 1.62 (s, 3H), 1.38 (m, 4H), 0.80 (m, 4H). The crude amino-phosphine (0.057 g, 0.113 mmol) was oxidized with DMD (4.0 mL, 0.064 M in acetone) in methylene chloride (8 mL). After 20 min, the reaction was complete and the resulting solution was concentrated *in vacuo* to give a colorless oil. Column chromatography (Al_2O_3, hexane:EtOAc=3:1) afforded pure N,N′-di-(3-methylbenzyl)-N-(diphenylphosphinous)-N′-hydroxy-(1R,2R)-cyclohexanediamine (**4g**) as an oil that on standing solidified to give a white solid (0.038 g, 78%); $[\alpha]_D$ −65.9 (c=0.81, $CHCl_3$); IR ($CHCl_3$) 3245 (brd), 2938, 2850, 1700, 1607, 1439, 1216, 1174, 1120, 1044, 869, 755, 695, 665 cm^{-1}; ^{1}H NMR (C_6D_6) δ 9.63 (s, 1H), 8.23–8.16 (m, 2H), 8.14–8.07 (m, 2H) 7.59 (s, 1H), 7.50 (d, 1H, $^1J_{HH}$=8.1 Hz), 7.29 (dd, 1H, $^1J_{HH}$=7.5, 7.2 Hz), 7.11–6.95 (m, 9H), 6.86 (d, 1H, J_{HH}=7.2 Hz), 6.63 (s, 1H), 4.43 (d, 1H, $^1J_{HH}$=13.5 Hz), 4.26 (d, 2H, $^3J_{HP}$=10.2 Hz), 3.82 (d, 1H, J_{HH}=13.2 Hz), 3.75 (m, 1H), 2.63 (ddd, 1H, J_{HH}=10.5, 10.5, 3.3 Hz), 2.28 (s, 3H), 2.06 (s, 3H), 1.99–1.97 (m, 1H), 1.86–1.70 (m, 2H), 1.43–1.36 (m, 1H), 1.30–1.12 (m, 2H), 0.75–0.65 (m, 2H); ^{13}C NMR (C_6D_6) δ 141.76 (d, $^3J_{CP}$=6.6 Hz), 140.30, 138.09, 138.04, 135.06 (d, $^1J_{CP}$=132.7 Hz), 133.64 (d, $^3J_{CP}$=9.0 Hz), 133.36 (d, $^3J_{CP}$=9.0 Hz), 133.30 (d, $^1J_{CP}$=124.5 Hz), 132.12 (d, $^2J_{CP}$=2.5 Hz), 131.95 (d, $^2J_{CP}$=2.5 Hz), 131.03, 129.66, 129.59, 129.04, 128.88, 128.53, 128.24, 127.21, 126.01, 64.92, 60.16, 58.62, 47.84 (d, $^2J_{CP}$=4.0 Hz), 34.62 (d, $^3J_{CP}$=5.6 Hz), 26.77, 25.52, 22.59, 21.97, 21.67; ^{31}P NMR (C_6D_6) δ 34.38 ppm. Anal. calcd for $C_{34}H_{39}N_2PO_2 \cdot 1.5H_2O$: C, 72.19; H, 7.48; N, 4.95. Found: C, 72.39; H, 7.17; N, 4.85.

3.9. General procedure for N-alkyl-N′-phosphines (10)

To a solution of the corresponding diamine **9** (0.76 mmol) in toluene under argon, was added triethylamine (0.76 mmol). The mixture was cooled in an ice bath, and chlorodiphenylphosphine (0.76 mmol) added dropwise, via syringe. The final mixture was warmed to room temperature and stirred for 4 hrs. The reaction mixture was vacuum filtered through anhydrous $MgSO_4$ in a glove box and the solvent evaporated *in vacuo* to give the crude product, which was purified by column chromatography (neutral Al_2O_3, hexane:EtOAc=3:1). Isolated yields and data for each ligand are given below.

