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Reactive intermediates in asymmetric cross-coupling catalysed by palladium P–N chelates

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Abstract

The palladium dibromide complexes of (*S*,*R*)-(1,1′-bis-diphenylphosphino)-2-ferrocenylethyldimethylamine and (*S*,*R*)-(1-diphenylphosphino)-2-ferrocenylethyldimethylamine have been reduced with dilithiocyclooctatetraene to form the corresponding Pd^0 cyclooctatetraene complexes. Their reactions with *E*-4-methoxy-2′-bromophenylethene, and then benzylmagnesium chloride at −60 to −30 °C, provide information on the structure of intermediates in asymmetric cross-coupling.

Introduction

A longer-term goal of our work in catalytic cross-coupling[1] is to gain sufficient understanding of the reaction mechanism to permit the rational design of ligands for asymmetric synthesis. Most of the impetus in this area has come from the research group of Kumada and Hayashi [2]. Their archetypal reaction involves nickel or palladium catalysts for the coupling of vinyl or *E*-alkenyl bromides with chiral benzylic organomagnesium or organozinc compounds in Et_2O. They assumed, without experimental verification, that racemisation at the chiral centre is faster than cross-coupling. A striking feature of their work is that the best ligands bear little structural relationship to those which are the best in Rh or Ru catalysed hydrogenation [3], olefin isomerisation [4], or Pt catalysed hydroformylation [5]. Whereas all these other reactions give highest optical yields with moderately rigid P–P chelates, the Kyoto group has convincingly demonstrated the superiority of P–N chelates in cross-coupling [2]. Other workers have tried various alternatives, with mixed success [6].

Two classes of P–N ligand have been employed. The first of these is typified by compound **1**, and the ligands can be synthesised simply from α-amino acids. Alternatively, the ease of synthesis of optically pure 1′-dimethylaminoethylferrocene [7] and its stereoselective lithiation has led to the synthesis of compounds **2** and **3**. A general lack of correlation between the efficiency of these and other ligands in

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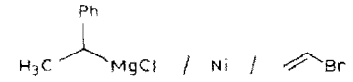
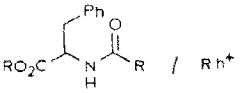
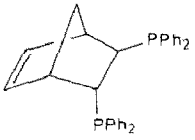
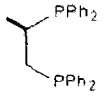
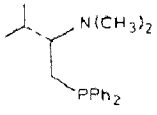
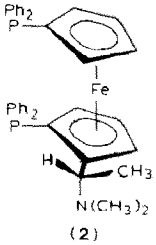
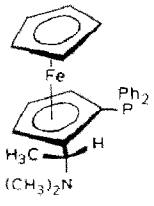
Table 1

Comparison of enantiomer excesses in (a) cross-coupling and (b) hydrogenation. Data from "*Asymmetric Catalysis*" Vol. 5, Chapters 3 and 5; J.D. Morrison (Ed.), Academic Press, New York, 1985 unless indicated

Ligand	Cross-coupling	Hydrogenation
		
	67*S*	95*S*
	0	90*S*
 (1)	81*S*	25*S* [a]
 (2)	65*R*	93*S*
 (3)	68*S*	80*S*

[a] Japanese Patent 56-29594; 1981. side-chain = benzyl.

cross-coupling and Rh asymmetric hydrogenation for defined standard reactions is displayed in Table 1. This implies that the molecular origin of enantioselection is very different in the two cases. In particular, comparison between the P–N chelate (**3**) and the P–P–N chelate (**2**) may indicate that asymmetric hydrogenation proceeds through a P–P-bonded complex for **2**, and cross-coupling through a P–N-

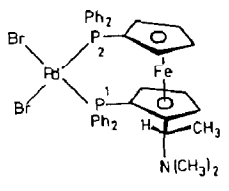
bonded complex in both cases. This may explain why the two ligands give the same product in cross-coupling, but opposite enantiomers of the hydrogenation product.

