Chiral Chelate Ligands Based on a Neopentane Framework; Introducing Indenyl and Fluorenyl Donor Groups

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Dedicated to Prof. Dr. H. Schmidbaur on the occasion of his 65th birthday

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The neopentane-derived functionalized oxetane $O(CH_2)_2C(CH_3)(CH_2OMs)$, **1**, reacts with indenyllithium (LiInd) or fluorenyllithium (LiFlu) to produce the derivatives $O(CH_2)_2C(CH_3)(CH_2R)$ (R = indenyl, fluorenyl), **2**. The oxetane ring of **2** undergoes nucleophilic ring-opening by reaction with $LiPR'_2$ to give the chiral chelate ligands $(HOCH_2)(CH_3)C(CH_2R)(CH_2PR'_2)$ (R = indenyl, fluorenyl), **5**. Nucleophilic ring-opening by LiInd or LiFlu is possible too, resulting in the functionalized *ansa*-Cp ligands $(HOCH_2)(CH_3)C(CH_2R)(CH_2R')$ (R, R′ = indenyl, fluorenyl), **12**. Electrophilic ring-opening of **2** with HBr to give $(HOCH_2)(CH_3)C(CH_2R)(CH_2Br)$ (R = indenyl, fluorenyl), **3**, is also possible. The alcohol function of **3** may be activated directly, whereas activation of this group in **5** is only possible after BH_3 protection of the phosphane function. The mesylates $(MsOCH_2)(CH_3)C(CH_2R)(CH_2Br)$ (R = indenyl, fluorenyl), **4**, undergo, under basic conditions, spiro cyclization to produce spirocyclobutane derivatives **9** with the α-carbons of the five-membered cycles acting as the spiro centres. Substitution of the mesylate group of **4** by PR_2 nucleophiles is therefore not possible. *Ansa*-Cp derivative $(MsOCH_2)(CH_3)C(CH_2Ind)(CH_2Flu)$, **12c** also reacts with $LiPPh_2$ with spiro cyclization to produce **9d**, instead of giving the substitution product. Tripodal ligands $(CH_3)C(CH_2R)(CHPPh_2)_2$ (R = indenyl, fluorenyl), **11**, are accessible by the reaction of $(MsOCH_2)(CH_3)C(CH_2PPh_2)_2$ with LiInd or LiFlu. All compounds are fully characterized by the usual spectroscopic and analytical techniques including single-crystal X-ray analyses in several cases.

Introduction

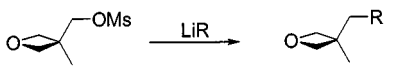
The coordination chemistry of neopentane-based tripodal ligands was extensively developed by L. Sacconi[1] and his school,[2] on the basis of $CH_3C(CH_2PPh_2)_3$ as the prototype ligand. The peculiar type of reactivity of the corresponding tripodal metal templates $CH_3C(CH_2PR_2)_3M$[1][2] indicates potential for this type of ligand, and modification of the donor groups appears to be a worthwhile goal. A number of methods have been developed for the introduction of different donor groups in $CH_3C(CH_2X)(CH_2Y)(CH_2Z)$ (X, Y, Z = PR_2, PR'_2, NR_2, SR, OR),[3−5] even enantioselectively.[3c,3e,3h] Introducing a Cp moiety as a constituent of this type of tripodal ligand calls for special procedures which have been worked out in some cases.[6] The ligands $[R'CH_2C(CH_2C_5H_4)(CH_2X)(CH_2Y)]^-$ (Y, Z = PR_2) lend themselves to the construction of $CpML_2$ templates in which the Cp ligand and the L donors are covalently linked by a neopentane scaffolding. The importance of $CpML_2$ templates in the metal-mediated transformation of organic substances is a stimulus for the interest in such tripodal CpL_2 ligands.[7] It is shown in this paper that the routes developed for the introduction of Cp donor groups into the tripodal ligands cannot be directly transferred to the synthesis of tripodal ligands containing indenyl or fluorenyl groups, due to complications arising from internal cyclization processes. Reaction sequences are nevertheless developed, which allow the introduction of these Cp derivatives into neopentane-based tripodal ligands.

Results and Discussion

Ligand Synthesis

The following reaction sequence was shown to be effective for converting functionalized oxetane **1** to Cp-functionalized tripodal ligands: 1. Substituting OMs by Cp. 2. Electrophilic opening of the oxetane ring by HBr. 3. Mesylation of the OH group resulting from step 2. 4. Nucleophilic substitution of the two leaving groups (OMs, Br) by PR_2.[6a]

The first step of this sequence (Scheme 1) also works when indenyl or fluorenyl needs to be introduced. Compound **2a** is obtained as a colourless oil, which tends to



1 **2a** R = Indenyl **2b** R = Fluorenyl

Scheme 1

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crystallize at −20°C. Compound **2b** forms a colourless microcrystalline powder, from which crystals, suitable for X-ray analysis, could be grown by slow evaporation from CH_2Cl_2/*n*-pentane solutions. NMR spectroscopic data (Table 1) and analytical data (Table 2) are consistent with the assigned constitution which is further proved by an X-ray analysis of **2b** (Figure 1, Table 3 and Table 4).

There are two independent molecules of **2b** in the unit cell (only one is shown in Figure 1). The scalar geometric parameters of these individual molecules are almost identical (Table 3). Even the relative orientation of the fluorenyl entity with respect to the oxetane moiety is closely similar in both molecules (see torsion angles C1−C2−C5−C6 in Table 3). The only significant difference is in the folding angles of the oxetane ring which is definitely different in the two independent species (cf. torsion angles C1−C2−C3−Y and C1−C2−C4−Y Table 3).

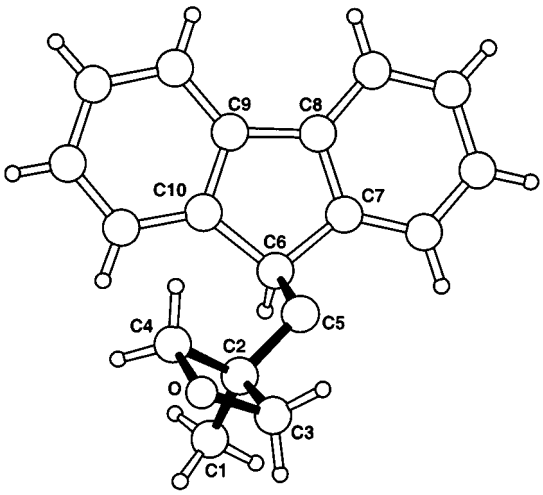


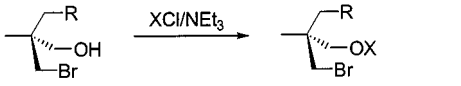
Figure 1. Structure of **2b**

Electrophilic opening of the oxetane rings of **2** by HBr results in compounds **3**; **3a** is obtained as a colourless oil and **3b** as a colourless microcrystalline material (Scheme 2). Analytical (Table 2) and spectroscopic data (Table 1) confirm the identity of **3**.

2a R = Indenyl
2b R = Fluorenyl

3a R = Indenyl
3b R = Fluorenyl

Scheme 2



3a R = Indenyl
3b R = Fluorenyl

4a R = Indenyl, X = Ms
4b R = Indenyl, X = SO_2Ph
4c R = Indenyl, X = $SiMe_3$
4d R = Fluorenyl, X = Ms

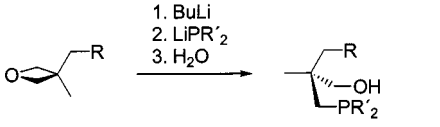
Scheme 3

Activation of the OH group of **3** by different reagents leads to compounds **4** (Scheme 3). Transformation of the $OSiMe_3$ group of **4c** into an iodine substituent by reaction with NaI/$ClSiMe_3$/acetonitrile was unsuccessful. The silyl derivative **4c** is obtained as a colourless oil, while the other compounds **4** form colourless microcrystalline solids. The analytical (Table 2) and the spectroscopic (Table 1) data are in accord with the assigned constitutions, which are further corroborated by single-crystal X-ray analyses of **4a** and **4b** (Figure 2, Table 3 and Table 4). The single crystals of **4a** and **4b** could be grown in test tubes from saturated CH_2Cl_2/*n*-pentane solutions by slow diffusion of the solvent into rubber stoppers.

Both these chiral neopentane derivatives crystallize in racemic form (Table 4). The arrangement of the individual substituents is such that steric congestion within the molecules is avoided by spreading out of the bulky groups (Figure 2). In both compounds the indenyl substituents are connected to the scaffolding via the α-carbon centre (C6) of the five-membered cycle. The alternating double and single bonds between the carbon atoms of these five-membered cycles are clearly evident from the corresponding distances (Table 3). The solid-state structures are in agreement with the NMR spectroscopic data (Table 1) which show that indenyl substitution is fully stereoselective with only C_α acting as the linking atom.

Nucleophilic opening of the oxetane group of **2** is also possible. This is done according to a procedure developed for Cp-substituted oxetanes.[6a] After deprotonation of the Cp-containing residue by *n*-butyllithium in THF, a THF solution of $LiPR_2$ is slowly added to the reaction mixture. After hydrolysis, the products **5** are extracted with diethyl ether and are obtained as colourless oils after evaporation of the solvent (Scheme 4). The crude products **5a** and **5b** are separated from the excess diphenylphosphane by chromatography while excess diethylphosphane is removed from **5c** in vacuo. The NMR spectroscopic data of **5** (Table 5) are consistent with the formulae given, as are the mass spectra and the elemental analyses (Table 2).

