Synthesis of (Indenylidene)phosphoranes – A Novel Class of Ligand Precursors for Main-Group and Transition Metal Organometallics[‡]

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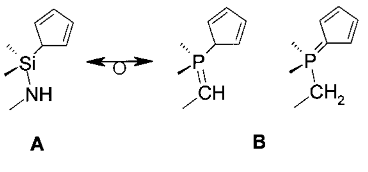
Dedicated to Professor Manfred Meisel on the occasion of his 65th birthday

Keywords: Bridging ligands / Constrained geometry catalysts / Cyclopentadienyl ligands / Isoelectronic analogues / Isolobal relationship / Phosphoranes / Phosphorus ylides / Indenyl / Sodium

$IndPPh_2$ (**1**) reacts with RCH_2Br to form the phosphonium salts $[RCH_2P(Ph)_2Ind]^+Br^-$ (**2**: R = Ph; **3**: R = C_6F_5) in high yields. Oxidation of **1** with H_2O_2 in THF proceeds smoothly to give the phosphane oxide $IndP(O)Ph_2$ (**4**). Dehydrobromination of **2** and **3** with NaH in THF yields the corresponding indenylidenephosphoranes $C_9H_6{=}P(Ph)_2CH_2R$ (**5**: R = Ph; **6**: R = C_6F_5). Further deprotonation of **6** with excess NaH results in formation of sodium 1-{[(pentafluorophenyl)methylidene]-diphenylphosphoranyl}indenide (**7**), isolated as a solvate with three THF molecules. A detailed NMR study of new ligand precursors and X-ray structure studies of **5** and **7** have been accomplished. A short F→Na coordination contact in the molecular structure of **7** has been detected.

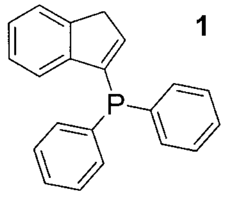
Introduction

Linked (cyclopentadienylsilyl)amine systems **A** (Scheme 1) became one of the best established and developed classes of specially designed ligand precursors[1–5] for bridged cyclopentadienyl–amido early transition metal complexes, the so-called "constrained geometry catalysts".[6] Depending on the nature of the ligand framework, these complexes give high molecular weight PE with long-chain branching. Furthermore, because of their more open coordination spheres (relative to *ansa*-metallocenes), they have the pronounced ability to incorporate higher olefins.[7–12] Isoelectronic analogues of systems **A** are the linked cyclopentadienylphosphoranylidene systems (**B**, left). These compounds do exist in the thermodynamically more stable form of the cyclopentadienylidenephosphoranes (**B**, right). Some examples of similar compounds are known from the literature;[13] however, neither a general synthetic route towards these ligand precursors for organometallic chemistry nor their organometallic derivatives have been explored.



Scheme 1

In this paper we describe a synthetic approach towards and a detailed NMR study of type **B** ligand precursors on the basis of stable Ph_2PInd (**1**), as well as the first alkali metal derivative of one such new ligand, along with their crystal structures.



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Results and Discussion

As the simple (cyclopentadienyl)phosphanes are eager to dimerise by Diels–Alder reaction, **1** was chosen for our preliminary studies. Of the two isomers of this compound, earlier described by Anderson and co-workers,[14] the thermodynamically most stable is the vinylic isomer. It was synthesised in 89% yield by a slightly modified procedure starting from IndLi and Ph_2PCl in toluene.[15] Quaternisation of **1** with bulky $tBuCH_2Br$ or Me_3SiCH_2Br was un-