Little mechanistic work has been carried out on asymmetric cross-coupling. The X-ray structures of Pd and Rh complexes derived from ligands **2** and **3** have been determined [8]. Hayashi and co-workers suggested that the function of the amine in the P–N chelate is to bind to Mg (or Zn) at the transition state for alkyl transfer to Pd (or Ni) [9], but there seems to be little precedent or experimental support for this idea. To clarify matters, we have applied techniques used earlier in the study of simple cross-coupling reactions [1], and now present information about reactive intermediates in the catalytic cycle.

Complexes derived from ligand 2

The initial step in catalytic cross-coupling is addition of the electrophilic component to zerovalent palladium or nickel. The catalyst is normally introduced as a dihalide complex, which must be reduced in situ, presumably by RMgX or RZnX. Although labile palladium(0) olefin complexes can be prepared and isolated [10], few examples of the $L_2Pd(C{=}C)$ (L_2 = chelate) type are known. Since they are excellent precursors for entry into the catalytic cycle of cross-coupling, a method for in situ generation has been developed [1].

Dilithiocyclooctatetraene [11], prepared in Et_2O or thf, reacts with the $PdBr_2$ complex (**4**) derived from ligand **2** at −80 to −60 °C. Initially the ^{31}P NMR of



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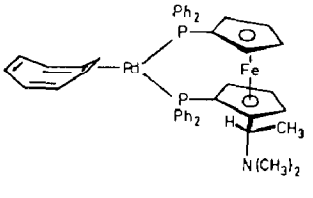

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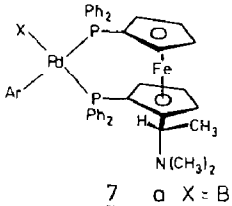
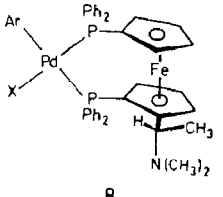


7 a X = Br (Ar as 6)
b X = I



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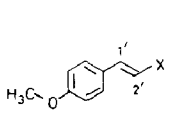

6 X = Br
10 X = I ; 2-^{13}C

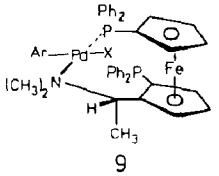

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Table 2

^{31}P and ^{13}C NMR spectroscopic data for compounds described in text, in tetrahydrofuran

	$\delta(P^1)$	$\delta(P^2)$	$J(P^1P^2)$ (Hz)	T (°C)
PPN series				
2	−21.3	−31.8	–	+30
4	30.3	19.5	22	+30
5	10.2	6.3	21	0
7a	7.5	19.5	24	−30
7b	8.1 [a]	12.4	30	10
ua	25.7	1.1	29	−30
8b	21.6	0.9 [a]	30	10
9a	18(br)	−28.5	–	−30
9b	16.5(br)	−27.7	–	10
	$\delta(P^1)$	$\delta(C)$	$J(PC)$ (Hz)	T (°C)
PN series				
12	3.7 [b]			−60
13	12.8	132.2	6	−30
14 [c]	5.8	172.0	128	−30
			[< 5] [d]	
15 [c]	0.4	149.6	18	−30
			[96] [d]	−30

[a] $J(CP)$ (*trans*) = 123 Hz in both cases. [b] A second singlet at 4.4 ppm is always present, but in minor amount. [c] Olefin C(1′)-labelled. [d] $PhCH_2MgCl$ labelled.

complex **4** exhibits an AB quartet at 30.2 and 19.5 ppm (thf), $J(P^1P^2) = 21$ Hz. In the parent ligand there are two singlets at −21.3 and −31.7, respectively. Since the parent 1,1′-bis(diphenylphosphino)ferrocene resonates at −19.5 ppm, it is assumed that the lower field resonance in both **2** and **4** is due to P^2 and the higher field resonance to P^1, shielded by the *ortho*-aminoalkyl substituent. After reaction with $COTLi_2$, the AB quartet of complex **4** is cleanly replaced by a new ABq, δ 10.2, 6.3 ppm. $J = 20$ Hz, assigned to the cyclooctatetraene complex **5**.

