Electron-Poor Olefin Polymerization Catalysts Based on Semi-Fluorinated Bis(phosphane)s

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Two semi-fluorinated bis(phosphane)s, *P,P′*-(1,2-ethanediyl)-bis[bis(2,4,5-trifluorophenyl)phosphane] (**3a**), *P,P′*-(1,2-ethanediyl)bis[bis(2,4-difluorophenyl)phosphane] (**3b**), and their corresponding Pd^{II}- and Pt^{II}-dichloro complexes (**4a**,**b** and **6a**,**b**) have been synthesized. Complexation of *P,P′*-(1,2-ethanediyl)bis{bis[3,5-di(trifluoromethyl)phenyl]phosphane} (**3c**) and *P,P′*-(1,2-ethanediyl)bis[bis(pentafluorophenyl)phosphane] (**3d**) afforded the related compounds **4c**,**d** and **6c**. The Pd^{II}-diiodo complexes **5c**,**d** have been obtained from **4c**,**d** by halide exchange with NaI. The solid-state structures of compounds **4b** and **5c**,**d** have been determined by single-crystal X-ray diffraction analysis. Activation of **4b**–**d** with MAO produced efficient catalysts for the polymerization of 2-norbornene, which have proved to be superior to the Pd^{II}-dichlorides derived from the more electron-rich, structurally related *P,P′*-(1,2-ethanediyl)bis(diphenylphosphane) (DPPE) or *P,P′*-(1,3-propanediyl)bis(diphenylphosphane) (DPPP).

Introduction

Bidentate phosphanes $R_2PCH_2CH_2PR_2$ (R = alkyl, aryl) play an important role in the synthesis of tailored organometallic complexes for catalytic purposes. Potential applications range from the field of asymmetric hydrogenation, as carried out with chiral rhodium(I) compounds, for example, to C−C bond-forming processes in the case of the Grignard cross-coupling reaction.[1−3] Apart from examples specific to isolated molecules, late transition metal complexes of bis(phosphane)s are also versatile catalysts for the construction of polymeric materials. With an appropriate choice of the ligand sphere, Ni^{II} compounds can be used to synthesize either high molecular weight poly(olefin)s or oligomeric products.[4,5]

Recently, bis(phosphane)s $(R^f)_2P(CH_2)_2P(R^f)_2$ (R^f may be, for instance, pentafluorophenyl- or perfluoroalkyl-) have attracted attention as a new class of chelating ligands.[6,7] The electron-withdrawing character of the fluorine substituents strongly alters the electronic behaviour of the phosphorus atoms, leading to ligands that show weak σ-donor characteristics, but a high level of π-acceptor capacity. Consequently, bis(phosphane)s of this type form electron-poor transition metal complexes, e.g. Cr, Mo, Fe, Pt, Ru, Rh, and Ir compounds.[8−15] For catalytic applications, it may be advantageous that, unlike most typical strong π-acceptor ligands such as CO, NO and PF_3, bis(phosphane)s can easily be modified in a steric or electronic way by changing their substitution pattern.

We report herein on the synthesis and structural characterization of new electron-poor Pd^{II} and Pt^{II} complexes based on ethylene-bridged ligands $(Ar^f)_2P(CH_2)_2P(Ar^f)_2$, which differ in the substitution patterns at their arene moieties. To explore the potential of this class of compounds as catalysts for the polymerization of olefinic substrates, polymerization experiments have been conducted with 2-norbornene as the monomer.

Results and Discussion

Ligands

Ethylene-bridged bis(phosphane)s are most conveniently prepared by reaction of *P,P′*-(1,2-ethanediyl)bis(dichlorophosphane) **(1)** with an organometallic reagent, usually a lithiated or Grignard compound.[16,17] This method not only circumvents the time-consuming and laborious synthesis of secondary phosphanes, it also proceeds smoothly to afford the desired bidentate phosphanes in a one-pot procedure.

For the syntheses of *P,P′*-(1,2-ethanediyl)bis[bis(2,4,5-trifluorophenyl)phosphane] **(3a)** and *P,P′*-(1,2-ethanediyl)-bis[bis(2,4-difluorophenyl)phosphane] **(3b)**, we employed fluorinated phenyllithiums as the metallated components, which were prepared from the corresponding bromo derivatives through halogen−metal exchange using *n*-butyllithium at −78 °C in diethyl ether (Figure 1). *P,P′*-(1,2-ethanediyl)bis{bis[3,5-di(trifluoromethyl)phenyl]phosphane} **(3c)** was prepared from the Grignard compound 3,5-bis(trifluoromethyl)benzenemagnesium bromide **(2c)**, generated according to a literature procedure from 1-bromo-3,5-bis(trifluoromethyl)benzene and magnesium tur-

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nings.[18] A multi-step synthesis of **3c** has been reported previously, but is less favourable from an economic viewpoint.[19] Compounds **3a** and **3b** exhibit ^{31}P absorptions at $\delta = -30.2$ and -31.9, respectively. These signals are situated upfield from the resonance reported for the unsubstituted *P,P'*-(1,2-ethanediyl)bis(diphenylphosphane) ($\delta = -12.5$),[20] whereas in the case of **3d** a ^{31}P chemical shift of $\delta = -44.5$ is observed.[7] This reflects the partial fluorination of the phenyl substituents in compounds **3a,b** and further suggests that they may also form electron-poor complexes, although this effect should be less pronounced than in the case of **3d**.