3.10. (1R,2R) N-Benzyl-N′-(diphenylphosphinyl)-1,2-cyclohexanediamine (10c)

The crude product was obtained as a yellow solid (92%) and was further purified by chromatography (Al_2O_3, hexane:EtOAc=3:1), (0.08 g, 30%). Mp 78.8–79.8°C; $[\alpha]_D$ −26.7 (c=0.12, C_6H_6); IR (KBr) 3448, 2950, 2932, 2850, 1733, 1655, 1508, 1350, 1125, 1105, 740, 695, 493 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39–7.22 (m, 14H), 7.13 (m, 1H), 3.87 (d, 1H, $^1J_{HH}$=12.9 Hz), 3.60 (d, 1H, $^1J_{HH}$=13.2 Hz), 2.89 (m, 1H), 2.60 (brd s, 1H), 2.37 (ddd or app. dt, 1H, J_{HH}=10.2, 10.2, 3.9 Hz), 2.18 (m, 2H), 2.07 (m, 1H), 1.72 (m, 2H), 1.30–1.10 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 143.67 (d, $^1J_{CP}$=28.2 Hz), 143.50 (d, $^1J_{CP}$=26.7 Hz), 140.65, 131.43 (d, $^3J_{CP}$=20.7 Hz), 131.12 (d, $^3J_{CP}$=20.6 Hz), 128.65, 128.51, 128.45, 128.37, 128.35, 126.96, 62.81 (d, $^2J_{CP}$=7.0 Hz), 61.55 (d, $^3J_{CP}$=24.2 Hz), 50.87, 36.13 (d, $^3J_{CP}$=6.0 Hz), 31.41, 25.62, 24.94; ^{31}P NMR ($CDCl_3$) δ 35.43 ppm. Anal. calcd for $C_{25}H_{29}N_2P$: C, 77.29; H, 7.52; N, 7.21. Found: C, 77.20; H, 7.52; N 7.21.

3.11. (1R,2R) N-(2,2-Dimethylpropyl)-N′-(diphenylphosphinyl)-1,2-cyclohexanediamine (10h)

The crude product was obtained as a yellow solid (50%) and was further purified by chromatography (Al_2O_3, hexane:EtOAc=3:1), (0.58 g, 56%). Mp 55.8–56.4°C; $[\alpha]_D$ −103.8 (c=0.13, C_6H_6); IR (KBr) 3300, 3052, 2922, 2852, 1740, 1655, 1508, 1466, 1434, 1290, 1260, 1126, 1100, 825, 740, 695, 613, 515 cm^{-1}; ^1H NMR (C_6D_6) δ 7.29 (m, 4H), 6.91–6.77 (m, 6H), 2.52 (m, 1H), 2.28 (dd, 1H, $^1J_{HH}$=6.0 Hz, $^3J_{HP}$=10.5 Hz), 2.09 (d, 1H, $^1J_{HH}$=11.1 Hz), 1.94 (m, 1H), 1.86 (m, 1H), 1.78 (d, 1H, $^1J_{HH}$=11.1 Hz), 1.64–1.59 (m, 1H), 1.23 (brd s, 2H), 0.86 (m, 3H), 0.59 (s, 9H); ^{13}C NMR (C_6D_6) δ 144.93 (d, $^1J_{CP}$=21.2 Hz), 144.76 (d, $^1J_{CP}$=24.2 Hz), 132.13 (d, $^3J_{CP}$=20.6 Hz), 131.81 (d, $^3J_{CP}$=20.1 Hz), 129.04 (d, $^2J_{CP}$=6.5 Hz), 64.67 (d, $^2J_{CP}$=7.5 Hz), 61.61 (d, $^3J_{CP}$=22.6 Hz), 59.66, 36.11 (d, $^3J_{CP}$=6.6 Hz), 32.41, 32.03, 28.27, 25.90, 25.73; ^{31}P NMR (C_6D_6) δ 33.89 ppm. Anal. calcd for $C_{23}H_{33}N_2P$: C, 74.97; H, 9.03; N, 7.60. Found: C, 74.90; H, 9.11; N 7.64.