When this species was treated with a 5 molar excess of alkenyl bromide (**6**) at −30 °C in thf, two new species were observed in 70/30 ratio. These two complexes are considered to be the regioisomers **7a** and **8a**, derived by oxidative addition of RBr to palladium. In contrast to observations on the achiral ferrocenylphosphine reaction [1], it was not possible to observe an intermediate olefin complex, the oxidative addition step proceeding too rapidly. On the basis of their respective chemical shifts (Table 2) isomer **7a** has P^1 *trans* to bromide, and isomer **7a** has P^2 *trans* to bromide. When the solution is warmed above −30 °C, the regioisomers undergo interconversion, so that only the more stable complex **8a** remains detectable after 10 min at 0 °C.

Repetition of the experiment in ether under otherwise identical conditions gave a very different result. When the alkenyl bromide **6** was added to complex **5** in Et_2O at −30 °C, complexes **7a** and **8a** were formed, together with a third species (**9a**) in ratio 3/1/1 (Fig. 1). This ratio did not change appreciably when the solution was warmed to 0 °C. The new species (**9a**) is characterised by a broad singlet at −28.5 ppm, and a very broad resonance centred at 18 ppm, data consistent with a P–N

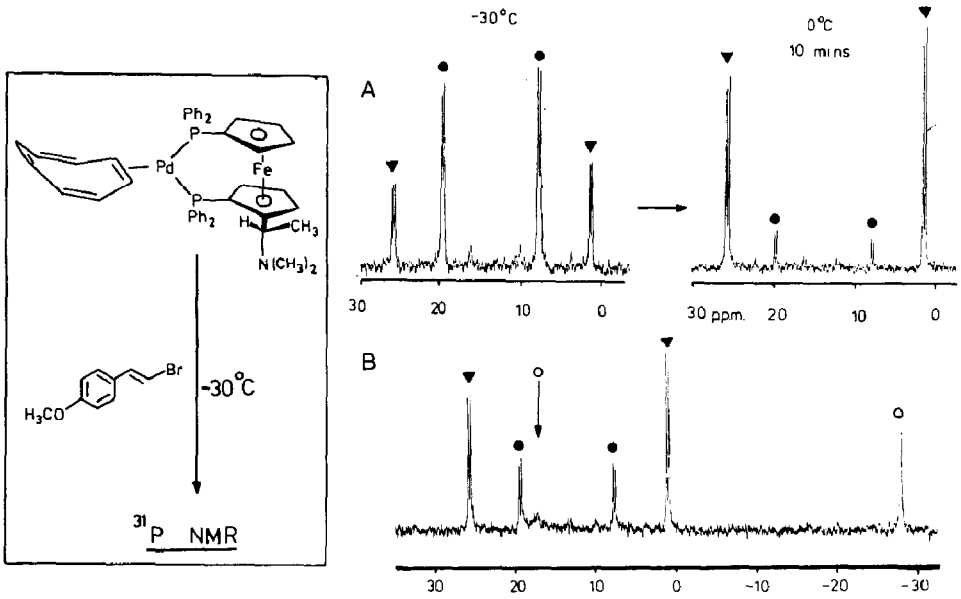

Fig. 1. ^{31}P NMR spectra of alkenyl bromide complexes formed by cyclooctatetraene displacement. A, thf, interconversion of regioisomers. B, Et_2O. ● = **7a**, ▲, **8a**, ○ = **9a**.

chelate structure. Surprisingly, it appears that the free phosphine is P^2, adjacent to the aminoethyl side-chain. We speculate that the structure of this intermediate is **9a**, with P and N *trans* in the coordination sphere. Participation of the second phosphine (e.g. in $P^2 \rightleftharpoons P^1$, equilibration) then leads to the observed dynamic broadening.