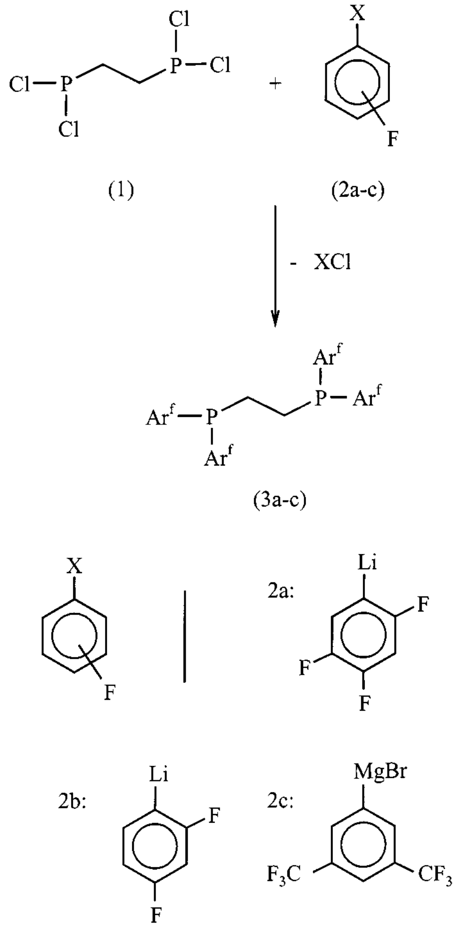

Figure 1. Synthesis of the semi-fluorinated bis(phosphane)s **3a**, **3b**, and **3c**

Complexes

For the synthesis of the Pd^{II}- and Pt^{II}-dichloro complexes of **3a–c** (denoted in Figure 2 as **4a–c** and **6a–c**, respectively) we used suitable organometallic precursors, which were reacted with the ligands at ambient temperature. Compound **4d** was prepared according to a modified literature procedure.[14] All the complexes were obtained as ivory-coloured, microcrystalline solids, except **4d**, which exhibited a distinct yellow aspect. Single crystals of **4b** were obtained from a tetrachloroethane solution.

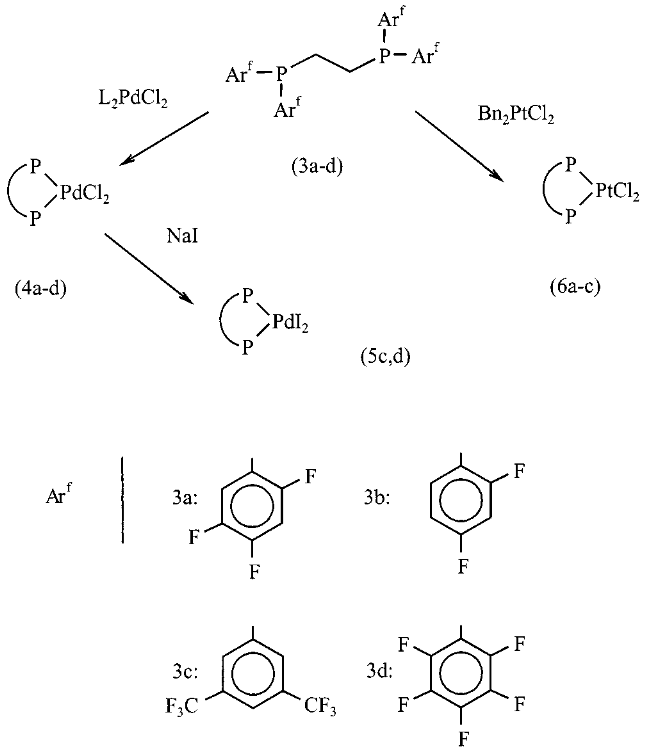

Figure 2. Preparation of the Pd^{II} and Pt^{II} complexes of the semi-fluorinated bis(phosphane)s **3a**, **3b**, **3c**, and **3d**; L_2 = COD (1,5-cyclooctadiene) in the synthesis of **4b** and **4d**; Bn = benzonitrile

Replacement of the chloride substituents of **4d** by treatment with sodium iodide yielded **5d** as a dark-red complex. Slow evaporation of the solvent from an acetone solution produced crystals suitable for an X-ray structure analysis. Halide exchange was also performed on **4c**, leading to a red product that was identified as **5c** (Figure 3, Table 1). Single crystals of this compound suitable for structure investigation could be grown from an acetone solution; their analysis allowed a direct comparison with **5d**, any influence of the different halide ligands being excluded.

In the case of compound **5c** (space group: *C*2/*c*), 3.5 molecules of acetone were found to be included within the unit cell, which are omitted from the ORTEP plot for the sake of clarity. One of the crystallographically determined acetone molecules was found to have a site occupancy factor of 0.75, both showing a slight disordering. The anisotropic displacement factors were also rather large for the CF$_3$ groups, but dividing the fluorine atoms into two positions could not be satisfactorily accomplished. Similar effects have been observed in an X-ray structure analysis of [{BISBI-(3,5-CF$_3$)}(PPh$_3$)Ir(CO)H].[21] Here, three out of four CF$_3$ moieties were found to be disordered at 133 K. These observations may serve to illustrate the fluxional behaviour of trifluoromethyl substituents in the solid state. The average C−F bond lengths in **5c** (1.301 Å) are in agreement with the literature data (1.338 Å).[19]

Only a few crystal structures of complexes of **3d** have hitherto been reported, specifically those of [(**3d**)$_2$Pt^0],[12] *trans*-[η^5-(C$_5$H$_5$)Mo(**3d**)(CO)Cl],[14] [(**3d**)Rh(PPh$_3$)Cl],[22]

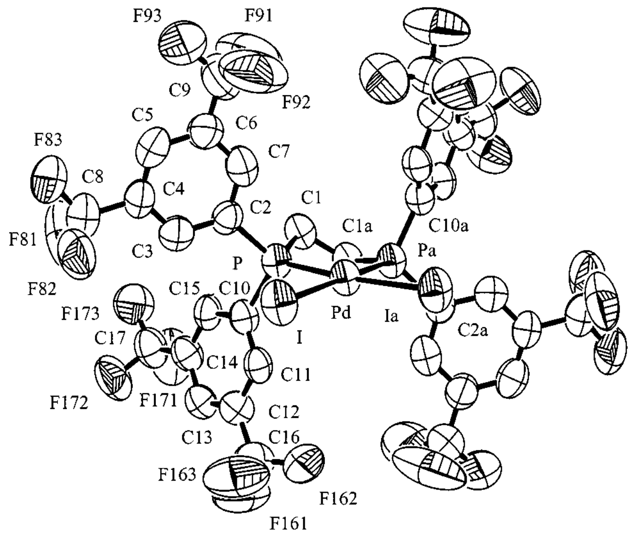

Figure 3. ORTEP plot of complex (**3c**)PdI$_2$, **5c**, showing the atom labelling scheme; atoms labelled *a* were generated by symmetry operations; thermal ellipsoids are depicted at a 50% probability level

Table 1. Selected bond lengths [Å] and angles [°] in **5c**

Distances		Angles	
Pd−I	2.6349(15)	P−Pd−Pa[a]	85.81(14)
Pd−P	2.244(3)	P−Pd−Ia[a]	88.83(8)
P−C10	1.807(11)	I−Pd−Ia[a]	96.70(7)
P−C2	1.811(10)	C10−P−C2	106.9(5)
P−C1	1.813(10)	C10−P−C1	103.6(5)
		C2−P−C1	106.3(5)

[a] Generated by symmetry operations: $-x + 1, y, -z + 1/2$.