Protection of the PR_2 group of **5** by BH_3 leads to the derivatives **6**, which are also fully characterized (Scheme 5, Table 5 and Table 2). [3f,8] Single crystals of **6b** were grown from saturated CH_2Cl_2/*n*-pentane solutions by slow diffusion of the solvent into rubber stoppers. X-ray analysis data of **6b** (Figure 3, Table 3 and Table 4) are in accord with the assigned constitution. In contrast to **4a**/**4b**, the bulky substituents are not spread out as far as possible; the fluorenyl substituent is apparently preferentially close to the phenyl groups, with a face to edge arrangement of these two groups resulting. Individual angles and distances within the compound are normal (Table 3); the P−B distance



2a R = Indenyl
2b R = Fluorenyl

5a R = Indenyl, R´= Ph
5b R = Fluorenyl, R´= Ph
5c R = Indenyl, R´= Et

Scheme 4

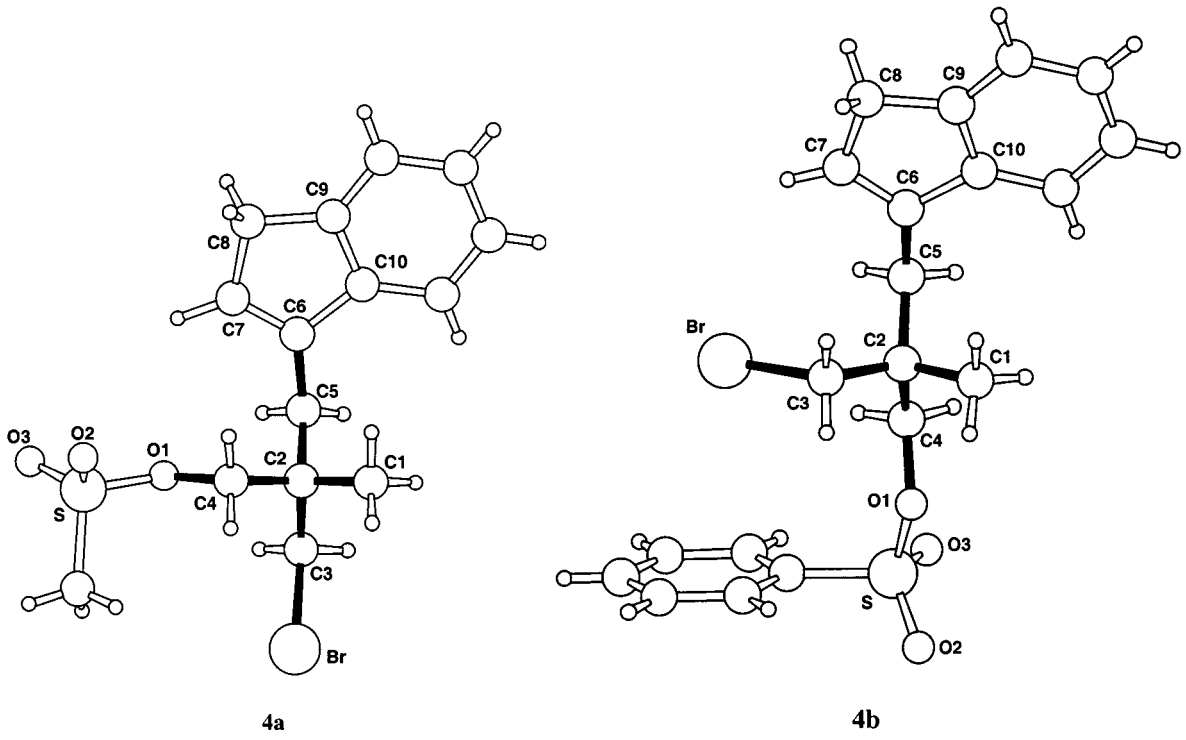


Figure 2. Structure of **4a** and **4b**

Table 1. NMR spectroscopic data of **2a**−**4d**[a,b,c]

No	R X Y	1[d] CH_3 [3H]	2[d] C_q	3[d] $CH_{2a,b}$ [2H]	4[d] $CH_{2a,b}$ [2H]	5[d] $CH_{2a,b}$ [2H]	6[d] $-CH_n-$ (n = 1−2)	7[d] −CH= [1H]	CH aromatic	Y
2a	Indenyl O	1.50 (s)	−	4.50, 4.76 (2 d) $^2J_{HH}$ = 5.6 Hz		2.99 (s)	3.45 (s) [2 H]	6.24 (s)	7.27−7.57 (m) [4 H]	−
	(Oxetane)	24.6 (s)	40.0 (s)	83.3 (s)		36.7 (s)	38.5 (s)		119.6−146.4 (8 s)	−
3a	Indenyl Br	1.15 (s)	−	3.57, 3.65 (2 d) $^2J_{HH}$ = 10.2 Hz	3.64, 3.72 (2 d) $^2J_{HH}$ = 11.0 Hz	2.81 (s)	3.49 (s) [2 H]	6.50 (s)	7.29−7.60 (m) [4 H]	2.51 (s) [1 H]
	OH	21.4 (s)	40.8 (s)	42.7 (s)	68.2 (s)	32.5 (s)	38.5 (s)		119.9−146.7 (8 s)	−
4a	Indenyl Br	1.16 (s)	−	3.49, 3.58 (2 d) $^2J_{HH}$ = 10.4 Hz	4.17, 4.24 (2 d) $^2J_{HH}$ = 9.5 Hz	2.80 (s)	3.45 (s) [2 H]	6.48 (s)	7.23−7.55 (m) [4 H]	3.08 (s) [3 H]
	OMs	21.3 (s)	39.7 (s)	40.9 (s)	74.2 (s)	32.3 (s)	38.6 (s)		119.8−146.1 (8 s)	37.6 (s)
4b	Indenyl Br	1.08 (s)	−	3.43, 3.51 (2 d) $^2J_{HH}$ = 10.4 Hz	4.02, 4.09 (2 d) $^2J_{HH}$ = 9.3 Hz	2.75 (s)	3.40 (s) [2 H]	6.38 (s)	7.27−8.03 (m) [9 H]	7.27−8.03 (m) [9 H]
	OSO_3Ph	21.3 (s)	39.7 (s)	40.8 (s)	74.4 (s)	32.3 (s)	38.5 (s)		119.8−146.1 (13 s)	119.8−146.1 (13 s)
4c	Indenyl Br	1.04 (s)	−	3.49, 3.60 (2 d) $^2J_{HH}$ = 9.5 Hz	3.50 (s)	2.74 (s)	3.44 (s) [2 H]	6.43 (s)	7.22−7.55 (m) [4 H]	0.21 (s) [9 H]
	OTMS	21.3 (s)	40.7 (s)	43.0 (s)	67.3 (s)	32.3 (s)	38.4 (s)		120.1−146.8 (5 s)	0.0 (s)
2b	Fluorenyl O	1.52 (s)	−	4.35, 4.5 (2 d) $^2J_{HH}$ = 5.6 Hz		2.35 (d) $^3J_{HH}$ = 6.6 Hz	4.06 (t) [1 H] $^3J_{HH}$ = 6.6 Hz	−	7.29−7.84 (m) [8 H]	−
	(Oxetane)	24.4 (s)	40.0 (s)	84.4 (s)		43.1 (s)	45.2 (s)	−	120.4−147.4 (6 s)	−
3b	Fluorenyl Br OH	1.05 (s)	−	3.38, 3.50 (2 d) $^2J_{HH}$ = 10.0 Hz	3.53 (m)	2.27, 2.37 (2 dd) $^2J_{HH}$ = 15.0 Hz $^3J_{HH}$ = 4.3 Hz	4.02 (t) [1 H] $^3J_{HH}$ = 4.3 Hz	−	7.29−7.80 (m) [8 H]	1.58 (bs) [1 H]
		21.8 (s)	40.7 (s)	43.1 (s)	68.0 (s)	37.8 (s)	44.6 (s)	−	120.3−148.7 (6 s)	−
4d	Fluorenyl Br	1.00 (s)	−	3.30, 3.40 (2 d) $^2J_{HH}$ = 10.4 Hz	3.99 (m)	2.40 (d) $^3J_{HH}$ = 4.4 Hz	3.99 (m) [1 H]	−	7.37−7.80 (m) [8 H]	3.02 (s) [3 H]
	OMs	21.7 (s)	39.8 (s)	41.5 (s)	74.5 (s)	37.2 (s)	44.6 (s)	−	120.5−147.6 (6 s)	37.5 (s)

[a] For ease of comparison the sequence of entries in this table does not follow the compound numbering sequence. − [b] Sequence of entries for each compound: ^1H NMR first lines, ^{13}C NMR last lines. − [c] Solvent: $CDCl_3$. − [d] Designation:

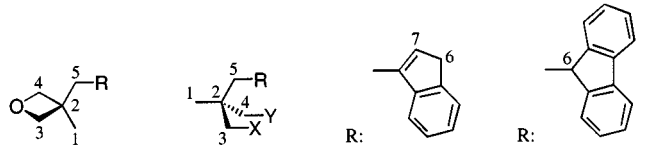


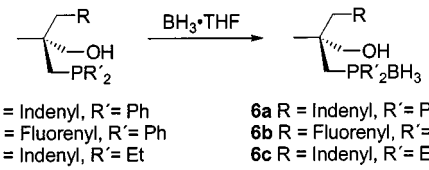
Table 2. Analytical data of **2a**−**12d**