However, if the reaction is carried out in thf and the sample kept at $-80\,^\circ C$ for several hours (i.e., the equilibration of complexes **7a** and **8a** is avoided), then the P–N chelate **9a** is clearly apparent.

Further clarification was obtained by carrying out reaction of complex **5** with the ^{13}C-labelled alkenyl iodide (**10**) [12] in thf at $-40\,^\circ C$. This led to a mixture of complexes **7b**, **8b** and **9b** in approximate ratio 3/1/1. For both **7b** and **8b** it is the upfield signal which shows a C–P coupling of ca. 120 Hz; none is observed in the case of complex **9b**. For the iodide, no change in ratio is apparent in standing the sample at $+10\,^\circ C$.

Several experiments were carried out in which the oxidative addition product(s) were treated with Grignard reagents at low temperatures. The dialkylpalladium intermediate was never observed as a definite species; even at $-60\,^\circ C$, complex **5** and other olefin complexes were detected. When a mixture of **7a** and **9a** was treated with a solution of PhCHMeMgCl in Et_2O at $-60\,^\circ C$, it became clear that the thermodynamically stable isomer **8a** accumulates as reaction proceeds and is substantially less reactive towards the Grignard reagent. When this thermodynamically stable isomer **8a** was treated *after* equilibration (in 95% of total complex) in thf with PhCHMeMgCl at $-60\,^\circ C$ the ^{31}P NMR spectrum indicated that the predominant products were P–N- rather than P–P-bonded, with free phosphine apparent at -29 ppm.

Complexes derived from ligand 3

With only a single spin-active heteroatom nucleus, the ^{31}P NMR spectra of complexes derived from the $PdBr_2$ adduct **11** are necessarily less informative than those for the previous series. For this reason extensive use was made of ^{13}C-labelled reagents.

Complex **11** reacted cleanly with dilithium cyclooctatetraenide in thf to give a single species (**12**), δ 3.7 ppm (thf, $-60\,^{\circ}C$). This reacted in turn with bromide (**6**) to give a single product (**13**), δ 12.8 ppm, (thf, $-30\,^{\circ}C$), which exhibited substantial dynamic broadening at lower temperatures. Repetition of the reaction with $1'$-^{13}C-labelled bromide (**6**) indicated that the stereochemistry is as shown, with P *trans* to Br ($\delta(^{13}C)$ 132.2, $J(CP) = 6$ Hz).

Reaction of complex **13** with $PhCH_2MgCl$ in thf at $-60\,^{\circ}C$ leads to a mixture of at least three products. Two of these are transient and disappear on warming to $-30\,^{\circ}C$, leaving the olefin complex **12** intact *. This implies observation of a single