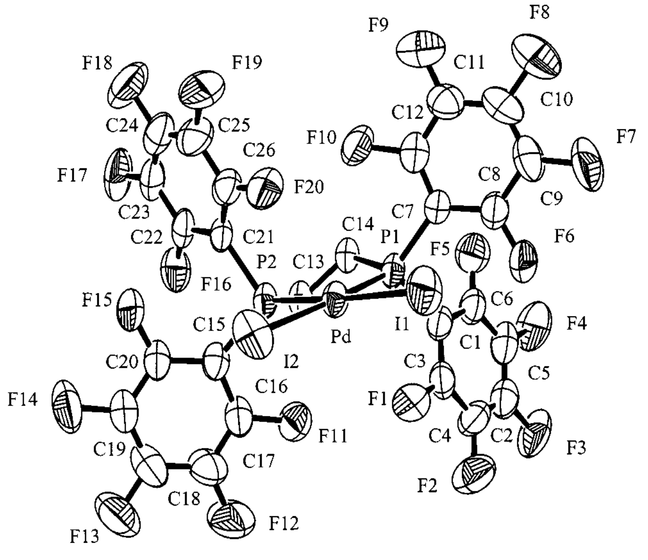

Figure 4. ORTEP plot of complex (**3d**)PdI$_2$, **5d**, showing the atom labelling scheme; thermal ellipsoids are depicted at a 50% probability level

Table 2. Selected bond lengths [Å] and angles [°] in **5d**

Distances		Angles	
Pd−P1	2.265(3)	P1−Pd−P2	85.48(12)
Pd−P2	2.247(3)	P1−Pd−I1	92.23(11)
Pd−I1	2.630(2)	P2−Pd−I2	88.09(11)
Pd−I2	2.645(2)	I1−Pd−I2	94.18(9)
P1−C7	1.814(10)	C15−P2−C13	108.2(5)
P1−C1	1.830(10)	C15−P2−C21	107.2(4)
P1−C14	1.850(9)	C13−P2−C21	102.5(5)
P2−C15	1.812(10)	C7−P1−C1	105.8(4)
P2−C13	1.831(10)	C7−P1−C14	107.5(5)
P2−C21	1.835(9)	C1−P1−C14	99.8(5)
C13−C14	1.531(13)		

and [M(Cp*)(**3d**)Cl]BF$_4$ (M = Rh, Ir).[23] The crystal structure of **3d** itself is also known.[23] As regards the bond distances between the phosphorus atoms and the metal, comparable results have been obtained for **5d** (space group: $P2_1/n$) and the Pt^0 complex (average Pt−P distance 2.288 Å), the values being somewhat lower for Pd^{II} (Figure 4, Table 2). The P−C bond lengths are in the same range as observed previously, but in the present study the shortest distances have been seen in [(**3d**)PdI$_2$] (**5d**).[12,14] The average C−F bond length calculated for **5d** (1.340 Å) matches the value determined for the Mo complex (1.344 Å).[16] The non-fluorinated complex diiodo-[*P*,*P*′-(1,2-ethanediyl)bis-(diphenylphosphane)]palladium(II) has Pd−I bond lengths of 2.6649(8)/2.6446(10) Å and Pd−P bond lengths of 2.2608(14)/2.2756 Å, which resemble the corresponding values found for **5c**,**d** (Table 1 and 2).[24] Moreover, the P−Pd−P bond angle of 85.59(5)° and the I−Pd−I bond angle of 92.73(3)° are similar to the results observed for the fluorinated species **5c**,**d**.

Complex **4b** (space group: *I*2/*a*) was found to crystallize with two molecules of tetrachloroethane (Figure 5, Table 3).

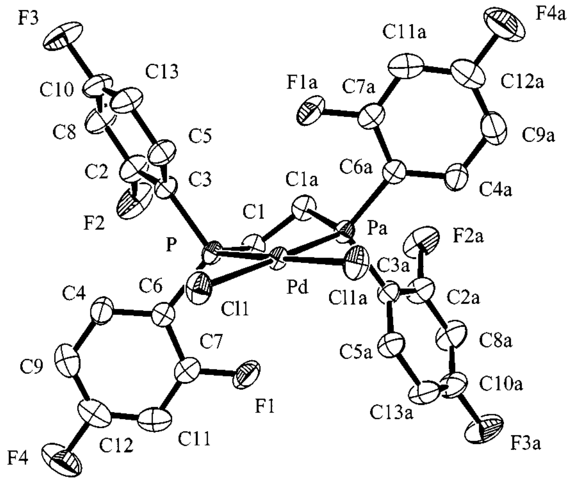

Figure 5. ORTEP plot of complex (**3b**)PdCl$_2$, **4b**, showing the atom labelling scheme; atoms labelled *a* were generated by symmetry operations; thermal ellipsoids are depicted at a 50% probability level

Table 3. Selected bond lengths [Å] and angles [°] in **4b**

Distances		Angles	
Pd−P	2.233(7)	P−Pd−Pa[a]	85.94(4)
Pd−Cl1	2.342(7)	Cl1−Pd−Cl1a[a]	92.11(4)
P−C6	1.804(3)	C6−P−C3	106.73(12)
P−C1	1.835(3)	C6−P−C1	106.79(13)
P−C3	1.812(3)	C3−P−C1	106.97(13)

[a] Generated by symmetry operations: $-x + 3/2, y, -z + 1$.