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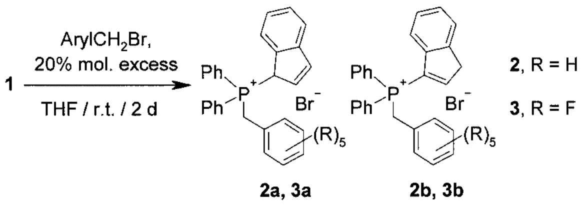
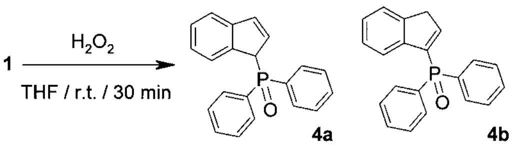
successful,[16] we therefore decided to use the more electrophilic $C_6H_5CH_2Br$ and $C_6F_5CH_2Br$. In both cases, using 20% molar excess of benzyl bromides, complete quaternisation was achieved in THF at room temperature after 2 d (Scheme 2). Corresponding phosphonium salts **2** and **3** are only slightly soluble in THF and were isolated as white powders in practically quantitative yields.[17]



Scheme 2

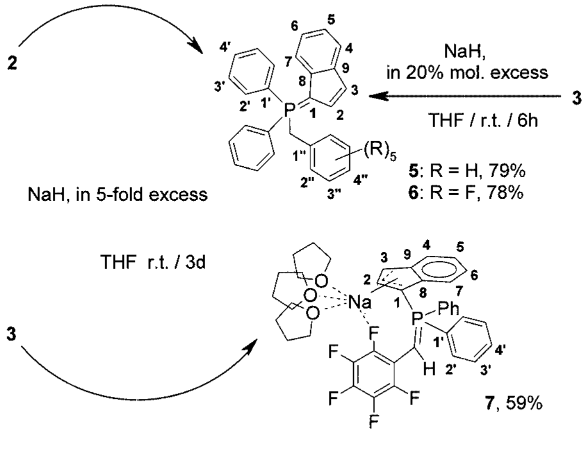
According to ^{31}P NMR spectroscopic data, **2** and **3** exist as mixtures of allylic (**2a**: δ = 32.8 ppm; **3a**: δ = 15.6 ppm) and vinylic (**2b**: δ = 31 ppm; **3b**: δ = 13 ppm) isomers depending on the position of the double bond in the indenyl ring. The ratio of isomers differs from one sample to another in an irregular way, which precludes accurate assignment of arylic and vinylic signals in ^{1}H and ^{13}C NMR spectra that have been measured in $[D_6]DMSO$. ^{1}H NMR benzylic signals are located between δ = 5.0 and 5.5 ppm and ^{13}C signals at δ = 30.0 ppm for **2** and δ = 19.0 ppm for **3**. Allylic signals of isomers **a** are located at $\delta \approx 6.3$ ppm ($^{2}J_{PH}$ = 21 Hz) and 44 ppm ($^{1}J_{P,C}$ = 42 Hz), while those of isomers **b** are shifted downfield to δ = 4 ppm and 42 ppm in the ^{1}H and ^{13}C NMR spectra, respectively.

Interestingly, a similar situation arises when phosphane oxide **4** is synthesised by oxidation of **1** with H_2O_2 in THF (Scheme 3).[18] Compound **4**, obtained quantitatively, exists as a 1:4 isomeric mixture of corresponding allylic and vinylic phosphane oxides **4a** and **4b**, respectively.[19]



Scheme 3

The reaction of the phosphonium salt **2** with a five-fold molar excess of NaH in THF was rather slow, took 3 d, and resulted in a dark green solution (Scheme 4). Upon concentration of the solution to one quarter of its initial volume, the desired indenylidenephosphorane **5** precipitated at −78 °C after 1 d as a yellow-green, light-sensitive microcrystalline powder.[20] Crystallisation from CH_2Cl_2 gave block crystals. The X-ray structure of **5** was determined and showed nearly ideal tetrahedral coordination of the central phosphorus atom with C−P−C angles between 104° and 116°. The C−P bond lengths are also not very different: 1.828(4) Å for $PhCH_2-P$, 1.797(4) Å for $C_{Ph}-P$ and 1.727(4) Å for $C_{Ind}=P$.[21,22] The molecular structure of **5** with thermal ellipsoids of 50% probability as well as selected bond lengths and angles are shown in Figure 1.



