

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

Konstantin A. Rufanov,^{*[a]} Burkhard Ziemer,^[a] Markus Hummert,^[b] and Stefan Schütte^[b]

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

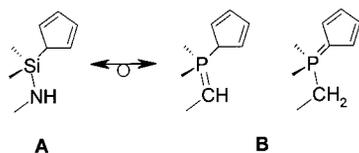
IndPPh₂ (**1**) reacts with RCH₂Br to form the phosphonium salts [RCH₂P(Ph)₂Ind]⁺Br⁻ (**2**: R = Ph; **3**: R = C₆F₅) in high yields. Oxidation of **1** with H₂O₂ in THF proceeds smoothly to give the phosphine oxide IndP(O)Ph₂ (**4**). Dehydrobromination of **2** and **3** with NaH in THF yields the corresponding indenylidenephosphoranes C₉H₆=P(Ph)₂CH₂R (**5**: R = Ph; **6**: R = C₆F₅). 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.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

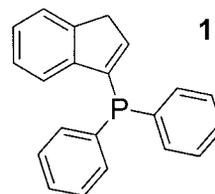
Linked (cyclopentadienylsilyl)amine systems **A** (Scheme 1) became one of the best established and developed classes of specially designed ligand precursors^[1–5] for bridged cyclopentadienyl–amido early transition metal complexes, the so-called “constrained geometry catalysts”.^[6] Depending on the 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



Scheme 1

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.

In this paper we describe a synthetic approach towards and a detailed NMR study of type **B** ligand precursors on the basis of stable Ph₂PInd (**1**), as well as the first alkali metal derivative of one such new ligand, along with their crystal structures.



Results and Discussion

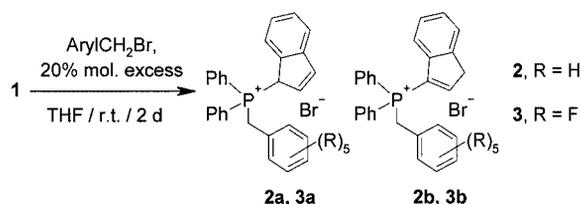
As the simple (cyclopentadienyl)phosphanes are eager to dimerise by Diels–Alder reaction, **1** was chosen for our preliminary studies. Of the two isomers of this compound, earlier described by Anderson and co-workers,^[14] the thermodynamically most stable is the vinylic isomer. It was synthesised in 89% yield by a slightly modified procedure starting from IndLi and Ph₂PCl in toluene.^[15] Quaternisation of **1** with bulky *t*BuCH₂Br or Me₃SiCH₂Br was un-

[‡] Organophosphorus(v) Ligands for Coordination and Organometallic Chemistry, 1

[a] Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489 Berlin, Germany

[b] Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany

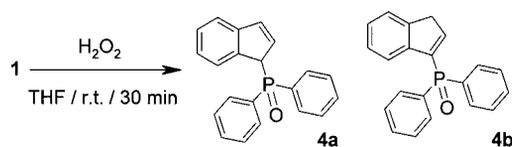
successful,^[16] we therefore decided to use the more electrophilic $C_6H_5CH_2Br$ and $C_6F_5CH_2Br$. In both cases, using 20% molar excess of benzyl bromides, complete quaternisation was achieved in THF at room temperature after 2 d (Scheme 2). Corresponding phosphonium salts **2** and **3** are only 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**: $\delta = 32.8$ ppm; **3a**: $\delta = 15.6$ ppm) and vinylic (**2b**: $\delta = 31$ ppm; **3b**: $\delta = 13$ 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 allylic and vinylic signals in 1H and ^{13}C NMR spectra that have been measured in $[D_6]DMSO$. 1H NMR benzylic signals are located between $\delta = 5.0$ and 5.5 ppm and ^{13}C signals at $\delta = 30.0$ ppm for **2** and $\delta = 19.0$ ppm for **3**. Allylic signals of isomers **a** are located at $\delta \approx 6.3$ ppm ($^2J_{PH} = 21$ Hz) and 44 ppm ($^1J_{PC} = 42$ Hz), while those of isomers **b** are shifted downfield to $\delta = 4$ ppm and 42 ppm in the 1H and ^{13}C NMR spectra, respectively.