Its P−C bonds are generally shorter than those in the structures of **5c**,**d**, whereas the C−P−C bond angles are seemingly widened. The C−F bond lengths to the *o*- and *p*-fluorines are on average 1.351 Å, slightly longer than in the pentafluorinated aromatics. Two crystal structures of the non-fluorinated parent compound, dichloro-{*P,P′*-(1,2-ethanediyl)bis[diphenylphosphane]}palladium(II) can be found in the literature.[25,26] These show significant deviations as regards, for example, the P−Pd−P bond angle [88.3(1)° vs. 85.82(7)°] and the Pd−P bond lengths [2.284(3) and 2.264(3) Å vs. 2.233(2) and 2.226(2) Å]. This has been attributed to a packing effect arising from the incorporation of one molecule of dichloromethane in the second case. The latter values are nevertheless in good agreement with the Pd−P bond length in **4b** [2.233(7) Å] and the associated P−Pd−P bond angle [85.94(4)°]. The Pd−Cl bond length in **4b** (2.342 Å) is also close to the values observed in the non-fluorinated complex [2.361(2) and 2.357(2) Å].

Polymerization

In contrast to early transition metal systems, complexes of the late transition metals are most often found to dimerize or oligomerize olefins as a result of a competition between chain propagation and β-hydride elimination.[27,28] This is illustrated by the fact that, until recently, just a few examples of late transition metal catalyzed formation of high molecular weight poly(ethylene) were known.[29−31] However, it has since been demonstrated that Pd^{II}- and Ni^{II}-based systems with bulky diimine ligands are not only capable of producing high molecular weight poly(ethylene), but even poly(α-olefin)s.[32,33] This finding was attributed to a blocking of β-hydride elimination by the sterically demanding ligand system. Since the ligands discussed in this work were not designed to meet this requirement, 2-norbornene was used as the monomer as, in this case, a chain termination process based on β-hydride elimination is thermodynamically unfavourable.[34,35] In the case of the semi-fluorinated complexes **4b−d**, addition of 2-norbornene to a solution of the MAO-activated[36] species led to the immediate precipitation of poly(norbornene). Due to the heat of reaction evolved in the polymerization process, this was accompanied by a warming of the reaction vessel. Under analogous experimental conditions, the structurally related complexes DPPE-$PdCl_2$, DPPP-$PdCl_2$,[37] and DPPP-$NiCl_2$[38] were found to give lower conversions, whereas the Pt^{II} complex **6c**[39] failed to produce any poly(norbornene) (Table 4).

Table 4. Polymerization results for semi-fluorinated complexes in comparison with the performances of structurally similar non-fluorinated compounds

	Catalyst	Reaction time (min.)	Monomer conversion (%)
1	DPPE-$PdCl_2$	15	51.4
2	DPPP-$PdCl_2$	15	49.7
3	4b	10	94.7
4	4c	15	100
5	4c	10	94.1
6	4d	15	85.7
7	6c	15	0
8	DPPP-$NiCl_2$	15	6.3

Polymer Characterization

The poly(norbornene)s synthesized in the course of this study were found to be completely insoluble in common organic solvents. In the case of the palladium-catalyzed norbornene polymerization, this lack of solubility has been proposed to originate from an *diisotactic* microstructure of the polymer, whereas Ni and Co complexes have been reported to produce *erythro-syndiotactic* material that shows satisfactory solubility up to molecular weights of one million and beyond.[35,40,41] In this regard, it is noteworthy that the polymer formed by DPPP-$NiCl_2$ was also found to be insoluble. As a consequence, polymer characterization could only be carried out by means of solid-state methods. The solid-state ^{13}C NMR spectrum features broad resonances in the range $\delta = 25-60$. Major absorptions are seen at $\delta = 52.5$, 48.6, 40.9, and 35.3 that are not fully baseline-resolved. This finding is due to the bicyclic nature of the monomer and can also be taken as evidence pointing to a complex polymer microstructure. As far as we can conclude from the spectral data, polymerization with the late transition metal catalysts examined here proceeds according to an insertion-type mechanism, since vinylic resonances resulting from a hypothetical ring-opening propagation step are not observed.[42−44] In the FT-IR (KBr) spectrum, strong bands are observed at 2946 cm^{-1} (CH_2 units) and 2867 cm^{-1} (CH units), resembling the typical C,H valence absorptions, whereas bands at 1478 cm^{-1} and 1454 cm^{-1} can be attributed to C,H bond deformation. A weak absorption at 707 cm^{-1} is assigned to CH_2 rocking. In accordance with the literature data, no glass transition below the onset of thermal decomposition could be detected for the prepared poly(norbornene)s by DSC methods.[34]

Conclusion

The treatment of novel electron-poor Pd^{II} complexes based on semi-fluorinated bis(phosphane)s with methylaluminoxane (MAO) affords active catalysts for the insertion polymerization of 2-norbornene, which display increased monomer conversions compared to catalysts derived from non-fluorinated, more electron-rich compounds. Comparisons of the crystallographic data of **4a** with those of the parent compound dichloro-[*P,P′*-(1,2-ethanediyl)bis(diphenylphosphane)]palladium(II), and those of **5c**,**d** with the data for diiodo-[*P,P′*-(1,2-ethanediyl)bis(diphenylphosphane)]palladium(II) revealed no significant structural differences. Therefore, despite the fact that there seems to be no clear relationship between the degree of fluorination and the monomer conversion, the improved polymerization results obtained with the fluorinated species may be ascribed to their altered electronic properties.

Owing to the comparatively low steric demand in the apical positions, the investigated catalysts are not suitable for the polymerization of α-olefins to high molecular weight poly(olefin)s since the competing displacement of β-H elimination products by incoming olefin molecules cannot be sufficiently suppressed.[27,28,32,33] Consequently, these complexes can be expected to act as oligomerization catalysts for α-olefins. In terms of activity towards the polymerization of 2-norbornene, ligand-free systems[35,40,41] based on simple metal salts, for instance Pd^{II}, Ni^{II}, or Co^{II} compounds, are presumably superior to the investigated catalysts, but lack the structural versatility of bis(phosphane) complexes, which potentially may be helpful in controlling olefin insertion processes. Thus, it should be interesting to combine a bulky ligand geometry, which meets the requirements outlined up above, with partial fluorination to obtain new late transition metal catalysts for the synthesis of poly(olefin)s.