No.	formula (M)	eluent (R_f)	MS (EI) *m/z* (%) [fragment]	$C_{calcd.}$ C_{found}	$H_{calcd.}$ H_{found}	$P_{calcd.}$ P_{found}	$S_{calcd.}$ S_{found}	$Br_{calcd.}$ Br_{found}	M.p.[a] [°C]	yield (%)
2a	$C_{14}H_{16}O$ (200.28)	PE/Et_2O 8/1 (0.27)	200 (14) [M^+]; 155 (18) [$M^+ - CH_2O - CH_3$]; 130 (100) [$C_{10}H_{10}^+$]; 129 (24) [CH_2Indenyl$^+$]; 115 (35) [Indenyl$^+$]	83.96 83.31	8.05 8.12				–	62
2b	$C_{18}H_{18}O$ (250.34)	PE/Et_2O 7/3 (0.33)	250 (9) [M^+]; 180 (94) [CH_2Fluorenyl$^+$]; 165 (100) [Fluorenyl$^+$]	86.36 86.35	7.25 7.34				101	52
3a	$C_{14}H_{17}BrO$ (281.19)	PE/Et_2O 7/3 (0.29)	281 (4) [M^+]; 130 (100) [$C_{10}H_{10}^+$]; 129 (48) [CH_2Indenyl$^+$]; 115 (12) [Indenyl$^+$]	59.80 59.73	6.09 6.08	– –	– –	28.42 28.02	–	>95
3b	$C_{18}H_{19}BrO$ (331.25)	PE/Et_2O 1/1 (0.43)	331 (18) [M^+]; 233 (26) [$M^+ - H_2O - Br$]	65.44 65.41	5.88 5.88	– –	– –	23.91 24.17	102	>95
4a	$C_{15}H_{19}BrO_3S$ (359.29)	PE/Et_2O 7/3 (0.18)	359 (12) [M^+]; 183 (45) [$M^+ - Br - SO_2CH_3$]; 128 (100) [CH_2Indenyl$^+$]; 115 (18) [Indenyl$^+$]	50.28 50.37	5.35 5.35	– –	8.93 8.73	22.04 22.30	109	74
4b	$C_{20}H_{21}BrO_3S$ (421.36)	PE/Et_2O 3/2 (0.47)	422 (22) [M^+]; 264 (10) [$M^+ - OSO_2Ph$]; 183 (46) [$M^+ - Br - OSO_2Ph$]; 170 (18) [$M^+ - Br - CH_2OSO_2Ph$]	57.01 56.93	5.02 4.98	– –	7.62 7.65	18.96 19.71	64	79
4c	$C_{17}H_{25}BrOSi$ (353.38)	PE/Et_2O 9/1 (0.74)	353 (3) [M^+]; 223 (5) [$M^+ - CH_2$Indenyl]; 144 (25) [$M^+ - CH_2$Indenyl $- Br$]; 143 (100) [$M^+ - CH_2$Indenyl $- HBr$]	57.94 57.98	7.16 7.15	– –	– –	22.41 22.46	–	75
4d	$C_{19}H_{21}BrO_3S$ (409.35)	PE/THF 3/1 (0.33)	409 (22) [M^+]; 314 (6) [$M^+ - OSO_2CH_3$]; 230 (31) [$M^+ - CH_2$Fluorenyl]	55.75 55.64	5.17 5.13	– –	7.83 7.67	19.52 20.13	99	86
5a	$C_{26}H_{27}OP$ (386.47)	PE/THF 5.6/1 (0.24)	386 (70) [M^+]; 355 (13) [$M^+ - CH_2OH$]; 257 (3) [$M^+ - CH_2$Indenyl]; 199 (30) [$M^+ - PPh_2$]	80.79 80.56	7.05 7.06	8.02 7.90			63	84
5b	$C_{30}H_{29}OP$ (436.53)	PE/THF 5.6/1 (0.27)	436 (25) [M^+]; 258 (8) [$M^+ - CH_2$Fluorenyl]	82.53 82.14	6.70 6.93	7.10 7.03			144	74
5c	$C_{18}H_{27}OP$ (290.38)	–	290 (58) [M^+]; 295 (11) [$M^+ - CH_2O$]; 161 (35) [$M^+ - CH_2$Indenyl]	–					–	93
6a	$C_{26}H_{30}BOP$ (400.32)	PE/THF 7/3 (0.40)	400 (21) [M^+]; 241 (100) [$M^+ - BH_3 - CH_2$Indenyl $- OH$]; 201 (28) [$M^+ - PPh_2BH_3$]; 186 (82) [$M^+ - CH_2PPh_2BH_3$]	78.01 77.59	7.55 7.70	7.74 n.d.			76−80 (dec.)	86
6b	$C_{30}H_{32}BOP$ (450.38)	PE/THF 3/1 (0.22)	449 (9) [$M^+ - H$]; 436 (5) [$M^+ - BH_3$]	80.01 79.97	7.16 7.24	6.88 6.47			160 (dec.)	>95
6c	$C_{18}H_{30}BOP$ (304.23)	PE/THF 4/1 (0.22)	304 (26) [M^+]; 290 (10) [$M^+ - BH_3$]; 189 (13) [M^+ − Indenyl]; 144 (60) [$M^+ - BH_3 - CH_2OH$ − Indenyl]	71.00 70.87	9.94 9.99	10.18 9.78			–	85
7a	$C_{27}H_{32}BO_3PS$ (478.40)	PE/THF 3/1 (0.24)	400 (21) [M^+]; 241 (100) [$M^+ - BH_3 - CH_2$Indenyl $- OH$]; 201 (28) [$M^+ - PPh_2BH_3$]; 186 (82) [$M^+ - CH_2PPh_2BH_3$]	67.76 66.98	6.74 6.93	6.48 n.d.	6.69 n.d.		50 (dec.)	71
7b	$C_{31}H_{34}BO_3PS$ (528.47)	PE/THF 7/3 (0.39)	528 (6) [M^+]; 515 (20) [$M^+ - BH_3$]; 433 (8) [$M^+ - OSO_2CH_3$]; 419 (10) [$M^+ - CH_2OSO_2CH_3$]	70.46 70.24	6.48 6.67	5.86 5.83	6.07 6.12		144 (dec.)	68
8a	$C_{27}H_{29}O_3PS$ (464.57)	PE/THF 3/1 (0.37)	465 (20) [M^+]; 370 (5) [$M^+ - OSO_2CH_3$]	69.81 69.16	6.29 6.56	6.67 n.d.	6.90 n.d.		–	76
8b	$C_{31}H_{31}O_3PS$ (514.63)	PE/THF 7/3 (0.36)	515 (1) [M^+]; 419 (30) [$M^+ - OSO_2CH_3$]; 240 (34) [$M^+ - OSO_2CH_3 - CH_2$Fluorenyl]	72.35 70.85	6.07 6.11	6.02 n.d.	6.23 n.d.		153	83
9a	$C_{26}H_{25}P$ (368.46)	PE/Et_2O 9/1 (0.64)	368 (90) [M^+]; 240 (69) [$M^+ - C_{10}H_8$]	84.75 84.25	6.84 6.80	8.41 8.31			–	54
9b	$C_{30}H_{27}P$ (418.52)	PE/Et_2O 19/1 (0.48)	418 (100) [M^+]	86.10 85.40	6.50 6.58	7.40 7.36			92	59
9c	$C_{15}H_{18}O_3S$ (278.37)	PE/Et_2O 1/1 (0.24)	278 (15) [M^+]; 182 (29) [$M^+ - OSO_2CH_3$]; 167 (100) [$M^+ - OSO_2CH_3 - CH_3$]; 153 (21) [$M^+ - CH_2OSO_2CH_3 - CH_3$]	64.72 64.48	6.52 6.55	– –	11.52 11.29		–	
9d	$C_{27}H_{24}$ (348.49)	–	348 (7) [M^+]; 178 (100) [CH_2Fluorenyl$^+$]; 129 (30) [CH_2Indenyl$^+$]; 115 (48) [Indenyl$^+$]	93.06 91.01	6.94 6.85				209	41
10	$C_{30}H_{32}O_3P_2S$ (534.59)	PE/THF 3/2 (0.56)	534 (5) [M^+]; 457 (56) [$M^+ - Ph$]; 439 (3) [$M^+ - OSO_2CH_3$]	67.40 67.23	6.03 6.10	11.59 11.36	6.00 5.82		–	79
11a	$C_{38}H_{36}P_2$ (554.65)	PE/THF 19/1 (0.32)	554 (55) [M^+]; 477 (54) [$M^+ - Ph$]; 425 (3) [$M^+ - CH_2$Indenyl]; 369 (100) [$M^+ - PPh_2$]	82.29 82.08	6.54 6.78	11.17 10.90			103	26
11b	$C_{42}H_{38}P_2$ (604.71)	PE/THF 9/1 (0.35)	605 (19) [M^+]; 528 (100) [$M^+ - Ph$]	83.41 83.03	6.34 6.64	10.25 9.99			65	30
12a	$C_{27}H_{26}O$ (366.50)	PE/Et_2O 7/3 (0.23)	366 (19) [M^+]; 335 (24) [$M^+ - CH_2OH$]; 178 (51) [CH_2Fluorenyl$^+$]; 165 (100) [Fluorenyl$^+$]	88.48 88.17	7.15 7.11				126	58
12b	$C_{19}H_{22}O$ (266.38)	PE/Et_2O 7/3 (0.32)	266 (100) [M^+]; 235 (51) [$M^+ - CH_2OH$]; 137 (74) [$M^+ - CH_2$Indenyl]; 129 (44) [CH_2Indenyl$^+$]; 79 (30) [CH_2Cp^+]	85.67 82.55	8.32 8.13				–	15
12c	$C_{28}H_{28}O_3S$ (444.59)	PE/Et_2O 3/2 (0.24)	444 (8) [M^+]; 349 (10) [$M^+ - OSO_2CH_3$]; 165 (100) [Fluorenyl$^+$]; 129 (23) [CH_2Indenyl$^+$]; 115 (20) [Indenyl$^+$]	75.64 75.87	6.35 6.23	– –	7.21 7.14		–	87
12d	$C_{30}H_{34}OSi$ (438.68)	PE/Et_2O 7/3 (0.77)	438 (22) [M^+]; 423 (13) [$M^+ - CH_3$]; 335 (35) [$M^+ - CH_2$OTMS]; 259 (14) [$M^+ - CH_2$Fluorenyl]	82.14 82.28	7.81 7.96				94	>95

[a] dec. = decomposition.

(191.7(2) pm) in the borane-protected phosphane group is also normal.[8c]

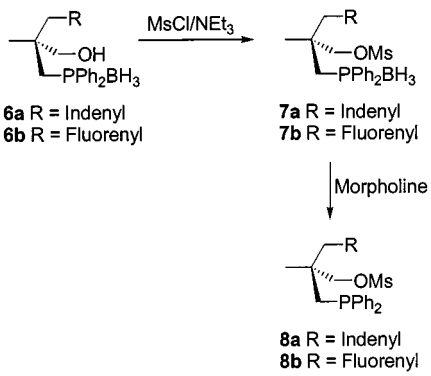
BH_3 protection allows the activation of the OH group.[8c] Thus **6a/6b** are transformed into **7a/7b** by mesylation (Scheme 6). Compounds **7** are fully characterized by their analytical and spectroscopic data (Table 5 and Table 2).



5a R = Indenyl, R´= Ph
5b R = Fluorenyl, R´= Ph
5c R = Indenyl, R´= Ph

6a R = Indenyl, R´= Ph
6b R = Fluorenyl, R´= Ph
6c R = Indenyl, R´= Ph

Scheme 5



6a R = Indenyl
6b R = Fluorenyl

7a R = Indenyl
7b R = Fluorenyl

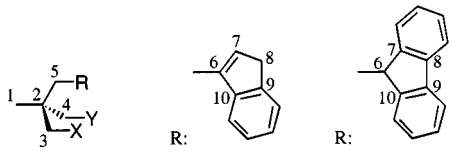
8a R = Indenyl
8b R = Fluorenyl

Scheme 6

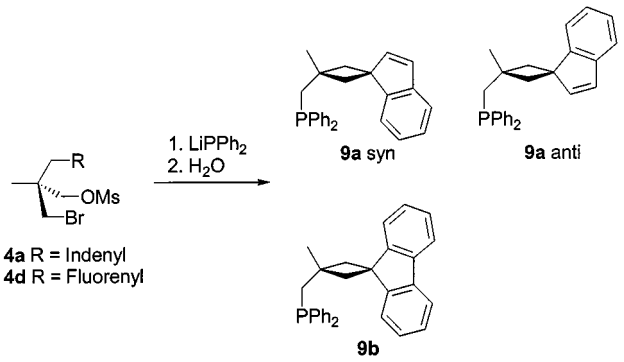
Table 3. Selected bond lengths [pm], bond angles [°], and torsion angles [°] for **2b**, **4a**, **4b**, **6b** and **12a**[a]