Scheme 4

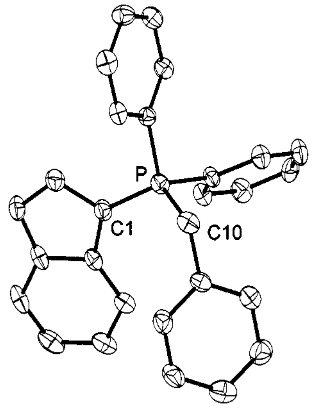


Figure 1. Molecular structure of **5** showing the atom numbering scheme with 50% probability thermal ellipsoids; all hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: C(1)−P(1) 1.733(4), C(1)−C(2) 1.420(5), C(10)−P(1) 1.832(4), C(1)−P(1)−C(10) 116.4(2); C(1)−P(1)−C(Ph) 108.9(2), C(Ph)−P(1)−C(Ph′) 108.3(2)

Under the same reaction conditions, phosphonium salt **3** was converted directly into the Na salt **7**. Obviously, CH acidity of the benzylic CH_2 group is much higher in the case of the pentafluorobenzyl derivative, and further deprotonation with NaH (applied in fivefold excess) proceeds quicker and results in the formation of sodium 1-{[(pentafluorophenyl)methylidene]diphenylphosphoranyl}-indenide (**7**).[23] The synthesis of **6** was achieved in another experiment using only 20% molar excess of NaH and a shorter reaction time: after 6 h in THF, it was obtained in 78% yield as a yellow powder.[24] Both indenylidenephosphoranes **5** and **6** are rather stable and can be handled in air without special care for several minutes. They are more soluble in ethereal and aromatic solvents than in aliphatic ones. Gold-yellow Na salt **7** crystallises with three THF molecules (coordinated by sodium) in the asymmetric unit.[25,26] While their O atoms occupy fixed positions around the sodium atom, all carbon atoms are disordered. The structure refinement of the latter had to be split on two sides in each case. For this reason only the C atoms of the major components could be refined anisotropically. The ratios between major and minor components vary from 64:36, 66:34 to 83:17, respectively. The sodium atom shows predominantly η^3-coordination with the allylic part of the indenyl fragment, with the shortest distance to the C2 atom (2.67 Å). Similar delocalisation of the carbanionic charge was found by Schmidbaur and co-workers in the crystal structure of the solvent-free potassium salt of dimethylphosphonium bis(benzylide) K[Me$_2$P(CHPh)$_2$]. The lattice did not contain discrete complex molecules, but was rather a coordination polymer; the metal atoms interacted preferentially with ylidic carbanions and the *ortho* and *para* positions of the benzylide rings.[27] In the molecular structure of **7**, a short F→Na coordination contact was found. The intramolecular distance between the sodium cation and one of the *ortho*-F atoms of the C$_6$F$_5$ group is only 2.67 Å, i.e. more than 1 Å shorter than the sum of the van der Waals radii of these elements (3.74 Å).[28] The molecular structure of **7** with thermal ellipsoids of 50% probability as well as selected bond lengths and angles are shown in Figure 2.