Experimental Section

Materials: *P,P′*-(1,2-ethanediyl)bis[bis(pentafluorophenyl)phosphane] (99%), *P,P′*-(1,2-ethanediyl)bis(dichlorophosphane) (min. purity 97%; received in a sealed glass ampoule, which was opened immediately prior to use), and dichlorobis(benzonitrile)platinum(II) (Bn_2PtCl_2) (99%) were purchased from Strem Chemicals; 1-bromo-2,4-difluorobenzene (98%+), 1-bromo-2,4,5-trifluorobenzene (98%+), and 1-bromo-3,5-bis(trifluoromethyl)benzene (98%+) were from Lancaster. Mg turnings and 2-norbornene were obtained from Merck. Dichloro[*P,P′*-(1,3-propanediyl)bis(diphenylphosphane)]nickel(II), dichloro[*P,P′*-(1,2-ethanediyl)bis(diphenylphosphane)]palladium(II), dichloro[*P,P′*-(1,3-propanediyl)bis(diphenylphosphane)]palladium(II), and *n*-butyllithium (0.1 M in *n*-hexane) were purchased from Fluka. MAO was supplied by WITCO (10% *w*/*w* in toluene). Dichlorobis(benzonitrile)palladium(II) (Bn_2PdCl_2) and dichloro(1,5-cyclooctadiene)palladium(II) ($CODPdCl_2$) were prepared according to literature procedures.[45,46] Tetrahydrofuran was distilled from sodium benzophenone ketyl, toluene from potassium benzophenone ketyl. Dichloromethane was refluxed with calcium hydride and distilled. Ethanol was dried with sodium/diethyl phthalate. Dry acetone (max. 0.01% H_2O) was purchased from Merck. All operations relating to the preparation and complexation of the bis(phosphane) ligands were carried out under an argon atmosphere employing standard Schlenk techniques. The synthesized complexes were found to be stable towards air and moisture and do not require any special conditions for storage.

Methods: ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AMX 500 spectrometer. Chemical shifts (δ) are given in ppm and were referenced to residual ^1H NMR signals and to the ^{13}C NMR signals of the deuterated solvents, respectively. ^{31}P chemical shifts were referenced to external 85% H_3PO_4. ^{19}F NMR spectra were recorded on a Bruker AC 200 spectrometer employing an external $CFCl_3$ standard for calibration. Solid-state ^{13}C NMR spectra (CP-MAS) were recorded on a Bruker DSX 400 spectrometer and referenced using glycine. − IR spectra were recorded on a Bruker IFS 113V spectrophotometer using samples in KBr pellets. − FAB mass spectra were measured on a Finnigan SSQ 7000 spectrometer using a matrix of 2-nitrophenyl octyl ether. − Elemental analyses were performed in the Microanalytical Section of the University of Ulm. − X-ray structure determinations of compounds **4b** and **5d** were carried out on a STOE IPDS diffractometer (Universität Ulm); **5c** was analyzed on a Rigaku AFC-7S diffractometer (University of Helsinki). All measurements were made using graphite-monochromated Mo-K_α radiation (wavelength 0.71073 Å; fine-focus sealed tube).

Synthesis of the Ligands L_2 (3a−c)

***P,P′*-(1,2-Ethanediyl)bis[bis(2,4,5-trifluorophenyl)phosphane] (3a):** In a 500-mL Schlenk flask equipped with a dropping funnel 1-bromo-2,4,5-trifluorobenzene (6.1 mL, 51.8 mmol) was dissolved in dry diethyl ether (50 mL) and the solution was cooled to −78 °C by employing a dry ice/2-propanol bath. Over a period of 30 min., a solution of *n*-butyllithium in *n*-hexane (32.4 mL, 1.6 M) was added by means of the dropping funnel. Following this addition, stirring was continued for 15 min. The funnel was then rinsed with dry diethyl ether (5 mL) and charged with a solution of *P,P′*-(1,2-ethanediyl)bis(dichlorophosphane) (2.0 g, 8.9 mmol) in diethyl ether (25 mL), which was added maintaining a temperature of −78 °C. The solution was then allowed to warm to room temperature. After hydrolysis with degassed water, the ethereal phase was separated and dried with anhydrous magnesium sulfate. The solvent was evaporated in vacuo to yield a yellowish product. Recrystallization from ethanol/acetone afforded **3a** as a white crystalline solid. Yield: 4.4 g (80.5%). − ^1H NMR ($CDCl_3$): δ = 7.03 (m, 4 H, Ar), 6.91 (m, 4 H, Ar), 2.17 (m, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 159.6 [d, $^1J(^{19}F,^{13}C)$ = 246.5 Hz], 151.4 [ddd, $^1J(^{19}F,^{13}C)$ = 242.7 Hz, $^2J(^{19}F,^{13}C)$ = 15.1 Hz, $^2J(^{19}F,^{13}C)$ = 12.6 Hz], 147.9 [dd, $^1J(^{19}F,^{13}C)$, = 249.0 Hz, $^2J(^{19}F,^{13}C)$ = 12.6 Hz], 121.1, 118.6, 106.3 [dd, $^2J(^{19}F,^{13}C)$ = 30.2 Hz, $^2J(^{19}F,^{13}C)$ = 8.8 Hz], 20.9. − ^{19}F NMR ($CDCl_3$): δ = −105.9 (m, *o*-F), −130.3 (m, *p*-F), −141.8 (m, *m*-F). − ^{31}P NMR ($CDCl_3$): δ = −30.2. − $C_{26}H_{12}F_{12}P_2$ (614.3): calcd. C 50.8, H 2.0; found C 50.6, H 2.1.