	2b/1	**2b/2**	**4a**	**4b**	**6b**	**12a**
C2−C_{sp3}	151.5(6)−154.8(6)	152.1(6)−154.2(6)	152.4(6)−155.1(6)	150.4(4)−156.4(4)	153.5(2)−155.5(2)	152.6(2)−154.9(2)
C3−X (C6′)[b]	142.8(5)	144.2(5)	196.8(5)	195.7(3)	182.6(2)	154.2(2)
C4−Y[b]	143.6(5)	143.9(5)	147.0(5)	146.8(4)	142.1(2)	142.6(2)
C5−C6	154.8(6)	156.4(5)	151.1(6)	150.4(4)	155.3(2)	150.4(2)
C6−C7 [C6′−C7′]	152.6(6)	151.7(5)	134.3(6)	133.9(5)	151.5(2)	134.7(2) [152.4(2)]
C6−C10 [C6′−C10′]	152.1(6)	152.7(6)	148.0(6)	147.7(4)	151.6(2)	147.8(2) [152.9(2)]
C7−C8 [C7′−C8′]	140.0(6)	140.7(6)	149.4(7)	150.7(5)	139.9(2)	150.1(2) [140.0(2)]
C8−C9 [C8′−C9′]	147.1(6)	147.2(6)	150.3(7)	149.9(5)	147.4(2)	150.9(2) [146.7(2)]
C9−C10 [C9′−C10′]	140.5(6)	140.8(6)	140.9(6)	140.9(5)	140.9(2)	140.0(2) [140.0(2)]
C_{ar}−C_{ar}[c]	138.1(6)−139.9(6)	138.3(6)−140.3(6)	138.2(6)−140.6(6)	138(1)−139.7(5)	138.3(3)−139.7(2)	138.2(2)−139.7(2) Indenyl 138.1(2)−139.8(2) Fluorenyl
C1−C2−C3	114.9(4)	112.2(4)	111.6(4)	106.4(2)	112.0(1)	110.4(1)
C1−C2−C4	116.6(4)	113.7(4)	107.0(4)	109.8(3)	105.6(1)	107.2(1)
C1−C2−C5	113.6(4)	113.7(3)	111.0(4)	111.4(2)	112.5(1)	110.2(1)
C3−C2−C4	83.3(3)	83.5(3)	111.0(4)	112.0(3)	110.9(1)	111.4(1)
C3−C2−C5	110.4(4)	111.7(3)	104.8(4)	112.4(3)	109.5(1)	107.2(1)
C4−C2−C5	114.5(4)	118.3(3)	111.6(4)	105.0(2)	106.0(1)	110.5(2)
C2−C3−X[b]	92.3(3)	92.2(3)	114.1(3)	114.3(2)	120.5(1)	116.0(1)
C2−C4−Y[b]	91.8(3)	92.4(3)	108.0(3)	108.7(3)	110.9(3)	112.0(1)
C2−C5−C6	118.9(3)	117.5(3)	115.6(4)	116.3(3)	122.2(1)	116.9(1)
C1−C2−C3−X (C6′)[b]	−123.4(4)	−105.4(4)	61.8(5)	−179.7(2)	−49.0(2)	−62.3(2)
C1−C2−C4−Y[b]	121.7(4)	103.8(4)	177.3(4)	54.5(3)	179.0(1)	−179.9(1)
C1−C2−C5−C6	52.5(5)	50.4(5)	−64.6(5)	−59.6(3)	−66.2(2)	58.8(2)

[a] The numbering scheme used refers to the graphic given here and is different from the numbering schemes for the individual atoms in the deposited data. − [b] X (Y) designates the atom which is directly bonded to the relevant carbon atom. − [c] C_{ar}−C_{ar} designates the distances within the annelated cycles, excluding C7−C8 (fluorenyl) and C9−C10 which are given explicitly.



The synthesis of tripodal ligands containing one indenyl- or fluorenyl group and two phosphorus donors appears straightforward from starting compounds such as **4**: with $CH_3C(CH_2C_5H_5)(CH_2Br)(CH_2OMs)$ as the starting material, substitution of the leaving groups by phosphorus donors is easily achieved through reaction with $KPPh_2$.[6a] When the same procedure is applied to **4a**, internal cyclization with formation of the spiro compounds **9a** ***syn***/**9a** ***anti*** occurs (Scheme 7). The higher nucleophilicity of the indenyl residue compared to that of the Cp residue apparently favours the reaction leading to internal cyclization rather than the one leading to external substitution by PPh_2. With C_α of the indenyl group forming the spiro centre, there are two diastereomeric forms of **9a**, one in which the CH_2PPh_2 residue and the annelated benzene part of the indenyl residue are on the same side of the cyclobutane ring (*syn*) and one



Scheme 7

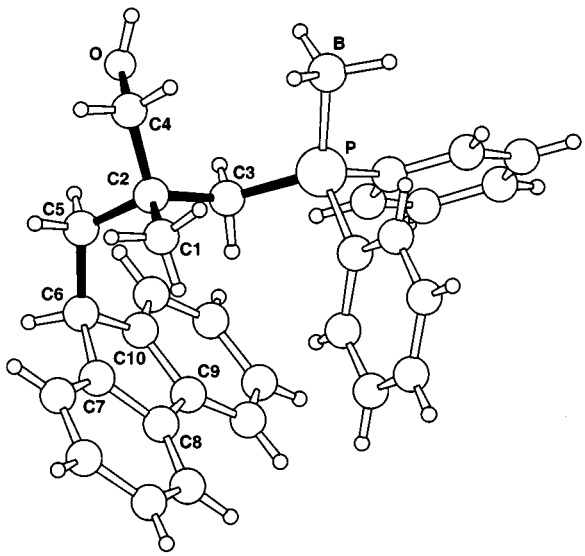


Figure 3. Structure of **6b**

Table 4. Crystal data for **2b**, **4a**, **4b**, **6b** and **12a**

Compound	**2b**	**4a**	**4b**	**6b**	**12a**
Formula	$C_{18}H_{17}O$	$C_{15}H_{19}BrO_3S$	$C_{20}H_{21}BrO_3S$	$C_{30}H_{32}BOP$	$C_{27}H_{25}O$
Molecular mass [g]	124.66	359.27	421.34	450.34	365.47
Crystal size [mm]	0.2 × 0.15 × 0.2	0.2 × 0.2 × 0.3	0.2 × 0.3 × 0.3	0.25 × 0.3 × 0.25	0.2 × 0.3 × 0.1
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group (No.)[15c]	$P2_1/c$ (14)	$P2_1/c$ (14)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P2_1/n$ (14)
a [pm]	2283(1)	1309.6(3)	787.8(1)	1010.3(2)	1547.3(3)
b [pm]	595.1(2)	817.4(3)	1069.3(2)	1015.1(2)	718.8(1)
c [pm]	2124(2)	1469.3(4)	1248.4(2)	1243.0(3)	1800.6(4)
α [°]	90.0	90.0	103.35(1)	88.08(3)	90.0
β [°]	72.62(4)	83.99(2)	94.08(1)	89.37(3)	92.10(3)
γ [°]	90.0	90.0	109.37(1)	71.25(3)	90.0
V [10^6 pm^3]	2754.0	1564.2	952.7	1206.4	2001.3
Z	8	4	2	2	4
d_x [g cm^{-3}]	1.203	1.526	1.469	1.240	1.213
T [K]	200	200	200	200	200
No. of rflns. for cell param. refinem.	33	36	31	–	–
Scan range	3.7° < 2Θ < 47.0°	5.6° < 2Θ < 51.0°	3.4° < 2Θ < 52.0°	3.3° < 2Θ < 52.1°	4.5° < 2Θ < 52.2°
Method	ω scan, Δω = 0.54°	ω scan, Δω = 0.54°	ω scan, Δω = 0.55°	ω scan, Δω = 2.0°	ω scan, Δω = 1.0°
Scan speed	$\dot{\omega}$ = 6° min^{-1}	$\dot{\omega}$ = 8° min^{-1}	$\dot{\omega}$ = 8° min^{-1}	–	–
s frame^{-1}	–	–	–	8	7
No. of measured rflns.	3765	2993	3960	19104	51425
No. of unique rflns.	3649	2863	3685	4758	3941
No. of observed rflns.	2184	1931	3025	3901	2304
Observation criterion	$I \geq 2\sigma$	$I \geq 2\sigma$	$I \geq 2\sigma$	$I \geq 2\sigma$	$I \geq 2\sigma$
No. of param. refined	349	257	230	315	353
resid. el. density [10^{-6} e pm^{-3}]	0.61	0.82	1.06	0.47	0.22
R_1/R_w [%] (refinement on F^2)	6.4/17.9	4.4/11.4	3.6/9.4	4.2/10.6	3.8/7.9

in which they are on opposite sides (*anti*). These two diastereomers are formed in a ratio of *syn*:*anti* = 7:4, as shown by NMR. Assignment of individual signals (Table 6) to the *syn*- and *anti* forms is based on the signals characterizing the CH_2 groups of the four-membered cycle. While the two CH_2 groups in each specific diastereomer are symmetrically equivalent, the protons of these groups are not so and this gives rise to two doublets. The type of spectrum observed for the indenyl spiro compounds **9** is exemplified in Figure 4 for **9a**. The resonances useful for the attribution of the structures of the *syn*- and *anti* isomers are shown as magnified inserts in Figure 4 (*syn* isomer in grey).

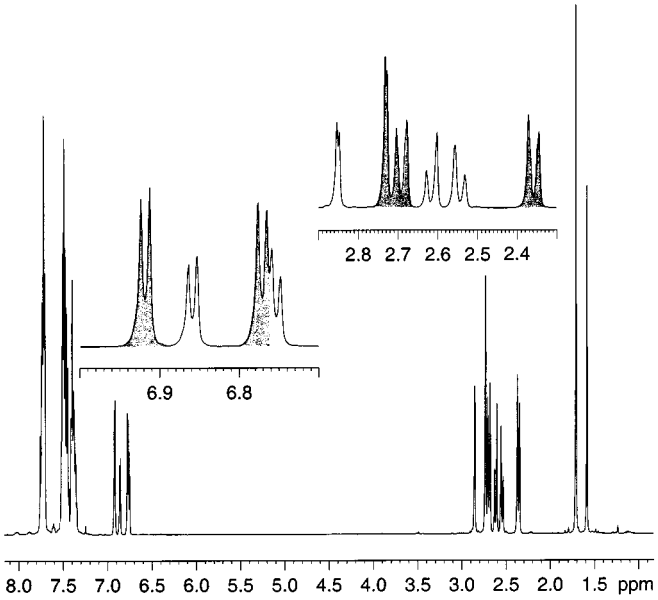
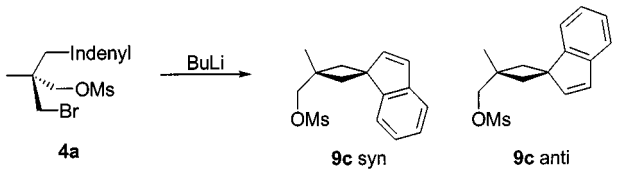
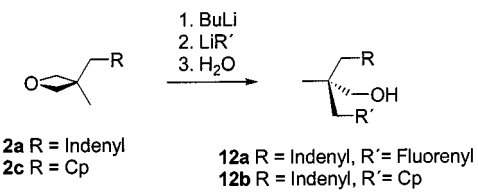