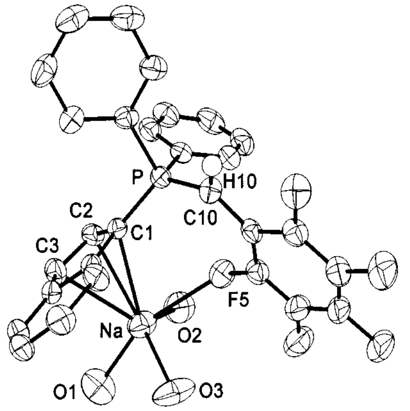


Figure 2. Molecular structure of **7** showing the atom numbering scheme with 50% probability thermal ellipsoids; all hydrogen atoms except for H(10) of the bridging moiety are omitted; only oxygen atoms of coordinated THF molecules are shown for clarity; selected bond lengths [Å] and angles [°]: P−C(10) 1.714(2), P−C(1) 1.747(1), P−C(Ph) 1.827(2), P−C(Ph′) 1.828(2), C(1)−C(2) 1.431(2), C(2)−C(3) 1.383(2), Na−C(1) 2.874(2), Na−C(2) 2.679(2), Na−C(3) 2.741(2), Na−O(1) 2.373(2), Na−O(2) 2.322(2), Na−O(3) 2.271(2), Na−F(5) 2.669(1), F(5)−C(C$_6$F$_5$) 1.374(2), F(3)−C(C$_6$F$_5$) 1.354(2); C(10)−P−C(1) 118.77(8), C(10)−P−C(Ph) 103.51(8), C(1)−P−C(Ph′) 109.02(8), C(1)−P−C(Ph) 106.37(7), C(Ph)−P−C(Ph′) 103.61(8), P−C(1)−Na 125.21(8), O(3)−Na−O(2) 116.93(6), O(3)−Na−O(1) 87.75(6), O(2)−Na−O(1) 88.00(6), O(3)−Na−F(5) 81.70(5), O(2)−Na−F(5) 78.87(5), O(1)−Na−F(5) 157.07(5), C(C$_6$F$_5$)−F(5)−Na 140.0(1)

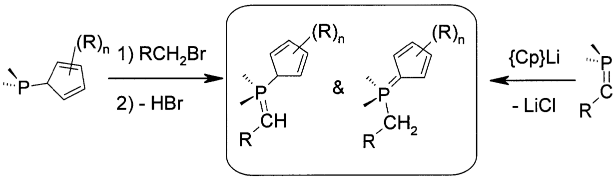
Because of the importance of **5**, **6** and **7** for further syntheses of organometallic derivatives, a detailed NMR study of these compounds has been performed using ^{1}H/^{13}C COSY, APT and DEPT methods and heteronuclear NMR spectroscopy. The complete set of data obtained is given in Table 1. It is interesting to note that in the ^{13}C NMR spectrum of **7** signals for C1 appear considerably shifted downfield, and the signals for C1′ and P*C*H are shifted upfield, relative to those in the spectrum of **6**. In the ^{19}F NMR spectrum the signals of *ortho*- and *para*-F substituents in **7** also appear at a much lower field than in **6**, while those of *meta*-F substituents are almost unaffected. Also, no difference between the *ortho*-F atoms can be detected, which indicates free rotation of the C$_6$F$_5$ substituent of **7** when it is in solution.

Table 1. Assignment of signals in ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra of **5**, **6** and **7**

	^{1}H: δ [ppm]			^{13}C/^{31}P/^{19}F: δ [ppm]		
	5	**6**	**7**	**5**	**6**	**7**
1	–	–	–	59.9 ($^1J_{P,C}$ = 110 Hz)	62.2 ($^1J_{P,C}$ = 118 Hz)	24.5 ($^1J_{P,C}$ = 135 Hz)
2	6.65, t	6.57, t	6.66, t	126.9 ($^2J_{P,C}$ = 15 Hz)	126.1 ($^2J_{P,C}$ = 16 Hz)	127.4 ($^2J_{P,C}$ = 16 Hz)
3	6.44. t	6.43, t	6.16, t	117.3 ($^3J_{P,C}$ = 13 Hz)	106.9 ($^3J_{P,C}$ = 15 Hz)	101.0 ($^3J_{P,C}$ = 14 Hz)
4, 7	7.57−7.02	7.62−7.39	7.32−7.26	120.1, 117.3	119.6, 117.1	119.6, 119.5
5, 6	6.76−6.57	6.77−6.55	6.57−6.46	117.2, 116.7	116.6, 116.3	115.8, 115.2
8	–	–	–	137.6	137.8	136.7
9	–	–	–	135.1	135.4	135.2
1′	–	–	–	124.6 ($^1J_{P,C}$ = 86 Hz)	123.1 ($^1J_{P,C}$ = 87 Hz)	137.5 ($^1J_{P,C}$ = 88 Hz)
2′	7.57−7.02	7.62−7.39	7.80−7.27	133.3($^2J_{P,C}$ = 10 Hz)	132.6 ($^2J_{P,C}$ = 10 Hz)	133.1 ($^2J_{P,C}$ = 9 Hz)
3′	7.57−7.02	7.62−7.39	7.80−7.27	128.8 ($^3J_{P,C}$ = 12 Hz)	128.5 ($^3J_{P,C}$ = 12 Hz)	128.1 ($^3J_{P,C}$ = 11 Hz)
4′	7.57−7.02	7.62−7.39	7.80−7.27	132.7 ($^4J_{P,C}$ = 3 Hz)	132.8($^4J_{P,C}$ = 3 Hz)	130.2($^4J_{P,C}$ = 2.5 Hz)
1′′	–	–	–	130.2 ($^2J_{P,C}$ = 8 Hz)	–	–
2′′	6.82−6.76	–	–	130.5	–	–
3′′	7.57−7.50	–	–	128.4	–	–
4′′	7.42−7.10	–	–	127.5	–	–
THF	–	–	3.61, 1.76	–	–	68.3, 26.4
P*CH*	4.14 ($^2J_{PH}$ = 14 Hz)	4.16 ($^2J_{PH}$ = 13 Hz)	2.73 ($^2J_{PH}$ = 11Hz)	33.9 ($^1J_{P,C}$ = 53 Hz)	22.0 ($^1J_{P,C}$ = 55 Hz)	81.4 ($^1J_{P,C}$ = 124 Hz)
P	–	–	–	9.7	8.9	4.7
o-F	–	–	–	–	−139	−153
m-F	–	–	–	–	−169	−170
p-F	–	–	–	–	−155	−190