***P,P′*-(1,2-Ethanediyl)bis[bis(2,4-difluorophenyl)phosphane] (3b):** Compound **3b** was synthesized according to the procedure described for **3a** starting from 1-bromo-2,4-difluorobenzene (10 g, 51.8 mmol) and 1,2-bis(dichlorophosphanyl)ethane (2.0 g, 8.9 mmol). Yield: 3.6 g (74.5%). − ^1H NMR ($CDCl_3$): δ = 7.22 (m, 4 H, Ar), 6.84 (m, 4 H, Ar), 6.76 (m, 4 H, Ar), 2.19 (m, 4 H, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 165.5 [dd, $^1J(^{19}F,^{13}C)$, = 56.6 Hz, $^2J(^{19}F,^{13}C)$ = 11.3 Hz], 163.4 [dd, $^1J(^{19}F,^{13}C)$ = 60.4 Hz, $^2J(^{19}F,^{13}C)$ = 12.6 Hz], 134.8 [dd, $^2J(^{19}F,^{13}C)$ = 15.1 Hz, $^2J(^{19}F,^{13}C)$ = 8.8 Hz], 118.6 (pseudo-triplet due to coupling with ^{19}F and ^{31}P; coupling constants are 20.1 Hz and 16.4 Hz but unequivocal assignment is not possible), 111.9 [d, $^2J(^{19}F,^{13}C)$ = 20.1 Hz], 104.3 [dd, $^2J(^{19}F,^{13}C)$ = 27.7 Hz, $^2J(^{19}F,^{13}C)$ = 25.2 Hz], 21.0. − ^{19}F NMR ($CDCl_3$): δ = −100.4 (m, *o*-F), −108.9 (m, *p*-F). − ^{31}P NMR ($CDCl_3$): δ = −31.9. − $C_{26}H_{16}F_8P_2$ (542.4): calcd. C 57.5, H 2.9; found C 57.3, H 2.8.

***P,P′*-(1,2-Ethanediyl)bis{bis[3,5-di(trifluoromethyl)phenyl]phosphane} (3c):** At 0 °C, a solution of bis(3,5-trifluoromethyl)phenylmagnesium bromide, prepared from magnesium turnings (1.75 g, 72.0 mmol) and 1-bromo-3,5-bis(trifluoromethyl)benzene (17.1 g, 58.4 mmol) in dry diethyl ether (130 mL) was added to a solution of *P,P′*-(1,2-ethanediyl)bis(dichlorophosphane) (2.0 g, 8.9 mmol) in dry diethyl ether (40 mL). Stirring was continued for 24 h at room temperature. The reaction mixture was then hydrolyzed with degassed water (100 mL) and the resulting precipitate was collected by filtration and extracted with warm acetone. Evaporation of the solvent left a slightly brownish solid, which was recrystallized from dichloromethane/acetone. Yield: 6.9 g (82.3%). − ^1H NMR ([D_6]acetone): δ = 8.10 (s, 8 H, Ar), 8.03 (s, 4 H, Ar), 2.73 (m, 4 H, CH_2). − ^{13}C NMR ([D_6]acetone): δ = 142.1, 134.2, 132.4 [q,

$^2J(^{19}F,^{13}C)$ = 34.0 Hz], 124.7 [q, $^1J(^{19}F,^{13}C)$ = 271.6 Hz, CF_3], 124.1, 23.5 [d, $^1J(^{31}P, ^{13}C)$ = 3.8 Hz]. − ^{19}F NMR ([D$_6$]acetone): δ = −62.6. − ^{31}P NMR ([D$_6$]acetone): δ = −3.4. − $C_{34}H_{16}F_{24}P_2$ (942.4): calcd. C 43.3, H 1.7; found C 43.3, H 2.1.

Preparation of the Complexes L_2PdCl_2 (4a−d)

Dichloro{*P,P'*-(1,2ethanediyl)bis[bis(2,4,5-trifluorophenyl)-phosphane]}palladium(II) (4a): Bn_2PdCl_2 (0.345 g, 0.9 mmol) was added to a solution of **3a** (0.61 g, 1.0 mmol) in dry CH_2Cl_2 (25 mL). After stirring for 16 h at room temperature, the yellowish white precipitate was collected by filtration, thoroughly washed with diethyl ether, and dried under high vacuum. Yield: 0.32 g (45.1%). − ^1H NMR ([D$_6$]DMSO): δ = 7.90 (m, 8 H, Ar), 2.85 (m, 4 H, CH_2). − ^{19}F NMR ([D$_6$]DMSO): δ = −99.1 (m, *o*-F), −124.1 (m, *p*-F), −140.3 (m, *m*-F). − ^{31}P NMR ([D$_6$]DMSO): δ = 64.4. − $C_{26}H_{12}Cl_2F_{12}P_2Pd$ (791.6): calcd. C 39.5, H 1.5; found C 39.1, H 1.5.

Dichloro{*P,P'*-(1,2-ethanediyl)bis[bis(2,4-difluorophenyl)-phosphane]}palladium(II) (4b): Compound **3b** (2.9 g, 53.5 mmol) was added to a solution of CODPdCl$_2$ (1.14 g, 40.0 mmol) in dry CH_2Cl_2 (75 mL). After stirring at room temperature for 16 h, the product was precipitated by pouring the reaction mixture into *n*-pentane (500 mL), collected by filtration, washed with *n*-pentane, and dried under high vacuum. Yield: 2.39 g (83.0%). − ^1H NMR ([D$_6$]DMSO): δ = 7.86 (m, 4 H, Ar), 7.58 (m, 4 H, Ar), 7.38 (m, 4 H, Ar), 2.74 (m, 4 H, CH_2). − ^{19}F NMR ([D$_6$]DMSO): δ = −94.4 (m, *o*-F), −100.7 (m, *p*-F). − ^{31}P NMR ([D$_6$]DMSO): δ = 64.3. − $C_{26}H_{16}Cl_2F_8P_2Pd$ (719.7): calcd. C 43.4, H 2.2; found C 43.6, H 2.7.

Dichloro[*P,P'*-(1,2-ethanediyl)bis{bis[3,5-di(trifluoromethyl)phenyl]-phosphane}]palladium(II) (4c): Compound **3c** (0.85 g, 0.9 mmol) was added to a solution of Bn_2PdCl_2 (0.345 g, 0.9 mmol) in dry acetone (20 mL). After stirring at room temperature for 16 h, the product was precipitated by pouring the reaction mixture into diethyl ether (50 mL). The yellowish-white solid was collected by filtration, washed with diethyl ether, and dried under high vacuum. Yield: 0.95 g (94.0%). − ^1H NMR ([D$_6$]acetone): δ = 8.76 (s, 4 H, Ar), 8.73 (s, 4 H, Ar), 8.34 (s, 4 H, Ar), 3.64 (m, 4 H, CH_2). − ^{19}F NMR ($CDCl_3$): δ = −62.5. − ^{31}P NMR ([D$_6$]acetone): δ = 67.7. − $C_{34}H_{16}Cl_2F_{24}P_2Pd$ (1119.7): calcd. C 36.5, H 1.4; found C 36.2, H 1.7.