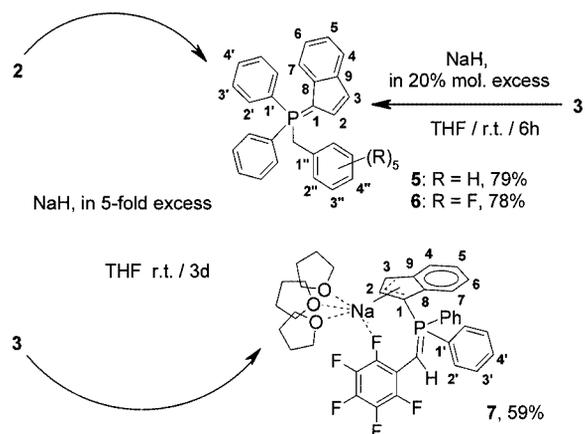
Interestingly, a similar situation arises when phosphane oxide **4** is synthesised by oxidation of **1** with H_2O_2 in THF (Scheme 3).^[18] Compound **4**, obtained quantitatively, exists as a 1:4 isomeric mixture of corresponding allylic and vinylic phosphane oxides **4a** and **4b**, respectively.^[19]



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

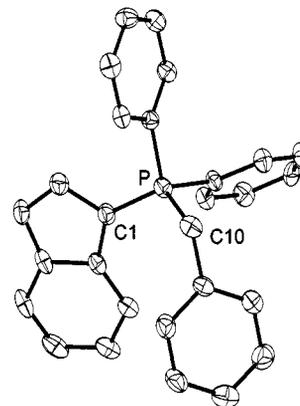


Figure 1. Molecular structure of **5** showing the atom numbering scheme with 50% probability thermal ellipsoids; all hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: C(1)–P(1) 1.733(4), C(1)–C(2) 1.420(5), C(10)–P(1) 1.832(4), C(1)–P(1)–C(10) 116.4(2); C(1)–P(1)–C(Ph) 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 Schmidbauer and co-workers in the crystal structure of the solvent-free potassium salt of dimethylphosphonium bis(benzylidene) $K[Me_2P(CHPh)_2]$. 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 benzylidene 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_6F_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.

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 $^1H/^{13}C$ 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 PCH 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**

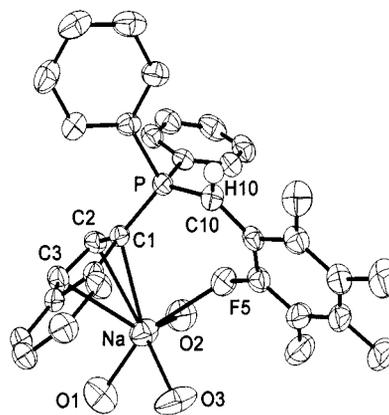


Figure 2. Molecular structure of **7** showing the atom numbering scheme with 50% probability thermal ellipsoids; all hydrogen atoms except for H(10) of the bridging moiety are omitted; only oxygen atoms of coordinated THF molecules are shown for clarity; selected bond lengths [Å] and angles [°]: P–C(10) 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_6F_5) 1.374(2), F(3)–C(C_6F_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_6F_5)–F(5)–Na 140.0(1)

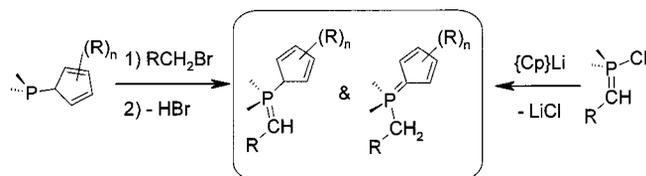
also appear at a much lower field than in **6**, while those of *meta*-F substituents are almost unaffected. Also, no difference between the *ortho*-F atoms can be detected, which indicates free rotation of the C_6F_5 substituent of **7** when it is in solution.