Conclusion

Series of phosphoranes **B** with different R substituents can be synthesised easily using the developed synthetic scheme or, alternatively, from chlorophosphonium ylides with sterically encumbered {Cp}-type anions. A combination of these two methods allows a wide range of the type **B** ligand precursors to be synthesised (Scheme 5).[29]



Scheme 5

In this preliminary work we have formed the basis for the further development and revival of organometallic chemistry in the so-called "post-metallocene" epoch. Systematic study of thus developed linked cyclopentadienylphosphoranylidene ligands for the syntheses of alkali, rare-earth and transition metal complexes is the subject of our current efforts.

Acknowledgments

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[15] **General Remarks:** All synthetic procedures were performed under purified argon using standard Schlenk techniques. Solvents were distilled from an appropriate drying agent and degassed prior to use. The ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were obtained with Bruker ARX-200, -300 or -400 spectrometers. Mass spectra were measured with a Varian CH-7a MAT device using electron impact with an excitation energy of 70 eV. Indene, Ph_2PCl, $C_6H_5CH_2Br$, $C_6F_5CH_2Br$, *n*BuLi and NaH were used as supplied (Merck, Aldrich). **Starting Phosphane, Ph_2PInd (1):** Indene (29 g, 250 mmol) was dissolved in pentane (900 mL). While the solution was stirred vigorously and cooled with an ice bath, *n*BuLi (110 mL 2.5 M solution in hexanes, 275 mmol) was added over a period of 2−3 h.. The mixture was stirred overnight. The white precipitate of IndLi was filtered off, washed with pentane (3 × 100 mL) and dried in vacuo for several hours. The thus obtained IndLi (12.2 g, 100 mmol) was suspended in toluene (400 mL), and under continuous stirring a solution of Ph_2PCl (22 g, 100 mmol) in toluene (100 mL) was added over a period of 4−5 h. The reaction mixture was stirred overnight, LiCl was filtered off, toluene was removed in vacuo, the crude product washed with hexane (4 × 50 mL) and dried in vacuo, to afford **1** in 89% yield and 95% purity as a light grey powder. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 7.52{-}6.98$ (m, 14 H, H_{Aryl}), 6.12 (dd, 1 H, vinylic H), 3.07 (t, 2 H, allylic H) ppm. ^{31}P NMR (200 MHz, C_6D_6, 25 °C): $\delta = -21$ ppm.

[16] No reaction was observed after stirring of **1** with 50% molar excess of RCH_2Br (R = *t*Bu or TMS) at room temperature in THF for 30 h.