Dichloro{*P,P'*-(1,2-ethanediyl)bis[bis(pentafluorophenyl)phosphane]}palladium(II) (4d): In a 250-mL Schlenk flask, CODPdCl$_2$ (0.358 g, 1.25 mmol) and **3d** (0.95 g, 1.25 mmol) were suspended in dry toluene (35 mL) and the mixture was heated to 110 °C for 5 h. After cooling to room temperature, the product was collected by filtration and washed with diethyl ether (2 × 25 mL). Drying under high vacuum yielded 1.1 g (94%) of a yellow powder. − ^1H NMR ([D$_6$]DMSO at 80 °C): δ = 3.21 (m, 4 H, CH_2). − ^{31}P NMR ([D$_6$]DMSO at 80 °C): δ = 37.8. − MS (FAB): *m*/*z* = 900.6 [M^+ − Cl], 863.8 [M^+ − 2Cl]. − $C_{26}H_4Cl_2F_{20}P_2Pd$ (935.6): calcd. C 33.4, H 0.4; found C 33.4, H 0.8.

Preparation of the Complexes L_2PdI_2 (5c,d)

[*P,P'*-(1,2-Ethanediyl)bis{bis[3,5-di(trifluoromethyl)phenyl]phosphane}]diiodopalladium(II) (5c): Compound **4c** (0.3 g, 0.27 mmol) was treated with NaI (0.12 g, 0.8 mmol) in dry acetone (30 mL). After evaporation of the solvent, the residue was extracted with CH_2Cl_2. The orange-red product was then precipitated from the concentrated CH_2Cl_2 solution by adding diethyl ether (50 mL). Yield: 0.23 g (65.9%). − ^1H NMR ([D$_6$]acetone): δ = 8.63 (d, 8 H, Ar), 8.35 (s, 4 H, Ar), 3.46 (m, 4 H, CH_2). − ^{19}F NMR ([D$_6$]acetone): δ = −62.5. − ^{31}P NMR ([D$_6$]acetone): δ = 69.3. − $C_{34}H_{16}F_{24}I_2P_2Pd$ (1302.6): calcd. C 31.4, H 1.2; found C 31.1, H 1.0.

{*P,P'*-(1,2-Ethanediyl)bis[bis(pentafluorophenyl)phosphane]}diiodopalladium(II) (5d): With gentle heating, **4d** (0.3 g, 0.32 mmol) was dissolved in dry acetone (60 mL). NaI (0.144 g, 0.96 mmol) was added, the mixture was stirred for 30 min, and then the solvent was removed in vacuo. The red residue was redissolved in the minimum volume of acetone and purified by column chromatography (SiO_2, particle size 0.063−0.200 mm, Merck) using acetone as the eluent. Evaporation of the solvent from the appropriate fraction left a red microcrystalline product. Yield: 0.27 g (73.7%). − ^1H NMR ([D$_6$]acetone): δ = 3.21 (m, 4 H, CH_2). − ^{31}P NMR ([D$_6$]acetone): δ = 33.6. − $C_{26}H_4F_{20}I_2P_2Pd$ (1118.5): calcd. C 27.9, H 0.4; found C 27.4, H 0.8.

Preparation of the Complexes L_2PtCl_2 (6a−c)

Dichloro{*P,P'*-(1,2-ethanediyl)bis[bis(2,4,5-trifluorophenyl)-phosphane]}platinum(II) (6a): Prepared analogously to **6c** from Bn_2PtCl_2 (0.33 g, 0.7 mmol) and **3a** (0.47 g, 0.77 mmol). Yield: 0.32 g (52.0%). − ^1H NMR ([D$_6$]DMSO): δ = 7.91 (m, 4 H, Ar), 7.86 (m, 4 H, Ar), 2.76 (m, 4 H, CH_2). − ^{31}P NMR ([D$_6$]DMSO): δ = 43.0 [$^1J(^{195}Pt, ^{31}P)$ = 3677.1 Hz]. − $C_{26}H_{12}Cl_2F_{12}P_2Pt$ (880.3): calcd. C 35.5, H 1.4; found C 35.7, H 1.2.

Dichloro{*P,P'*-(1,2-ethanediyl)bis[bis(2,4-difluorophenyl)-phosphane]}platinum(II) (6b): Prepared analogously to **6c** from Bn_2PtCl_2 (0.25 g, 0.53 mmol) and **3b** (0.30 g, 0.56 mmol). Yield: 0.35 g (81.7%). − ^1H NMR ([D$_6$]acetone): δ = 7.98 (m, 4 H, Ar), 7.26 (m, 8 H, Ar), 2.85 (m, 4 H, CH_2). − ^{19}F NMR ([D$_6$]acetone): δ = −95.4 (m, *o*-F), −102.4 (m, *p*-F). − ^{31}P NMR ([D$_6$]acetone):

Table 5. Crystal data and structure refinement for **4b**

Empirical formula[a]	$C_{30}H_{20}Cl_{10}F_8P_2Pd$
Formula weight	1055.30
Crystal size [mm]	0.38 × 0.29 × 0.23
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	*I*2/*a*
Unit cell dimensions [Å, °]	a = 20.855(2) b = 8.528(6), c = 23.200(2) β = 104.291(12)
Volume [Å^3]	3998.2(6)
Z	4
Calculated density [g/cm^3]	1.753
Absorption coefficient [mm^{-1}]	1.274
F (000)	2072
Θ range [°]	2.02 to 25.93
Index ranges	$25 \geq h \geq -25$, $10 \geq k \geq -10$, $28 \geq l \geq -28$
Reflections collected/unique	27301/3810 [R(int) = 0.0329]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3810/0/231
Goodness-of-fit on F^2	1.059
Final *R* indices, [$I > 2\sigma(I)$]	$R1$ = 0.032, $wR2$ = 0.0848
R indices (all data)	$R1$ = 0.0372, $wR2$ = 0.0888
Largest diff. peak and hole [e/Å^{-3}]	0.860 and −0.684

[a] Data collection, cell refinement and data reduction were performed with STOE IPDS. For structure solution SHELXS-97 and structure refinement SHELXL-97 (both Sheldrick, 1997) were used. Molecular Graphics: ORTEP III. Non hydrogen-atom sites were obtained with direct methods and are anisotropically refined. Hydrogen atoms are refined by riding model on calculated positions.