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

1H : δ [ppm]			$^{13}C/^{31}P/^{19}F$: δ [ppm]			
5	6	7	5	6	7	
1	–	–	59.9 ($^1J_{PC} = 110$ Hz)	62.2 ($^1J_{PC} = 118$ Hz)	24.5 ($^1J_{PC} = 135$ Hz)	
2	6.65, t	6.57, t	126.9 ($^2J_{PC} = 15$ Hz)	126.1 ($^2J_{PC} = 16$ Hz)	127.4 ($^2J_{PC} = 16$ Hz)	
3	6.44, t	6.43, t	117.3 ($^3J_{PC} = 13$ Hz)	106.9 ($^3J_{PC} = 15$ Hz)	101.0 ($^3J_{PC} = 14$ Hz)	
4, 7	7.57–7.02	7.62–7.39	120.1, 117.3	119.6, 117.1	119.6, 119.5	
5, 6	6.76–6.57	6.77–6.55	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 ($^1J_{PC} = 86$ Hz)	123.1 ($^1J_{PC} = 87$ Hz)	137.5 ($^1J_{PC} = 88$ Hz)	
2'	7.57–7.02	7.62–7.39	133.3 ($^2J_{PC} = 10$ Hz)	132.6 ($^2J_{PC} = 10$ Hz)	133.1 ($^2J_{PC} = 9$ Hz)	
3'	7.57–7.02	7.62–7.39	128.8 ($^3J_{PC} = 12$ Hz)	128.5 ($^3J_{PC} = 12$ Hz)	128.1 ($^3J_{PC} = 11$ Hz)	
4'	7.57–7.02	7.62–7.39	132.7 ($^4J_{PC} = 3$ Hz)	132.8 ($^4J_{PC} = 3$ Hz)	130.2 ($^4J_{PC} = 2.5$ Hz)	
1''	–	–	130.2 ($^2J_{PC} = 8$ 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	
PCH	4.14 ($^2J_{PH} = 14$ Hz)	4.16 ($^2J_{PH} = 13$ Hz)	2.73 ($^2J_{PH} = 11$ Hz)	33.9 ($^1J_{PC} = 53$ Hz)	22.0 ($^1J_{PC} = 55$ Hz)	81.4 ($^1J_{PC} = 124$ Hz)
P	–	–	9.7	8.9	4.7	
<i>o</i> -F	–	–	–	–139	–153	
<i>m</i> -F	–	–	–	–169	–170	
<i>p</i> -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 cyclopentadienylphosphoranylidenes ligands for the syntheses of alkali, rare-earth and transition metal complexes is the subject of our current efforts.

Acknowledgments

K. R. thanks Dr. Heinz-Jürgen Kroth for multinuclear NMR experiments, Profs. Herbert Schumann (Berlin Technical University) and Igor Fedushkin (Razuvaev-Institute of Chemistry, Nizhny Novgorod, Russian Federation) for fruitful discussions and the Graduate College Programme 352 of the DFG for a postdoctoral fellowship.

- ^[1] P. J. Shapiro, E. E. Bunel, W. P. Schaefer, J. E. Bercaw, *Organometallics* **1990**, *9*, 867.
^[2] J. Okuda, *Chem. Ber.* **1990**, *123*, 1649.
^[3] J. Okuda, *Top. Curr. Chem.* **1991**, *160*, 97.
^[4] J. C. Stevens, F. J. Timmers, G. W. Rosen, G. W. Knight, S. Y. Lai (Dow Chemical Co.), Eur. Pat. Appl. EP0416815A2, **1991**.
^[5] J. A. Canich (Exxon Chemical Co.), Eur. Pat. Appl. EP0420436A1, **1991**.
^[6] J. C. Stevens, *Stud. Surface Sci. Cat.* **1994**, *89*, 277.
^[7] W. Kaminsky, *J. Chem. Soc., Dalton Trans.* **1998**, 1413.
^[8] K. Soga, T. Uozumi, S. Nakamura, T. Toneri, T. Teranishi, T. Sano, T. Arai, *Macromol. Chem. Phys.* **1996**, *197*, 4237.
^[9] Y.-X. Chen, C. L. Stern, S. Yang, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 12451.
^[10] L. Jia, X. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1997**, *16*, 842.
^[11] A. L. McKnight, R. M. Waymouth, *Chem. Rev.* **1998**, *98*, 2587.
^[12] G. J. P. Britovsek, V. C. Gibson, D. F. Weiss, *Angew. Chem.* **1999**, *111*, 448.
^[13] G. Becker, in *Methoden Org. Chem. (Houben-Weyl)*, Georg Thieme Verlag, Stuttgart, **1985**, Bd. VI/2c, p. 494.
^[14] K. A. Fallis, G. K. Anderson, N. P. Rath, *Organometallics* **1992**, *11*, 885.
^[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 ¹H, ¹³C, ¹⁹F and ³¹P 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,