[17] **Phosphonium Salts $[C_6H_5CH_2P(Ph)_2Ind]^+Br^-$ (2) and $[C_6F_5CH_2P(Ph)_2Ind]^+Br^-$ (3)**: $C_6H_5CH_2Br$ (8.5 g, 50 mmol) or $C_6F_5CH_2Br$ (13 g, 50 mmol) was added at once to a solution of **1** (12 g, 40 mmol) in THF (300 mL). The reactions were very slow and only after 3 d complete, resulting in a white precipitate of **2** or **3**, which was filtered off, washed with THF and pentane, and dried in vacuo. Yields in both cases > 95%. **2**: M.p. 253−255 °C. EIMS: *m*/*z* (%) = 391.0 (100) $[M]^+$. **3**: M.p. 228−230 °C. EIMS: *m*/*z* (%) = 481.0 (100) $[M]^+$.

[18] **Phosphane Oxide IndP(O)Ph_2 (4)**: A 34% aqueous solution of H_2O_2 (2 mL, 20 mmol) was slowly added with a syringe to a stirred solution of **1** (3.0 g, 10 mmol) in THF (50 mL). After 30 min, the solution was quickly dried with Na_2SO_4, and THF was removed in vacuo, yielding an off-white microcrystalline powder of **4**. Yield: 3.15 g (100%). M.p. 137−138 °C. EIMS: *m*/*z* (%) = 316.1 (32) $[M]^+$, 201.0 (100) $[M^+ - \text{Ind}]$. $C_{21}H_{17}OP$ (316.34): calcd. C 79.73, H 5.42; found C 80.07, H 5.66.

[19] NMR measured in CD_2Cl_2: ^{1}H: **4a:** $\delta = 7.8{-}6.9$ (m, aryl, Ph), 6.83, 6.38 (AB system, $^3J_{AB} = 3$ Hz, vinylic protons), 4.72 (d, $^2J_{PH} = 25$ Hz, allylic H); **4b:** $\delta = 7.8{-}6.9$ (m, aryl, Ph), 6.71 (dt, vinylic H), 3.5 (br. s, 2 allylic H) ppm. ^{31}P: **4a:** $\delta = 32.3$ ppm; **4b:** $\delta = 23.2$ ppm.

[20] **Indenylidenephosphorane $C_9H_6{=}P(Ph)_2CH_2C_6H_5$ (5):** NaH (2.4 g, 100 mmol) was added under argon to a stirred suspension of **2** (9.42 g, 20 mmol) in THF (100 mL). Slowly the solution began to darken. The reaction was complete after 48 h, resulting in a dark green solution and white precipitate, which was filtered off. The filtrate was concentrated to one quarter of its initial volume (ca. 20−25 mL). The desired ylide **5** precipitated from the solution at −78 °C after 1 d as a yellow-green, light-sensitive microcrystalline powder. Yield: 6.16 g (79%). M.p. 224−226 °C. EIMS: *m*/*z* (%) = 390.1 (73) $[M]^+$, 299.0 (18) $[M^+ - C_7H_8]$, 276.1 (22) $[M^+ - \text{Ind}]$, 185.1 (100) $[Ph_2P]^+$. $C_{28}H_{23}P$ (390.47): calcd. C 86.13, H 5.94; found C 86.19, H 5.70.

[21] **X-ray Crystallographic Study:** Crystallisation of **5** was achieved from CH_2Cl_2. A suitable light-yellow, nearly colourless crystal with linear dimensions of 0.35 × 0.20 × 0.18 mm was mounted on the end of a glass fibre and investigated with a Siemens SMART CCD at 173(2) K, using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Data were collected with an area detector by use of ω scans. The structure was solved by direct methods and expanded by difference Fourier syntheses using the SHELX-97 software package; the intensities were corrected for Lorentz, polarisation and absorption effects using SADABS ($T_{\text{min.}} = 0.9601$, $T_{\text{max.}} = 0.9777$). G. M. Sheldrick, SADABS, *Programme for absorption correction*, University of Göttingen, **1996**; G. M. Sheldrick, *Programme for the refinement of crystal structures, SHELX-97*, University of Göttingen, **1997**.