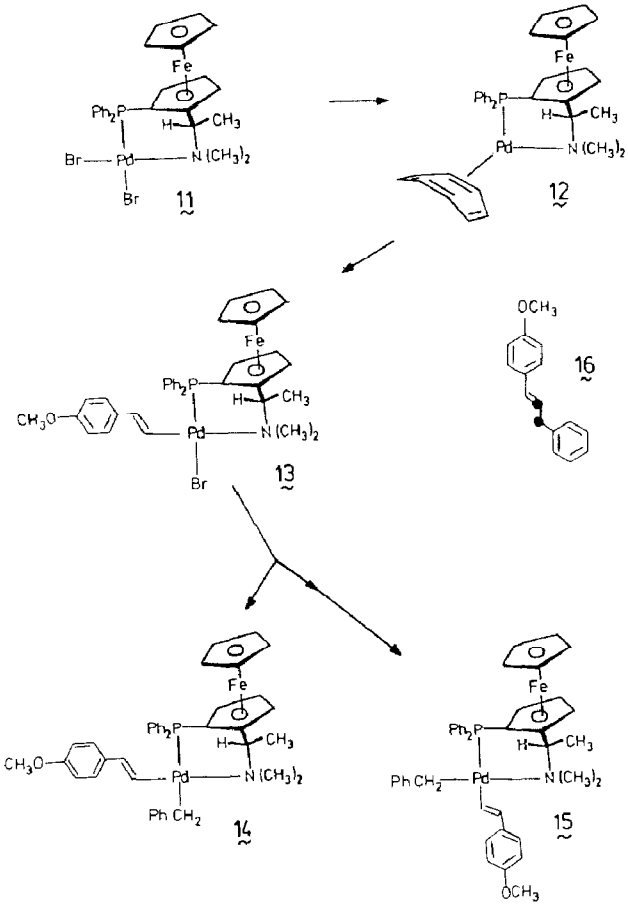

Fig. 2. Reactive intermediates in cross-coupling revealed by ^{13}C labelling on derivatives of ligand **3**. See text for reaction conditions.

* Complex **12** is formed by displacement of the product stilbene from the coordination sphere by cyclooctatetraene subsequent to reductive elimination.

turnover of the catalytic cycle, and further information on the transient intermediates was sought. When the reaction was carried out at $-60\,^{\circ}C$ with ^{13}C-labelled complex (vide supra) and $PhCH_2MgCl$, one of the transient species **14** exhibited a strong CP coupling (δ 5.8 ppm, $J(CP) = 128$ Hz) while the other (**15**) was only weakly coupled ($\delta = 0.4$ ppm, $J(CP) = 18$ Hz). The ^{13}C spectrum confirmed this coupling, with **14** resonating at 172.0 and **15** at 149.6 ppm. After warming to $-30\,^{\circ}C$ this ^{13}C spectrum contains ^{13}C-labelled olefin displaced from coordination. A similar experiment was carried out with ^{13}C-labelled Grignard reagent and halide (**6**); the ^{31}P spectrum then contains **14** merely broadened by ^{13}C coupling but **15** showing strong coupling ($J(CP) = 96$ Hz). An experiment with both components labelled served to characterise the olefinic product **16** (δ(C) 126.4, 40.2, $J(CC) = 43$ Hz, for labelled carbons)

The reactions revealed by these experiments are summarised in Fig. 2.

Discussion

As a first step towards elucidating the mechanism of asymmetric cross-coupling, key intermediates in the reaction cycle have been identified in solution and shown to undergo interconversion under conditions appropriate to catalysis. At this stage some caution is required in the interpretation of the results. One of the most critical factors in successful asymmetric synthesis is the solvent. It proves more convenient to carry out mechanistic work in thf, in which Pd complexes are generally satisfactory soluble at low temperature. The most effective asymmetric cross-couplings are carried out in Et_2O, and Table 3 shows the results of a direct comparison between these two solvents under specific experimental conditions. A further feature is that we have not been able to obtain evidence of intermediates using chiral Grignard reagents, so the work does not give information on the origin of enantioselection. The marked difference in optical efficiency between Et_2O and thf may relate to the structure of Grignard reagents in those two solvents. In Et_2O, the preferred form of RMgCl is a chloride-bridged cyclic dimer, whereas solvated monomers are dominant in thf [13].

In summary, we have shown that the palladium (PPN) ligand system gives rise to three possible alkenyl halide complexes, one of which (**8**) is strongly predominant

Table 3

Optical yields (*T*-enentiomer) in catalytic cross-coupling reactions with 1-(chloromagnesio)phenylethane and *E*-4-methoxy-2′-bromophenylethene (cf. Ref. 2)

Catalyst	Solvent	e.e. (%) [a]
(2) $PdCl_2$	Et_2O	58
(2) $PdCl_2$	THF	0
(3) $PdCl_2$	Et_2O	75
(3) $PdCl_2$	THF	20
(3) $PdCl_2$	Et_2O/CH_2Cl_2	~ 0
(3) $PdCl_2$	Et_2O/C_7H_8	64
(3) $PdCl_2$	Et_2O	73 [b]