3.12. (1R,2R) N-(2-Methylbenzyl)-N′-(diphenylphosphinyl)-1,2-cyclohexanediamine (10f)

The crude product was obtained as a yellow solid (68%) and was further purified by chromatography (Al_2O_3, hexane:EtOAc=3:1), (0.09 g, 52%). Mp 76.9–77.3°C; $[\alpha]_D$ −52.8 (c=0.20, C_6H_6); IR (KBr) 3276, 3070, 2920, 2853, 1742, 1458, 1434, 1293, 1098, 1026, 880, 826, 739, 695, 626, 504 cm^{-1}; ^1H NMR (C_6D_6) δ 7.18 (m, 4H), 6.94–6.74 (m, 10H), 3.46 (d, 1H, $^1J_{HH}$=12.6 Hz), 3.14 (d, 1H, $^1J_{HH}$=12.6 Hz), 2.54 (m, 1H), 2.02 (m, 1H), 1.91 (s, 3H), 1.89 (m, 1H), 1.71 (m, 1H), 1.23 (m, 2H), 1.02 (brd s, 1H), 0.90 (m, 3H), 0.69 (m, 1H); ^{13}C NMR (C_6D_6) δ 144.74 (d, $^1J_{CP}$=22.2 Hz), 144.56 (d, $^1J_{CP}$=23.2 Hz), 139.89, 136.99, 132.10 (d, $^3J_{CP}$=20.4 Hz), 131.76 (d, $^3J_{CP}$=20.1 Hz), 130.78, 128.51, 129.41, 128.90 (d, $^2J_{CP}$=6.0 Hz), 127.45, 126.48, 63.78 (d, $^2J_{CP}$=7.0 Hz), 61.58 (d, $^3J_{CP}$=23.1 Hz), 49.53, 36.03 (d,

$^3J_{CP}$=7.1 Hz), 32.05, 25.89, 25.56, 19.44; ^{31}P NMR (C_6D_6) δ 34.27 ppm. Anal. calcd for $C_{26}H_{31}N_2P$: C, 77.58; H, 7.76; N, 6.96. Found: C, 77.30; H, 7.83; N 6.91.

3.13. General asymmetric alkylation procedure

The ligand (0.034 mmol) was added to $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ (0.011 mmol) in dry THF. The mixture was degassed and stirred for 0.5 h, at room temperature. The substrate, 1,3-diphenyl-2-propenyl acetate **7** (1.1 mmol), was added to the catalyst solution and the mixture was stirred for 0.5 h. A solution of sodium dimethyl malonate, generated from dimethyl malonate (3.4 mmol) and sodium hydride (60% dispersion in oil, 0.13 g, 3.4 mmol) in dry THF, was added and the final reaction mixture was stirred until the reaction was complete. The mixture was quenched with a saturated solution of NH_4Cl, diluted with diethyl ether, then transferred to a separatory funnel, and the aqueous layer extracted with Et_2O. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel) to give the desired alkylated product **8**.

3.14. Synthesis of palladium allyl complex (6)

Ligand **2c** (0.1 mmol) was added to a solution of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ (0.044 mmol) in CH_2Cl_2 (2 mL). The mixture was degassed three times through a freeze–pump–thaw cycle, then was stirred for 1 h, at r.t., under argon. The reaction mixture was treated with $AgPF_6$ (0.087 mmol) in MeOH (2 mL), and was stirred at r.t., in the dark, for 1 h. The AgCl precipitate was filtered off on a Celite plug, to give a yellowish solution. Et_2O was added slowly and upon standing pale yellow crystals formed.

3.15. X-Ray structure determination

Data collection was performed using a Siemens CCD automated single crystal X-ray diffractometer for **2c** and a Siemens P4RA single crystal X-ray diffractometer for **6**, using graphite monochromated Mo-Kα radiation. SMART software package[12] was used for data collection as well as frame integration for **2c**, and the raw data was corrected for systematic errors using SADABS.[13] Data collection and data reduction were carried out using XSCANS[15] for **6**. Structure solution and least-squares refinement for all compounds were achieved by using SHELXTL.[14] Crystal data and intensity data collection parameters, the final residual values and relevant structure refinement parameters, a complete list of bond distances and bond angles, positional and isotropic displacement coefficients for hydrogen atoms and a list of anisotropic displacement coefficients for the non-hydrogen atoms, and calculated and observed structure factors have been deposited in the Cambridge Crystallographic Data Base.

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