Figure 4. ^{1}H NMR spectrum of **9a** in $CDCl_3$

Assignment of the NMR resonances to individual diastereomers is based on the assumption that, within the *syn* diastereomer, two of these protons are in close vicinity of the CH_2PPh_2 group and the annelated benzene ring, whereas the other two protons stick out to the far less congested side of the four-membered cycle, so that the environments of these two pairs of protons are very different. The proton signals corresponding to these protons should therefore have significantly different shift values. With the *anti* isomer, both sides of the ring are congested, so that the



Scheme 8

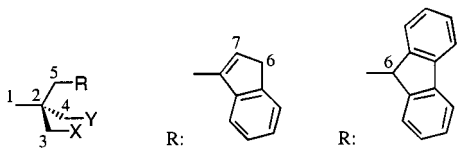


Scheme 9

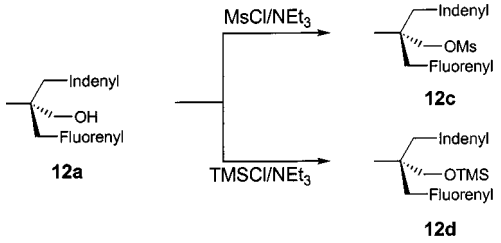
Table 5. NMR spectroscopic data of **5a**−**8b**[a,b,c]

No.	R X Y	1[d] CH_3 [3 H]	2[d] C_q	3[d] $CH_{2a,b}$ [2 H]	4[d] $CH_{2a,b}$ [2 H]	5[d] $CH_{2a,b}$ [2 H]	6[d] $-CH_n-$ (n = 1−2)	7[d] −CH= [1 H]	CH aromatic	X {^{31}P NMR}	Y
5a	Indenyl PPh_2 OH	1.06 (s)	−	2.38, 2.48 (2 dd) $^2J_{HH}$ = 14.4 Hz $^2J_{HP}$ = 3.6 Hz	3.54 (s)	2.78, 2.85 (2 d) $^2J_{HH}$ = 14.2 Hz	3.39 (s) [2 H]	6.33 (s)	7.20−7.80 (m) [14 H]	1.48 (bs) [1 H]	
		23.9 (d) $^3J_{CP}$ = 9.0 Hz	40.4 (d) $^2J_{CP}$ = 13.1 Hz	38.6 (d) $^1J_{CP}$ = 14.1 Hz	69.9 (d) $^3J_{CP}$ = 8.5 Hz	36.1 (d) $^3J_{CP}$ = 7.5 Hz	38.4 (s)		120.2−147.0		−
8a	Indenyl PPh_2 OMs	1.12 (s)	−	2.51 (d) $^2J_{HP}$ = 3.4 Hz	4.22 (s)	2.91 (s)	3.45 (s) [2 H]	6.43 (s)	7.28−7.63 (m) [14 H]	2.86 (s) [3 H]	
		23.7 (d) $^3J_{CP}$ = 9.8 Hz	39.3 (d) $^2J_{CP}$ = 14.0 Hz	38.2 (d) $^1J_{CP}$ = 16.8 Hz	76.0 (d) $^3J_{CP}$ = 10.5 Hz	35.7 (d) $^3J_{CP}$ = 8.5 Hz	38.5 (s)		120.0−146.5	37.3 (s)	
6a	Indenyl PPh_2BH_3 OH	0.93 (s)	−	2.74 (m)	3.60, 3.74 (2 d) $^2J_{HH}$ = 11.2 Hz	2.80, 2.92 (2 d) $^2J_{HH}$ = 13.6 Hz	3.43 (s) [2 H]	6.38 (s)	7.28−7.89 (m) [14]	2.28 (bs) [1 H]	
		23.3 (d) $^3J_{CP}$ = 3.9 Hz	41.2 (s)	34.0 (d) $^1J_{CP}$ = 31.6 Hz	68.9 (d) $^3J_{CP}$ = 4.6 Hz	37.0 (d) $^3J_{CP}$ = 8.2 Hz	38.5 (s)		120.2−146.8	−	
7a	Indenyl PPh_2BH_3 OMs	1.02 (s)	−	2.71 (m)	4.30 (s)	2.90 (m)	3.41 (s) [2 H]	6.41 (s)	7.20−7.83 (m) [14 H]	3.01 (s) [3 H]	
		22.9 (d) $^3J_{CP}$ = 5.0 Hz	39.8 (s)	33.7 (d) $^1J_{CP}$ = 32.2 Hz	75.7 (d) $^3J_{CP}$ = 3.5 Hz	36.2 (d) $^3J_{CP}$ = 7.0 Hz	38.6 (s)		120.1−146.3	37.6 (s)	
5b	Fluorenyl PPh_2 OH	1.10 (s)	−	2.20, 2.37 (2 dd) $^2J_{HH}$ = 14.4 Hz $^2J_{HP}$ = 3.6 Hz	3.55 (m)	2.35 (m)	4.04 (bs) [1 H]	−	7.28−7.79 (m) [18 H]	1.39 (bs) [1 H]	
		24.3 (d) $^3J_{CP}$ = 10.5 Hz	40.4 (d) $^2J_{CP}$ = 13.1 Hz	39.2 (d) $^1J_{CP}$ = 16.6 Hz	69.8 (d) $^3J_{CP}$ = 9.0 Hz	42.1 (d) $^3J_{CP}$ = 7.0 Hz	44.8 (s)	−	120.1−149.5	−	
8b	Fluorenyl PPh_2 OMs	1.05 (s)	−	2.25, 2.35 (2 dd) $^2J_{HH}$ = 14.6 Hz $^2J_{HP}$ = 2.8, 3.6 Hz	4.07, 4.13 (2d) $^2J_{HH}$ = 9.7 Hz	2.45, 2.58 (2 dd) $^2J_{HH}$ = 15.1 Hz $^3J_{HH}$ = 4.4 Hz	4.07, 4.13 (2d) [3 H] $^2J_{HH}$ = 9.7 Hz	−	7.27−7.84 (m) [18 H]	2.81 (s) [3 H]	
		24.4 (d) $^3J_{CP}$ = 10.0 Hz	39.6 (d) $^2J_{CP}$ = 13.6 Hz	38.5 (d) $^1J_{CP}$ = 17.1 Hz	76.8 (d) $^3J_{CP}$ = 11.1 Hz	41.2 (d) $^3J_{CP}$ = 7.5 Hz	45.1 (s)	−	120.4−148.4	37.2 (s)	
6b	Fluorenyl PPh_2BH_3 OH	0.70 (s)	−	2.18−2.58 (m)	3.42, 3.78 (2 d) $^2J_{HH}$ = 11.6 Hz	2.18−2.58 (m)	4.02 (t) [1 H] $^3J_{HH}$ = 4.2 Hz	−	7.27−7.81 (m) [18 H]	1.93 (bs) [1 H]	
		24.1 (d) $^3J_{CP}$ = 3.5 Hz	41.5 (s)	34.0 (d) $^1J_{CP}$ = 31.2 Hz	68.6 (d) $^3J_{CP}$ = 3.0 Hz	42.3 (d) $^3J_{CP}$ = 9.1 Hz	45.1 (s)	−	120.2−148.9	−	
7b	Fluorenyl PPh_2BH_3 OMs	0.70 (s)	−	2.12, 2.31 (2 dd) $^2J_{HH}$ = 15.0 Hz $^2J_{HP}$ = 9.4, 14.8 Hz	4.10, 4.25 (2 d) $^2J_{HH}$ = 9.5 Hz	2.44, 2.80 (2 dd) $^2J_{HH}$ = 15.2 Hz $^3J_{HH}$ = 4.4, 4.6 Hz	4.17 (m) [1 H]	−	7.30−7.92 (m) [18 H]	2.96 (s) [3 H]	
		24.0 (d) $^3J_{CP}$ = 4.5 Hz	40.5 (s)	33.1 (d) $^1J_{CP}$ = 31.2 Hz	76.9 (s)	40.5 (d) $^3J_{CP}$ = 8.5 Hz	45.7 (s)	−	120.5−147.5	37.6 (s)	
5c	Indenyl PEt_2 OH	1.04 (s)	−	1.61 (m)	3.55 (s)	2.70, 2.76 (2 d) $^2J_{HH}$ = 13.7 Hz	3.40 (s) [2 H]	6.35 (s)	7.23−7.58 (m) [4 H]	1.14, 1.50 (2 m) [10 H] {−34.4 (s)}	2.54 (bs) [1 H]
		23.7 (d) $^3J_{CP}$ = 9.0 Hz	39.7 (d) $^2J_{CP}$ = 10.5 Hz	36.8 (d) $^1J_{CP}$ = 15.6 Hz	70.3 (d) $^3J_{CP}$ = 7.5 Hz	36.0 (d) $^3J_{CP}$ = 7.5 Hz	38.3 (s)		120.2−147.0 (8 s)	10.0 (d) $^2J_{CP}$ = 11.5 Hz 20.4 (d) $^1J_{CP}$ = 10.0 Hz	−
6c	Indenyl PEt_2BH_3 OH	1.06−1.25 (m)	−	1.80−2.00 (m)	3.57, 3.70 (2 d) $^2J_{HH}$ = 11.2 Hz	2.80 (s)	3.41 (s) [2 H]	6.35 (s)	7.19−7.55 (m) [4 H]	1.06−1.25 (m) [6 H] 1.61−1.80 (m) [4 H] {11.7 (bs)}	2.08 (bs) [1 H]
		23.3 (s)	40.4 (s)	30.9 (d) $^1J_{CP}$ = 28.7 Hz	68.8 (d) $^3J_{CP}$ = 3.5 Hz	36.5 (d) $^3J_{CP}$ = 7.0 Hz	38.5 (s)		120.2−146.9 (85)	18.3 (d) $^1J_{CP}$ = 35.7 Hz 18.4 (d) $^1J_{CP}$ = 37.2 Hz, 7.2 (s)	−

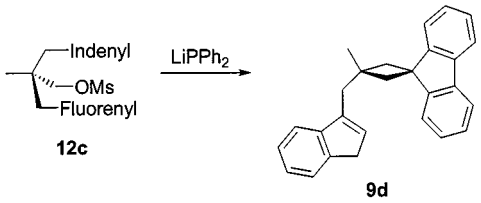
[a] For ease of comparison the sequence of entries in this table does not follow the compound numbering sequence. − [b] Sequence of entries for each compound: ^{1}H NMR first lines, ^{13}C NMR last lines. − [c] Solvent: $CDCl_3$. − [d] Designation:



surroundings of the two protons should not be as different as in the *syn* isomer. The difference in shift between these protons should then be smaller for the *anti* isomer than for the *syn* isomer. The pair of doublets at δ = 2.36 and 2.69



Scheme 10



Scheme 11

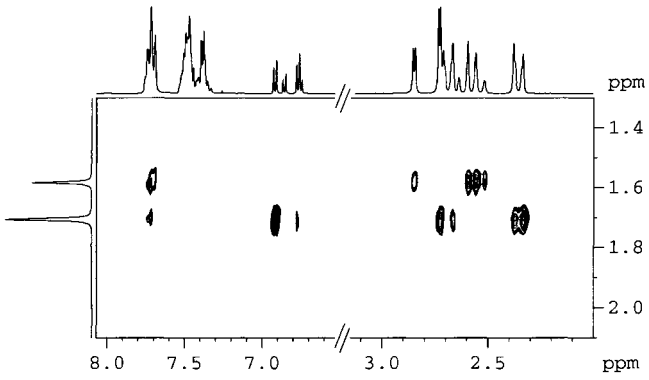
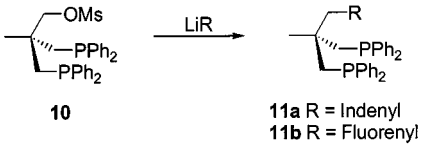


Figure 5. NOESY spectrum of **9a** in $CDCl_3$

is therefore assigned to the *syn* isomer, with the *anti* isomer giving rise to a doublet at δ = 2.55 and 2.61 (Table 6).