All reactions were carried out with 2 mol% catalyst at 25 °C described in the Experimental Section. [a] Determined by integration of the CH-O protons at ~ 5.9 ppm in the NMR spectra of derived methylmandelate esters. [b] Conducted with 2′-bromophenylethene.

after equilibration. Although this is PP complexed, it reacts with a benzylic Grignard reagent to form PN complexed intermediates. The regiochemical preference for **8** may be steric in origin, since it places the bulky phenylvinyl group distant from the PPh_2 group constrained by an aminoethyl side-chain. For the palladium (PN) ligand system, only a single alkenyl halide complex is formed, with the phosphorus *trans* to Br. On alkylation, both regioisomeric dialkyl complexes are formed; if the initial displacement of PdBr is stereospecific, then isomerisation must occur under very mild conditions.

These experiments emphasise the importance of P-N chelation in asymmetric cross-coupling. At this stage there is no need to invoke N-coordination to magnesium or zinc [2] to explain the sequence of catalysis. Similar conclusions have been reached by the Utrecht group working in a related series [22].

Experimental

All reactions were carried out by standard inert atmosphere techniques with solvents purified by distillation under Ar.

The following starting materials were prepared by published procedures: 1,5-cyclooctadienepalladium dibromide [14], (*S,R*)-dppfa(2) [7] (*S,R*)-ppfa(3) [7], 1-chloroethylbenzene [15], *E*-2′-bromo-4-methoxyphenylethane [16] [1′-^{13}C]=benzylchloride [14] and ^{13}C-bromoform [18].

Dilithium cyclooctatetraene dianion [11] was prepared from finely-divided lithium, which reduced the reaction time from 16 to 2 h.

Grignard reagents were prepared, in ether or tetrahydrofuran at −5 °C, in concentrations varying from 0.02 to 0.4 *M*. Aldrich "Gold Label" magnesium, preactivated with 1,2-dibromoethane (ca. 10 μl), was employed in all cases.

E-2′-Bromo-4-methoxyphenyl-[2′-^{13}C]ethene

Anisaldehyde (0.90 cm^3, 7.4 mmol) and ^{13}C-bromoform (1.80 g, 7.1 mmol) were added to a stirred suspension of $CrCl_2$ (3.50 g, 28.5 mmol) in tetrahydrofuran (50 cm^3) at 0 °C. The dark brown mixture was stirred at 0 °C for 2 h, then refluxed for 30 min to ensure complete reaction. Water (30 cm^3) was added, and the crude product was extracted with Et_2O (4 × 50 cm^3). Removal of the solvent from the extract and flash chromatography of the residue, with elution with petroleum ether (b.p. 30–40 °C), gave a mixture of the title compound and its chloride analogue in the ratio 60/40 (combined yield = 0.97 g, 71%).

The two products were separated by gas-liquid chromatography (OV 225, 15′, 200 °C, relative retention times of RCl and RBr 0.63/1) and the bromide (δ(C) ($CDCl_3$): 104.1 ppm) collected.

In situ NMR studies

The techniques employed in the preparation of samples for in situ NMR studies are illustrated by the following experiment.

A suspension of Pd(dppfa) Br_2 (0.0300 g, 0.034 mmol) in thf was degassed by three freeze/thaw cycles and recooled to −70 °C. A solution of dilithium cyclooctatetraene dianion (0.29 *M* in thf, 0.120 cm^3, 0.035 mmol) was added dropwise during 5 min. The resulting bright yellow solution was transferred via a steel cannula to a degassed, cooled NMR tube, which was sealed with a rubber

septum. Solutions of the cyclooctatetraene complex prepared in this manner could be stored without degradation for up to 8 h at −70 °C.