[22] **Crystal Data and Structure Refinements Details:** $C_{28}H_{23}P$, M = 390.43, triclinic, a = 9.5646(3) Å, b = 9.7692(3) Å, c = 11.8500(4) Å, α = 98.242(2)°, β = 94.528(2)°, γ = 109.004(2)°, V = 1026.70(5) Å^3, space group $P1$, Z = 2, μ = 0.145 mm^{-1}, $D_{\text{calcd.}}$ = 1.263 g·cm^{-3}, θ range 1.75−26.00°, 6798 reflections measured, 3971 unique (R_{int} = 0.0990) which were used in all calculations. GoF (on F^2) = 0.861. The final residuals R_F and $wR_F{}^2$ were 0.0723 [$I > 2\sigma(I)$] and 0.1638 (all). CCDC-233977 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc. cam. ac. uk].

[23] **Sodium 1-{[(Pentafluorphenyl)methylidene]diphenylphosphoranyl}indenide (7):** NaH (0.61 g, 25 mmol) was added under argon to a stirred suspension of **3** (2.72 g, 4.9 mmol) in THF (50 mL). The reaction proceeded exothermally with the evolution of a large amount of gas (H_2). The yellow solution was stirred over a weekend. After concentration of the reaction mixture, it was filtered and an equal amount of pentane was slowly poured onto the solution. Crystallisation began immediately, yielding gold-yellow crystals of Na salt **7** at 0 °C after 1 d. Yield: 1.5 g (59%).

[24] **Indenylidenephosphorane $C_9H_6{=}P(Ph)_2CH_2C_6F_5$ (6)**: Analogous to the preparation of **5** starting from **3** (5.6 g, 10 mmol) and NaH (0.29 g, 12 mmol) but with a shorter reaction time (6 h). Yield: 3.74 g (78%). M.p. 180−182 °C. EIMS: m/z (%) = 480.1 (9) [M$^+$], 366.1 (18) [M$^+$ − Ind], 299.0 (10) [M$^+$ − $C_6F_5CH_3$], 185.1 (50) [Ph_2P^+]. $C_{28}H_{18}F_5P$ (480.42): calcd. C 70.00, H 3.78; found C 68.15, H 4.20.

[25] **X-ray Crystallographic Study**: Crystallisation of **7** was achieved from THF. A suitable gold-yellow specimen with linear dimensions of 0.48 × 0.24 × 0.22 mm was mounted on the end of a glass fibre and investigated with a Siemens SMART CCD at 153(2) K, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data were collected with an area detector by use of ω scans. The structure was solved by direct methods and expanded by difference Fourier syntheses using the SHELX-97 software package; the intensities were corrected for Lorentz, polarisation and absorption effects using SADABS ($T_{\text{min.}}$ = 0.9324, $T_{\text{max.}}$ = 0.9682). G. M. Sheldrick, SADABS, *Programme for absorption correction*, University of Göttingen, **1996**; G. M. Sheldrick, *Programme for the refinement of crystal structures, SHELX-97*, University of Göttingen, **1997**.

[26] **Crystal Data and Structure Refinements Details:** $C_{40}H_{41}F_5NaO_3P$, M = 718.69, monoclinic, a = 12.0079(2) Å, b = 15.8221(2) Å, c = 20.3386(3) Å, $\alpha = \gamma$ = 90°, β = 106.918(1)°, V = 3696.90(9) Å^3, space group $P2_1/c$, Z = 4, μ = 0.148 mm^{-1}, $D_{\text{calcd.}}$ = 1.291 g·cm^{-3}, θ range 1.77−25.50°, 22 887 reflections measured, 6866 unique (R_{int} = 0.0993), which were used in all calculations. GoF (on F^2) = 1.012. The final residuals R_F and $wR_F{}^2$ were 0.0637 [$I > 2\sigma(I)$] and 0.1488 (all). CCDC-233976 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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