Table 6. Crystal data and structure refinement for **5c**

Empirical formula[a]	$C_{44.5}H_{37}F_{24}I_2O_{3.5}P_2Pd$
Formula weight	1505.88
Crystal size [mm]	0.45 × 0.35 × 0.25
Temperature [K]	193(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions [Å, °]	a = 24.969(9), b = 8.705(7), c = 27.843(8), β = 107.09(3)
Volume [Å^3]	5785(5)
Z	4
Calculated density [g/cm^3]	1.729
Absorption coefficient [mm^{-1}]	1.558
F (000)	2920
Θ range [°]	2.61 to 23.99
Index ranges	$28 \geq h \geq 0$, $9 \geq k \geq 0$, $30 \geq l \geq -31$
Reflections collected/unique	4163/4065, [R(int) = 0.0503]
Completeness to Θ = 23.99 (%)	89.8
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4065/108/361
Goodness-of-fit on F^2	1.114
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0786$, $wR2 = 0.1980$
R indices (all data)	$R1 = 0.0951$, $wR2 = 0.2101$
Largest diff. peak and hole [e/Å^{-3}]	0.474 and −0.260

[a] Data collection, cell refinement and data reduction were performed with TEXSAN (Molecular Structure Corporation, 1993). For structure solution SHELXS-97 and structure refinement SHELXL-97 (both Sheldrick, 1997) were used. Molecular Graphics: ORTEP III. Non-hydrogen atom positions were obtained with direct methods and are anisotropically refined. Hydrogen atoms are refined by riding model on calculated positions. One solvent acetone molecule is partly disordered, namely C(21)−C(22)-[O(1)]−C(23), and has a site occupation factor of 0.75. A SWAT parameter was introduced for diffuse solvent modelling

Table 7. Crystal data and structure refinement for **5d**

Empirical formula[a]	$C_{26}H_4F_{20}I_2P_2Pd$
Formula weight	1118.43
Crystal size [mm]	0.15 × 0.23 × 0.38
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions [Å, °]	a = 11.617(10), b = 14.958(8), c = 19.931(19), β = 95.05(11)
Volume [Å^3]	3450(5)
Z	4
Calculated density [g/cm^3]	2.153
Absorption coefficient [mm^{-1}]	2.548
F (000)	2088
Θ range [°]	2.05 to 24.01
Index ranges	$13 \geq h \geq -13$, $17 \geq k \geq -17$, $22 \geq l \geq -22$
Reflections collected/unique	31481/5290 [R(int) = 0.1043]
Completeness to Θ = 24.01 (%)	93.3
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5290/0/460
Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0637$, $wR2 = 0.1691$
R indices (all data)	$R1 = 0.0900$, $wR2 = 0.1870$
Largest diff. peak and hole [e/Å^{-3}]	1.181 and −1.702

[a] A relatively suitable crystal for diffraction was cut out of a soft crystalline bulk. This "crystal" diffracted only up to 24 degrees. Since the faces of the crystal were arbitrary they could not be used for conducting an absorption correction. The measured intensities were corrected for Lorentz and polarization effects. Data collection, cell refinement and data reduction were performed with STOE IPDS. The structure determination was done by direct methods using XMY (Debaerdemaeker, 1993),[47] for structure refinement SHELXL-97 (Sheldrick, 1997) was utilized. The positions of the hydrogen atoms were calculated (riding model) and refined isotropically. Molecular Graphics: ORTEP III.

δ = 42.5 [^1J (^{195}Pt, ^{31}P) = 3663.2 Hz]. − $C_{26}H_{16}Cl_2F_8P_2Pt$ (808.3): calcd. C 38.6, H 2.0; found C 38.9, H 2.3.

Dichloro[*P,P'*-(1,2-ethanediyl)bis{bis[3,5-di(trifluoromethyl)phenyl]-phosphane}]platinum(II) (6c): Compound **3c** (0.35 g, 0.37 mmol) was added to a solution of Bn_2PtCl_2 (0.159 g, 0.33 mmol) in dry CH_2Cl_2 (20 mL). The yellow colour of the starting material faded within a few minutes as a white precipitate formed. After stirring for 16 h at room temperature, the precipitate was collected by filtration, washed with diethyl ether and *n*-pentane, and dried under high vacuum. Yield: 0.31 g (78.5%). − ^{1}H NMR ([D$_6$]acetone): δ = 8.72 (d, 8 H, Ar), 8.34 (s, 4 H, Ar), 3.49 (m, 4 H, CH$_2$). − ^{31}P NMR ([D$_6$]acetone): δ = 50.9 [^1J(^{195}Pt, ^{31}P) = 3582.5 Hz]. − $C_{34}H_{16}Cl_2F_{24}P_2Pt$ (1208.4): calcd. C 33.8, H 1.3; found C 33.6, H 1.1.

General Procedure for the Polymerization of 2-Norbornene: A 250-mL Schlenk flask was evacuated and purged with argon three times. The vessel was then charged with the appropriate pre-catalyst (usually 3.74×10^{-5} mol) suspended in the requisite volume of dry toluene such that, together with the MAO solution, a final total volume of 100 mL was obtained. Addition of the MAO solution (10% *w*/*w* in toluene) led to an immediate conversion of the pre-catalyst, as was evident from the dissolution of the suspended material and the formation of a clear red-brown solution. Following the introduction of 2-norbornene (4.75 g, 50.5 mmol), the reaction was usually allowed to proceed for 10−15 min. and then the polymerization was quenched by pouring the mixture into a glass beaker containing MeOH (500 mL)/conc. hydrochloric acid (5 mL). The product was collected by filtration and dried under high vacuum at 80 °C for 24 h to yield a fine white powder. − ^{13}C NMR (CP-MAS): Resonances not baseline-resolved; peaks at δ = 57.4, 55.8, 52.5, 48.6, 40.9, 35.3, 30.1. − FT-IR (KBr): $\tilde{\nu}$ = 2946, 2867, 1478, 1454, 1300, 707 cm^{-1}.

Crystallographic Data: Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-136063 (**4b**, Table 5), -135995 (**5c**, Table 6), and -136062 (**5d**, Table 7). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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