NOE measurements confirm this assignment: In the NOESY spectrum of **9a** a strong correlation between the methyl group at δ = 1.71 and the olefinic proton 6 of the five-membered cycle at δ = 6.91 is observed (Figure 5). No



Scheme 12

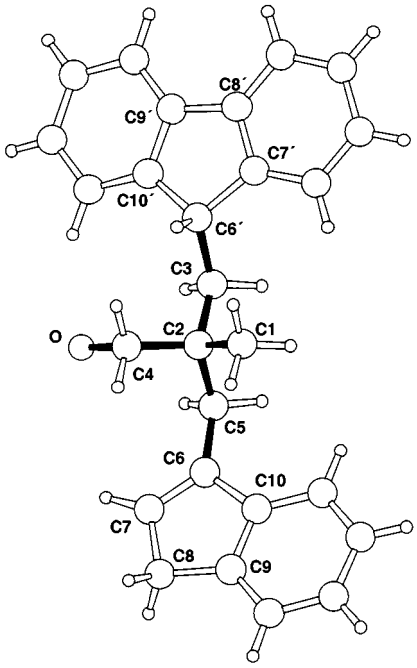


Figure 6. Structure of **12a**

correlation between these two types of protons is found for the *anti* isomer. The NOESY correlation between the pairs of diastereotopic protons in the four-membered cycles and the methyl groups also correspond to this assignment. Only

Table 6. NMR spectroscopic data of **9a**–**9d**[a,b]

No.	X	1[e] CH_3 [3 H]	2[e] C_q	3[e] $CH_{2a,b}$ [2 H]	4[e] $CH_{2a,b}$ [4 H]	5[e] C_q	6[e] −CH= [1 H]	7[e] −CH= [1 H]	CH aromatic	X {^{31}P NMR}
9a syn[c]	PPh_2	1.71 (s)	–	2.73 (s)	2.36, 2.69 (2 d) $^2J_{HH}$ = 10.0 Hz	–	6.77, 6.91 (2 d) $^3J_{HH}$ = 5.0 Hz		7.34–7.78 (m)	{−26.5, −24.9 (2 s)}
		29.8 (d) $^3J_{CP}$ = 10.0 Hz	33.0 (d)	44.9 (d) $^1J_{CP}$ = 15.0 Hz	42.5 (d) $^3J_{CP}$ = 8.3 Hz	48.7 (s)			121.1–152.5	
9a anti[c]	PPh_2	1.58 (s)	–	2.85 (s)	2.55, 2.61 (2 d) $^2J_{HH}$ = 15.0 Hz	–	6.75, 6.85 (2 d) $^3J_{HH}$ = 5.0 Hz		7.34–7.78 (m)	{−26.5, −24.9 (2 s)}
		30.5 (d) $^3J_{CP}$ = 11.0 Hz	$^2J_{CP}$ = 15.6 Hz	43.9 (d) $^1J_{CP}$ = 15.0 Hz	42.4 (d) $^3J_{CP}$ = 8.3 Hz	48.0 (s)			121.1–152.5	
9c syn[c]	OMs	1.56 (s)	–	4.28 (s)	2.25, 2.74 (2 d) $^2J_{HH}$ = 13.4 Hz	–	6.71, 6.82 (2 d) $^3J_{HH}$ = 5.4 Hz		7.26–7.66 (m)	3.15 (s)
		24.9 (s)	32.5 (s)	77.3 (s)	37.1 (s)	47.5 (s)			121.2–152.0	37.7 (s)
9c anti[c]	OMs	1.53 (s)	–	4.38 (s)	2.41, 2.60 (2 d) $^2J_{HH}$ = 13.6 Hz	–	6.71, 6.76 (2 d) $^3J_{HH}$ = 5.4 Hz		7.26–7.66 (m)	3.14 (s)
		25.6 (s)	32.6 (s)	77.1 (s)	37.6 (s)	47.3 (s)			121.2–152.0	37.7 (s)
9b[c]	PPh_2	1.68 (s)	–	2.90 (m)	2.58, 2.67 (d) $^2J_{HH}$ = 12.7 Hz	–	–	–	7.30–7.72 (m) [18 H]	{−25.3 (s)}
		29.5 (d) $^3J_{CP}$ = 12.0 Hz	31.5 (d) $^2J_{CP}$ = 16.1 Hz	44.3 (d) $^1J_{CP}$ = 16.6 Hz	47.4 (d) $^3J_{CP}$ = 8.0 Hz	45.6 (s)	–	–	119.9–153.7	
9d[d]	Indenyl	1.65 (s)	–	3.17 (s)	2.60, 2.89 (2 d) $^2J_{HH}$ = 13.5 Hz	–	–	–	7.28–7.83 (m) [12 H]	3.45 (s) [2 H] 6.35 (s) [1 H]
		27.8 (s)	31.6 (s)	40.1 (s)	46.1 (s)	45.6 (s)	–	–	119.7–153.9	38.4 (s)

[a] For ease of comparison the sequence of entries in this table does not follow the compound numbering sequence. – [b] Sequence of entries for each compound: ^{1}H NMR first lines, ^{13}C NMR last lines. – [c] Solvent: $CDCl_3$. – [d] Solvent: CD_2Cl_2. – [e] Designation:

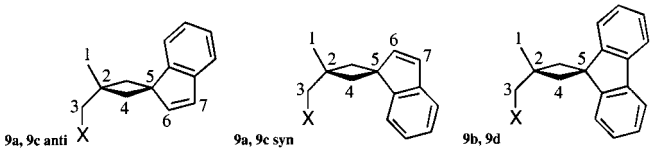
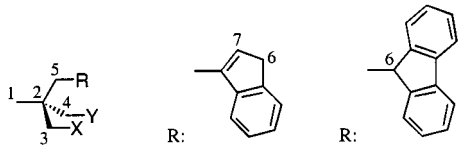


Table 7. NMR spectroscopic data of **10**−**12d**[a,b,c]

No.	R X Y	1[d] CH_3 [3 H]	2[d] C_q	3[d] $CH_{2a,b}$ [2 H]	4[d] $CH_{2a,b}$ [2 H]	5[d] $CH_{2a,b}$ [2 H]	6[d] $-CH_n-$ (n = 1−2)	7[d] −CH= [1 H]	CH aromatic	X {^{31}P NMR}	Y {^{31}P NMR}
10	OMs	1.13 (s)	−	2.49, 2.61 (2 dd)		4.26 (s)	−	−	−	7.30−7.55 (m)	
	PPh_2			$^2J_{HH}$ = 14.6 Hz; $^2J_{HP}$ = 2.4 Hz						{−28.6 (s)}	
	PPh_2	25.1 (t) $^3J_{CP}$ = 9.0 Hz	39.1 (t) $^2J_{CP}$ = 14.0 Hz	39.0 (dd) $^1J_{CP}$ = 17.9 Hz; $^3J_{CP}$ = 9.1 Hz		77.0 (t) $^3J_{CP}$ = 10.1 Hz	−	−	−	128.9−139.5	
11a	Indenyl	1.24 (s)	−	2.67 (m)		3.07 (s)	3.48 (s) [2 H]	6.41 (s)	7.35−7.65 (m) [24 H]		
	PPh_2									{−27.0 (s)}	
	PPh_2	28.6 (t) $^3J_{CP}$ = 9.4 Hz	39.7 (t) $^2J_{CP}$ = 13.5 Hz	42.4 (dd) $^1J_{CP}$ = 15.9 Hz; $^3J_{CP}$ = 8.6 Hz		40.0 (t) $^3J_{CP}$ = 8.7 Hz	38.6 (s)		120.5−147.2		
11b	Fluorenyl	1.13 (s)	−	2.46, 2.58 (2 dd)		2.61 (d)	4.18 (bs) [1 H]	−	7.32−7.88 (m) [28 H]		
	PPh_2			$^2J_{HH}$ = 14.4 Hz; $^2J_{HP}$ = 3.0 Hz		$^3J_{HH}$ = 4.2 Hz				{−27.8 (s)}	
	PPh_2	28.9 (t) $^3J_{CP}$ = 9.5 Hz	39.6 (t) $^2J_{CP}$ = 13.0 Hz	43.1 (dd) $^1J_{CP}$ = 16.0 Hz; $^3J_{CP}$ = 9.1 Hz		45.7 (t) $^3J_{CP}$ = 8.8 Hz	45.5 (s)	−	120.3−149.2		
12a	Indenyl	1.15 (s)	−	2.30, 2.43 (2 dd)	3.60 (pt)	2.78, 2.90 (2 d)	3.46 (s) [2 H]	6.38 (s)	7.30−7.86 (m)	4.11 (t)[1 H]	1.63 (s)
	Fluorenyl			$^2J_{HH}$ = 14.8 Hz	$^2J_{HH}$ = 11.4 Hz	$^2J_{HH}$ = 13.6 Hz			[12 H]	$^3J_{HH}$ = 4.0 Hz	[1 H]
	OH			$^3J_{HH}$ = 4.0 Hz							
		23.0 (s)	40.3 (s)	41.5 (s)	68.9 (s)	35.9 (s)	38.5 (s)		120.0−149.9		
12b	Indenyl	1.02 (s)	−	2.52−2.84 (m)	3.48 (bs)	3.11 (s)	3.48 (bs) [2 H]	6.40 (s)	7.26−7.58 (m)	2.52−2.84 (m)	1.86 (bs)
	Cp								[4 H]	6.22−6.60 (m) [3 H]	[1 H]
	OH	22.4, 22.6 (2 s)	40.3, 40.5 (2s)	38.5, 39.0 (2 s)	69.2 (s)	35.1 (s)	38.5 (s)		120.1−147.1		
12c	Indenyl	1.09 (s)	−	2.38, 2.47 (2 dd)	4.03, 4.11 (2 d)	2.80 (s)	3.44 (s) [2 H]	6.39 (s)	7.28−7.83 (m)	2.94 (s)	
									[12 H]		
	Fluorenyl			$^2J_{HH}$ = 14.8 Hz	$^2J_{HH}$ = 9.2 Hz					4.15 (m)	[3 H]
										[1 H]	
	OMs			$^3J_{HH}$ = 4.4 Hz							
		22.9 (s)	39.4 (s)	41.0 (s)	75.7 (s)	35.4 (s)	38.6 (s)		119.9−148.8		37.5 (s)
										44.6 (s)	
12d	Indenyl	1.29 (s)	−	2.45 (m)	3.73 (s)	2.94, 3.03 (2 d)	3.55 (s) [2 H]	6.47 (s)	7.40−7.95 (m) [12 H]		0.37 (s)
	Fluorenyl					$^2J_{HH}$ = 13.6 Hz				4.22 (t) [1 H]	[9 H]
	OTMS									$^3J_{HH}$ = 3.7 Hz	
		23.1 (s)	40.1 (s)	41.6 (s)	69.2 (s)	35.7 (s)	38.5 (s)		120.1−150.5		0.1 (s)
											44.6 (s)