The ^{31}P NMR spectrum of **5** was recorded in order to check the efficiency of formation of this complex. The sample was then transferred to a cold bath at −30 °C and a solution of 2′-bromo-4-methoxyphenylethene (0.0365 g, 0.17 mmol) in thf (0.100 cm^3) was added. The ^{31}P NMR spectra were recorded at 10° intervals from −30 to 0 °C.

The solution of **8a** was then cooled to −70 °C and 1-(chloromagnesio)phenylethane (0.37 *M* in thf, 0.100 cm^3, 0.037 mmol) was added. The ^{31}P NMR spectra were recorded at 10° intervals from −70 to 20 °C.

The catalysts were deactivated with HCl (0.01 *M*, 0.100 cm^3) and the solvent was evaporated. The products were extracted with petroleum ether (b.p. 30–40 °C, 10 cm^3) and the solution was dried over $NaSO_4$. After filtration, the solvent was removed, in vacuo, and the ^1H NMR spectra of the products recorded; δ ($CDCl_3$): 1.49 ($CHCH_3$, d, $J = 7$ Hz) 3.65 ($CHCH_3$, dq), 3.82 ($-OCH_3$, s), 6.28 ($=CH_2CHCH_3$, dd, $J = 7$ Hz) 6.40 ($CH{=}CH{-}CH$, d, $J = 16$ Hz) 6.84–7.37 (Ar).

NMR spectra were recorded on a Bruker AM 250 at the appropriate temperature in an 8.4 mm tube placed in a 10 mm tube containing CD_3OD as lock. For ^{13}C-labelled substrates, ^{31}P and ^{13}C spectra were recorded sequentially without removal of the sample from the probe.

Catalytic reaction of E-4-methoxy-2′-bromophenylethene with 1-(chloromagnesio)phenylethane

A solution of the $PdCl_2$ complex of ligand **3** (0.012 g, 0.02 mmol) 2 mol%) was suspended in dry, degassed Et_2O (2 ml) and cooled to −60 °C with stirring. To this suspension was added $COTLi_2$ (0.245 *M*, ca. 250 μ), a clear rust-coloured solution being obtained. To this solution was added first halide **6** (0.213 mg, 1 mmol) and then 1-(chloromagnesio)phenylethane (6 ml, 0.034 *M* solution in Et_2O, iodide-free) [19]. The solution was stirred in a bath at −25 °C overnight and then dilute HCl (5 mol) was added. Work-up by standard procedures followed by chromatographic separation (60 μ silica gel, 4% Et_2O/hexane) gave a golden-yellow oil (0.100 g), which was used directly for the analysis.

A 50 ml round-bottomed flask was charged with CH_3CN (2 ml) CCl_4 (2 ml) H_2O (3 ml) $NaIO_4$ (0.877 g) and product above (30 μl, 0.014 mmol). To the stirred biphasic solution was added $RuCl_3 \cdot 3H_2O$ (0.005 g), and vigorous stirring pursued for 2 h at 20 °C [20]. After this time CH_2Cl_2 (10 ml) was added and the phases were separated. Standard aqueous workup left a residue which was diluted with Et_2O, filtered through Celite and concentrated.

S-(+)-Methyl mandelate (0.026 g) was dissolved in dry CH_2Cl_2 (2 ml). 4-Dimethylaminopyridine (0.0012 g) and *N*,*N*′-dicyclohexylcarbodiimide (0.041 g) were added and the stirred solution cooled to −10 °C. The mixture of acids prepared as above was added, and stirring maintained at this temperature for 3 h. The precipitate of dicyclohexylurea was removed by filtration, and the mandelate ester purified by preparative TLC on silica gel (1/1 petroleum ether (40–60 °C)/ethyl acetate, R_f 0.57).

The enantiomeric excess was determined from the ^1H NMR spectra of the mandelate ester at 500 MHz, cf. Table 3 [21].

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