Ph₂PCL, C₆H₅CH₂Br, C₆F₅CH₂Br, *n*BuLi and NaH were used as supplied (Merck, Aldrich). **Starting Phosphane, Ph₂PInd (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 Ph₂PCL (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. ¹H NMR (200 MHz, C₆D₆, 25 °C): δ = 7.52–6.98 (m, 14 H, H_{Ar(yl)}), 6.12 (dd, 1 H, vinylic H), 3.07 (t, 2 H, allylic H) ppm. ³¹P NMR (200 MHz, C₆D₆, 25 °C): δ = –21 ppm.

^[16] No reaction was observed after stirring of **1** with 50% molar excess of RCH₂Br (R = *t*Bu or TMS) at room temperature in THF for 30 h.

^[17] **Phosphonium Salts [C₆H₅CH₂P(Ph)₂Ind]⁺Br[–] (2) and [C₆F₅CH₂P(Ph)₂Ind]⁺Br[–] (3):** C₆H₅CH₂Br (8.5 g, 50 mmol) or C₆F₅CH₂Br (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)Ph₂ (4):** A 34% aqueous solution of H₂O₂ (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 Na₂SO₄, 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⁺ – Ind]. C₂₁H₁₇OP (316.34): calcd. C 79.73, H 5.42; found C 80.07, H 5.66.

^[19] NMR measured in CD₂Cl₂: ¹H: **4a:** δ = 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:** δ = 7.8–6.9 (m, aryl, Ph), 6.71 (dt, vinylic H), 3.5 (br. s., 2 allylic H ((*AUTHOR: Change ok?*))) ppm. ³¹P: **4a:** δ = 32.3 ppm; **4b:** δ = 23.2 ppm.

^[20] **Indenylidene phosphorane C₉H₆=P(Ph)₂CH₂C₆H₅ (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⁺ – C₇H₈], 276.1 (22) [M⁺ – Ind], 185.1 (100) [Ph₂P]⁺. C₂₈H₂₃P (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 CH₂Cl₂. 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 (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*_{min} = 0.9601, *T*_{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, $\alpha = 98.242(2)^\circ$, $\beta = 94.528(2)^\circ$, $\gamma = 109.004(2)^\circ$, $V = 1026.70(5)$ Å³, space group $P1$, $Z = 2$, $\mu = 0.145$ mm⁻¹, $D_{\text{calcd.}} = 1.263$ g·cm⁻³, θ range 1.75–26.00°, 6798 reflections measured, 3971 unique ($R_{\text{int}} = 0.0990$) 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-[(Pentafluorophenyl)methylidene]diphenylphosphoranylindenide (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 (H₂). 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] **Indenylidene phosphorane C₉H₆=P(Ph)₂CH₂C₆F₅ (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⁺ – C₆F₅CH₃], 185.1 (50) [Ph₂P⁺]. C₂₈H₁₈F₅P (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 ($\lambda = 0.71073$ 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 ($T_{\text{min.}} = 0.9324$, $T_{\text{max.}} = 0.9682$). 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:** C₄₀H₄₁F₅NaO₃P, $M = 718.69$, monoclinic, $a = 12.0079(2)$ Å, $b = 15.8221(2)$ Å, $c = 20.3386(3)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 106.918(1)^\circ$, $V = 3696.90(9)$ Å³, space group $P2_1/c$, $Z = 4$, $\mu = 0.148$ mm⁻¹, $D_{\text{calcd.}} = 1.291$ g·cm⁻³, θ range 1.77–25.50°, 22 887 reflections measured, 6866 unique ($R_{\text{int}} = 0.0993$), 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].
- [27] H. Schmidbaur, U. Deschler, B. Milewski-Mahrla, B. Zimmer-Gasser, *Chem. Ber.* **1981**, *114*, 608.
- [28] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.
- [29] K. Rufanov, *Chem. Eur. J.*, manuscript in preparation.

Received July 29, 2004