[a] For ease of comparison the sequence of entries in this table does not follow the numbering scheme. − [b] Sequence of entries for each compound: ^{1}H NMR first lines, ^{13}C NMR last lines. − [c] Solvent: $CDCl_3$. − [d] Designation:



the protons that are on the same sides of the four-membered cycles as the methyl groups show a strong correlation (Figure 5).

The spectroscopic and analytical properties of the fluorenyl residue of **9b** (due to the symmetry of the fluorenyl spiro substituent only one isomer is possible) are in accordance with the assigned constitution (Table 6 and Table 2).

The formation of the spiro compounds **9a/9b** is not due to any specific properties of $LiPPh_2$ as a base; the same type of reaction is observed when **4a** is treated with *n*-butyllithium.

The *syn*- and *anti* isomers of **9c** are formed in a ratio of 2:1 (Scheme 8); **9c** gives rise to a ^{1}H NMR spectrum (Table 6) similar to that of **9a** shown in Figure 4.

Towards the synthesis of tripodal ligands, the formation of the spiro products **9** is a dead end. Spiro cyclization appears to be the more favoured reaction for the more sterically congested compounds such as these neopentane-derived ones, which contain an indenyl or a fluorenyl group together with an electrophilically activating group. Here substitution by an external nucleophile is slowed down, whereas internal substitution is not drastically retarded by steric crowding. Taking this into account, it is not really probable that nucleophilic oxetane-ring-opening reaction sequences starting with the substituted oxetane **2**, shown to lead to **8** (Scheme 4, Scheme 5, and Scheme 6) might finally lead to the desired tripodal ligands. If, on the other hand, the oxetane ring of **2** would be amenable to nucleophilic ring-opening by indenyl- or fluorenyllithium, this would give a simple access to *ansa*-Cp ligands containing a functionalizable -CH_2−$C(CH_3)(CH_2OH)$−CH_2- linker. Compounds **2** were found to undergo this type of ring-opening reaction when treated with indenyl- or fluorenyllithium (Scheme 9). The OH group of **12** may be activated as shown by the transformation of **12a** into the corresponding mesylate **12c**, or trimethylsilyl ether **12d** (Scheme 10). Compounds **12** are fully characterized by their spectroscopic (Table 7) and analytical (Table 2) data. Except for **12b**, which is a colourless oil, compounds **12** are obtained as colourless microcrystalline solids. Single crystals suitable for X-ray analysis could be grown for **12a** (Figure 6, Table 3, and Table 4). The crystals were grown from saturated

CH_2Cl_2/*n*-pentane solutions by slow diffusion of the solvent into rubber stoppers.

The constitution of **12a** as derived from spectroscopy (Table 7) is confirmed by its structure. The angles and distances are in the normal ranges (Table 3). In contrast to **6b** where the fluorenyl substituent and the bulky PPh_2BH_3 group are in close vicintity to each other, the fluorenyl and indenyl substituents of **12a** are as distant from each other as possible (Figure 6) with a well spread-out molecular shape as had also been observed for **4a**/**4b**. As expected, phosphinylation of **12c** is not possible: When **12c** is treated with $LiPPh_2$ (Scheme 11), the spiro compound **9d** is formed which is characterized analytically (Table 2) as well as by its typical NMR pattern (Table 6). The transformation **12c** → **9d** is selective. No indication of spiro cyclization involving the indenyl substituent is observed.

The above results suggest that, in order to introduce an indenyl or a fluorenyl group into a tripodal ligand, this group has to be introduced last. This contrasts strongly to the synthesis of tripodal ligands containing a C_5H_5 group, where the optimal reaction route relies upon introducing the Cp group at the very beginning of the sequence.[6a] The reason for this difference is the inherent tendency of fluorenyl- and indenyl derivatives to undergo spiro cyclization.

Tripodal ligands containing an indenyl or a fluorenyl donor group are accessible from **10**, which is obtained from **10**•$2BH_3$ by deprotection with morpholine.[8c,9] The deprotected form **10** has to be used because using **10**•$2BH_3$ itself as the starting compound reduces yield and selectivity. Compound **10** reacts with indenyllithium to produce **11a** and with fluorenyllithium to give the tripodal ligand **11b** (Scheme 12). To obtain acceptable yields, the lithium reagents have to be activated by the addition of TMEDA or 18-crown-6. Under these conditions, the yields of **11** after chromatographic workup are around 30%. Compounds **11** are off-white solids, which are obtained in microcrystalline form. Depending on the handling procedure, **11b** may be orange, presumably due to some very minor dyestuff impurity which is not apparent from the analytical and spectroscopic data (Table 7 and Table 2). Both products **11a**/**11b** and starting material **11** are fully characterized by spectroscopy (Table 7) and elemental analysis (Table 2).

Conclusion

Neopentane-based tripodal ligands $CH_3C(CH_2PR_2)_2(CH_2R')$ (R = aryl, alkyl; R′ = indenyl, fluorenyl) are accessible by a synthetic procedure in which the indenyl or fluorenyl residues are introduced in the last step. This contrasts to the synthesis of the analogous Cp-containing tripodal ligands $[CH_3C(CH_2PR_2)_2(CH_2C_5H_4)]^-$, where the Cp group had to be the first one to be introduced.[6a]

Neopentane derivatives of the type $(RCH_2)(CH_2R')C(CH_2Indenyl)(CH_2X)$ (X = electrophilically activating group) undergo spiro cyclization when treated with bases, to produce spiro cyclobutanes with the indenyl α-carbon atom acting as the spiro centre. The basic nucleophiles (e.g., $KPPh_2$) therefore do not react by substitution, they act as bases, initiating spiro cyclization. The same type of reactivity is observed with fluorenyl as the neopentane-bound substituent.

Neopentane-derived oxetanes $O(CH_2)_2C(CH_3)(CH_2R)$ (R = Cp, indenyl) react with indenyl- or fluorenyllithium by nucleophilic opening of the oxetane ring to produce functionalizable chiral *ansa*-Cp ligands $(HOCH_2)(CH_3)C(CH_2R)(CH_2R')$ (R, R′ = Cp, indenyl, fluorenyl), in fair yields

Experimental Section

General: All manipulations involving phosphanes were carried out under argon by means of standard Schlenk techniques and were monitored by TLC (Macherey−Nagel Co., Polygram SIL G/UV_{254}). All solvents were dried by standard methods[10] and distilled under argon. The solvents $CDCl_3$ and CD_2Cl_2 used for NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried with 4-Å molecular sieves. − NMR: Bruker Avance DPX 200 at 200.12 MHz (^1H), 50.323 MHz ($^{13}C\{^1H\}$), 81.015 MHz ($^{31}P\{^1H\}$), T = 298 K; chemical shifts (δ) with respect to $CHCl_3$ (^1H: δ = 5.32; ^{13}C: δ = 53.5) as internal standards. ^{31}P chemical shifts (δ) with respect to 85% H_3PO_4 (^{31}P: δ = 0) as external standard. − MS: Finnigan MAT 8320, EI (70 eV) − Melting points: Gallenkamp MFB-595010; uncorrected values. − Elemental analyses: Microanalytical Laboratory of the Organisch-Chemisches Institut, Universität Heidelberg.

Materials: Silica gel (Kieselgel z.A. 0.06−0.2 mm, J. T. Baker Chemicals B. V.) used for chromatography was degassed at 1 mbar for 24 h and saturated with argon. A solution of 2.5 M *n*BuLi in hexane was used for deprotonations. $HPEt_2$,[11] $HPPh_2$,[12] 3-methanesulfonoxymethyl-3-methyloxetane (**1**),[13] 1-methanesulfonoxymethyl-2,2-bis(diphenylphosphanylmethyl)propane−*P,P*-bis(borane) (**10**•$2BH_3$)[3f] and 3-cyclopentadienylmethyl-3-methyloxetane (**2c**)[6a] were prepared according to or by adaptation of literature procedures. All other chemicals were obtained from commercial suppliers and were used without further purification.

General Procedure for the Synthesis of Compounds 2: Indene or fluorene (37 mmol, 1.3 equiv.) was dissolved in 100 mL of THF and was deprotonated by the dropwise addition of *n*BuLi at 0°C. This solution was stirred for 2 h at room temperature; after this period the solution was heated to 60°C and a solution of 3-methanesulfonoxymethyl-3-methyloxetane (28 mmol) in THF (50 mL) was added dropwise over a period of 45 min. The resulting mixture was then heated to reflux for 3 h. After cooling to room temperature, the mixture was hydrolysed by addition of 30 mL water. The organic phase was separated, and the aqueous layer was extracted with three 30 mL portions of diethyl ether. The combined organic phases were washed with saturated NaCl solution (pH: neutral) and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by column chromatography (eluent, R_f, and yield given in Table 2).

General Procedure for the Synthesis of Compounds 3: Compound **2** (10 mmol) was dissolved in 50 mL THF and cooled to 0°C. At this temperature 30 mmol (3 equiv.) of a 48% aqueous solution of hydrobromic acid was added dropwise. After it was stirred for 1 h at 0°C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h.

For 3a: The mixture was again cooled to 0°C and 15 mL of 10% caustic soda solution was added to reverse the HBr addition at the

double bond of the indene residue, which had occurred in part during the first step (c.f.[6a]). Stirring was continued for 1 h at 20°C. The organic phase was separated, and the aqueous layer was extracted with three 30 mL portions of diethyl ether. The combined organic phases were washed with saturated NaCl solution (pH: neutral) and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by column chromatography (eluent, R_f, and yield are given in Table 2).

For 3b: The organic phase was separated, and the aqueous layer was extracted with three 30 mL portions of diethyl ether. The combined organic phases were washed with saturated NaCl solution (pH: neutral) and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by column chromatography (eluent, R_f, and yield are given in Table 2).

General Procedure for the Synthesis of Compounds 4a, 4d, 7, and 12c: The starting material (10 mmol) was dissolved in CH_2Cl_2 (60 mL)and 1.5 equiv. of triethylamine was added to the solution. The mixture was cooled to 0°C and 1.3 equiv. of methanesulfonyl chloride was added dropwise. After half the amount of methanesulfonyl chloride had been added, a white precipitate formed. After 20 min at 0°C, stirring was continued for another 6 h at 20°C. The mixture was hydrolysed by the addition of 20 mL of water. The organic phase was separated, and the aqueous layer was extracted with three 30 mL portions of CH_2Cl_2. The combined organic phases were washed with saturated NaCl solution (pH: neutral) and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue purified by column chromatography (eluent, R_f, and yield are given in Table 2).

General Procedure for the Synthesis of Compounds 5: Oxetane **2** (6−15 mmol) was dissolved in THF (40−60 mL)and deprotonated by the dropwise addition of 1 equiv. *n*BuLi at 0°C. The solution was stirred for 1 h. The phosphane HPR'_2 (1.2 equiv.) was dissolved in THF (40−60 mL) and was deprotonated in the same manner by the dropwise addition of 1 equiv. *n*BuLi at 0°C. This solution was stirred for 30 min at 20°C. The phosphide solution was added dropwise to the deprotonated oxetane over a period of 45 min. The resulting mixture was stirred for 6 h at room temperature and heated to reflux (**5a**, **5c** 1 h; **5b** 3 h). After it had cooled to room temperature, the mixture was hydrolysed by addition of 20 mL of water. The organic phase was separated, and the aqueous layer was extracted with three portions of 30 mL diethyl ether. The combined organic phases were washed with saturated NaCl solution (pH: neutral) and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by column chromatography (not in case of **5c**, which seems to decompose on silica gel) (eluent, R_f, and yield are given in Table 2).

General Procedure for the Synthesis of Compounds 6: Compound **5** (5−12 mmol) was dissolved in THF (50 mL) and cooled to 0°C. At this temperature, BH_3 (1.3 equiv.) in THF was added dropwise. The reaction mixture was stirred for 45 min. The solvent was removed in vacuo and the remaining residue was purified by column chromatography (eluent, R_f, and yield are given in Table 2).

General Procedure for the Synthesis of Compounds 8 and 10: The starting material was dissolved in a sufficient amount of morpholine (no undissolved parts remained). The mixture was heated 15 min at 70°C. All volatile components were removed in vacuo and the remaining residue was purified by column chromatography (eluent, R_f, and yield are given in Table 2).

General Procedure for the Synthesis of Compounds 9a and 9b: Diphenylphosphane (12 mmol, 3 equiv.) was dissolved in THF (30 mL) and deprotonated by the dropwise addition of 1 equiv. *n*BuLi at 0°C. This solution was stirred for 1 h at room temperature, after which a solution of 4 mmol starting material (**4a**, **4d**) in 30 mL THF was added dropwise over a period of 2 min. The resulting mixture was stirred for 2 h at room temperature and heated to reflux (**9a** 2 h; **9b** 3 h). After cooling to room temperature the mixture was hydrolysed by addition of 20 mL of water. The organic phase was separated and the aqueous layer was extracted with three portions of 20 mL diethyl ether. The combined organic phases were washed with saturated NaCl solution (pH: neutral) and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by column chromatography (eluent, R_f, and yield are given in Table 2).

Synthesis of Compound 9c: Compound **4a** (1.4 mmol) was dissolved in 10 mL of THF and deprotonated by the dropwise addition of 1 equiv. *n*BuLi at −70°C. This solution was stirred for 2 h at room temperature and heated to reflux for 2 h. After cooling to room temperature the mixture was hydrolysed by addition of 10 mL of water. The organic phase was separated and the aqueous layer was extracted with three portions of 10 mL diethyl ether. The combined organic phases were washed with saturated NaCl solution (pH: neutral) and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by column chromatography (eluent, R_f, and yield are given in Table 2).

Synthesis of Compound 9d: Diphenylphosphane (2.8 mmol, 2.5 equiv.) was dissolved in 15 mL of THF and deprotonated by the addition of 1 equiv. KO*t*Bu at 0°C. This solution was stirred for 1 h at room temperature, then a solution of 1.9 mmol **12c** in 20 mL THF was added dropwise over a period of 1 min. The resulting mixture was stirred for 12 h at room temperature. The mixture was hydrolysed by addition of 10 mL of water. The organic phase was separated and the aqueous layer was extracted with three portions of 20 mL diethyl ether. The combined organic phases were washed with saturated NaCl solution (pH: neutral) and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by column chromatography. Elution with PE/Et_2O = 1/1 removed contaminants while **9d** did not migrate at all. It was subsequently eluted with toluene/THF 1/1. On evaporation of the solvent from the eluate, the purified compound **9d** was obtained in microcrystalline form (yield are given in Table 2).

General Procedure for the Synthesis of Compounds 4c and 12d (Silylation): Starting material (5 mmol) was dissolved in 40 mL CH_2Cl_2 and 1.5 equiv. of triethylamine was added. The solution was cooled to 0°C and 1.3 equiv. of trimethylsilyl chloride was added dropwise. After the reaction mixture was stirred for 1 h, all volatile parts were removed in vacuo. The remaining residue was purified by column chromatography (eluent, R_f, and yield are given in Table 2).

Synthesis of Compound 4b: Compound **3a** (10 mmol) was dissolved in a solution consisting of 20 mL CH_2Cl_2 and 20 mmol pyridine (2 equiv.). The mixture was cooled to 0°C and 14 mmol benzenesulfonyl chloride (1.4 equiv.) was added dropwise. Stirring was continued at 20°C for 15 h. The mixture was hydrolysed by addition of 20 mL water. The organic phase was separated, and the aqueous layer was extracted with three portions of 30 mL CH_2Cl_2. The combined organic phases were washed and neutralized with saturated NaCl solution and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by column chromatography (eluent, R_f, and yield are given in Table 2).

Synthesis of Compound 11a: Indene (4.6 mmol, 2.2 equiv. related to **10**) was dissolved in 40 mL THF and deprotonated by the dropwise addition of an equimolar amount *n*BuLi at 0°C. This solution was stirred for 10 min. Dibenzo-18-crown-6-ether (4.6 mmol) was ad-

ded. Stirring was continued for another 2 h at 20°C. The mixture was heated to 60°C and a solution of **10** (2.1 mmol) in 10 mL THF was added dropwise over a period of 5 min (After the first drops the reaction mixture turned a deep violet colour). The mixture was heated to reflux for another 5 h. After cooling to 20°C, it was hydrolysed by the addition of 20 mL water. The precipitated white substance (crown ether) was filtered off and washed twice with diethyl ether. The organic phase was separated, and the aqueous layer was extracted with three portions of 30 mL diethyl ether. The combined organic phases were washed and neutralized with saturated NaCl solution until neutral pH was obtained, and it was then dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by column chromatography (eluent, R_f, and yield are given in Table 2).

Synthesis of Compound 11b: Fluorene (5.6 mmol, 3 equiv. with respect to **10**) was dissolved in 40 mL THF and deprotonated by the dropwise addition of an equimolar amount *n*BuLi at 0°C. After stirring for 10 min, TMEDA (5.6 mmol) was added. Stirring was continued for another 2 h at 20°C. The mixture was heated to 60°C and a solution of 1.9 mmol **10** in 10 mL THF was added dropwise over a period of 5 min (after the first drops the reaction mixture adopted a deep violet colour). The mixture was then heated to reflux for 5 h. The mixture was hydrolysed by addition of 20 mL water. The organic phase was separated and the aqueous layer was extracted with three portions of 30 mL diethyl ether. The combined organic phases were washed and neutralized with saturated NaCl solution and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by column chromatography (eluent, R_f, and yield are given in Table 2).

General Procedure for the Synthesis of Compounds 12a and 12b: Indene (in the case of **12b**) or fluorene (in the case of **12a**) (30 mmol, 3 equiv. with respect to **2**), for the generation of the nucleophile, was dissolved in 40 mL THF and deprotonated by the dropwise addition of 30 mmol *n*BuLi at 0°C. Stirring was continued 2 h at 20°C. Compound **2c** (in case of **12b**) or **2a** (in case of **12a**) (10 mmol) was dissolved in 30 mL THF and deprotonated by the dropwise addition of 10 mmol *n*BuLi at 0°C. The solution was stirred at 20°C (**2c** 1 h, **2a** 2 h). To this solution the nucleophile was added dropwise. The reaction mixture was heated to reflux for 4 h. The mixture was hydrolysed by the addition of 20 mL water. The organic phase was separated, and the aqueous layer was extracted with three portions of 30 mL diethyl ether. The combined organic phases were washed and neutralized with saturated NaCl solution and dried with Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by column chromatography (eluent, R_f, and yield are given in Table 2).

X-ray Structure determinations: Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil and fixed to a glass capillary at 200 K. The measurements for **2b**, **4a**, and **4b** were carried out on a Siemens P4 four-circle diffractometer (equipped with a low temperature unit) with graphite-monochromated Mo-K_α radiation. The measurements for **6b** and **12a** were carried out on a Nonius-Kappa CCD diffractometer (low temperature unit, graphite-monochromated Mo-K_α radiation). In case of the Siemens P4 four-circle diffractometer measurements, the intensities of three control reflections (measured every 100 reflections) remained constant throughout the data collection, thus indicating crystal and electronic stability. The data collected on a Siemens P4 four-circle diffractometer were corrected in the standard manner, including experimental absorption correction. The data from the Nonius Kappa CCD device were processed by standard Nonius software.[14] All Calculations were performed using the SHELXT-PLUS software package.[15] Structures were solved by direct methods with the SHELXS-97 program[15a] and refined with the SHELXL-97 program.[15b] Graphical handling of the structural data during solution and refinement was performed with XPMA.[16] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares calculations. Data for the structure determinations are compiled in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-124896 (**2b**), CCDC-124900 (**4a**), CCDC-124899 (**4b**), CCDC-124897 (**6b**), and CCDC-124898 (**12a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-(0)1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

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