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Tetrahedron Letters 48 (2007) 8326–8330
Tetrahedron Letters

Various P^*-chiral phosphite-type ligands: their synthesis, stereochemistry and use in Pd-catalysed allylation

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Received 20 May 2007; revised 7 September 2007; accepted 19 September 2007
Available online 22 September 2007

Abstract—A new family of readily available modular phosphite, phosphoramidite and diamidophosphite ligands with P^*-stereocentres have been prepared from inexpensive optically active precursors. Using these novel ligands, up to 91% ee was achieved in Pd-catalysed asymmetric allylic amination. The catalytic performance is affected greatly by the structure of the phosphocentre of the ligand.

Optically active phosphite-type compounds are a very attractive and developing class of phosphorus-containing ligands. As a whole, the most important advantages of chiral phosphites include their pronounced π-acidity, oxidation stability, as well as their synthetic availability and low cost.[1] In particular, phosphites provide broad opportunities for fine tuning of their donor–acceptor and steric properties by the incorporation of oxygen and nitrogen into the first coordination sphere of phosphorus and wide variation of the O- and/or N-containing building blocks. Most phosphites can be synthesised rather simply and in high yield from a variety of optically active precursors. This makes it possible to perform the direct one-pot phosphorylation of chiral compounds, whereas the synthesis of the corresponding phosphine derivatives requires preliminary modification. In addition, these compounds exhibit higher oxidative stability because of the absence of P–C bonds. Hence, this makes it possible to develop protocols for the whole process including ligand synthesis that do not necessitate the use of a glove box.

Surprisingly, there are only a few examples of very promising P^*-chiral monodentate phosphite-type ligands in the literature. The structures of the most efficient examples are shown in Figure 1. Compounds $\mathbf{L_a}$ have demonstrated high enantioselectivity in the Pd-catalysed allylic substitution reactions of (*E*)-1,3-diphenylallyl acetate and methyl (2-phenyl*ortho*-carboran-1-yl)phenyl acetate; [2] $\mathbf{L_b}$ and $\mathbf{L_c}$ are highly enantioselective in the Rh-catalysed hydrogenation of functionalised olefins.[3]

We designed and synthesised a library of novel P^*-chiral monodentate phosphite, phosphoramidite and diamidophosphite ligands having five- and six-membered phosphacycles and OMe or NEt_2 exocyclic substituents. These were easily prepared by direct phosphorylation of the appropriate bifunctional compounds and purified by vacuum distillation. They possess modular properties, allowing fine-tuning of their steric and electronic characteristics (Scheme 1).[4] The starting optically active

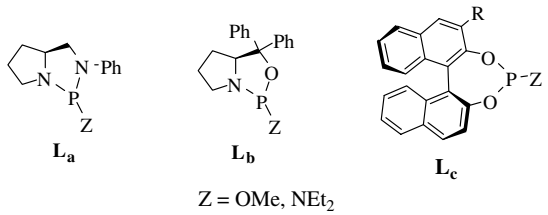

Figure 1.

Keywords: Asymmetric reactions; Phosphorus ligands; Palladium; Allylation.
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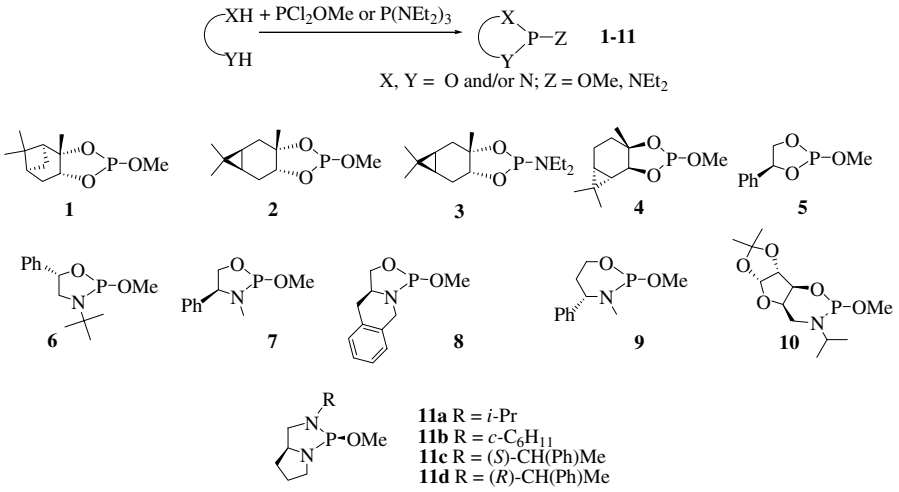
doi:10.1016/j.tetlet.2007.09.125



Scheme 1.

diols, aminoalcohols and diamines used were commercially available or were synthesised from (+)-2- and 3-carenes; (*S*)-mandelic, (*S*)-2-amino-2-phenylacetic, (*S*)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic and malonic acids; D-xylofuranose and (*S*)-*oxo*-proline.[5] Since all these precursors are inexpensive and readily available, ligands **1**–**11** can be prepared on multigram scales.

The ^{31}P NMR spectroscopic data for ligands **1**–**11** are summarised in Table 1. Ligand **3** possesing an NEt_2 exocyclic fragment was formed as a single stereoisomer, while ligands **1**, **2** and **4**–**11** each contain from 2% to 38% of the epimeric form at the P^*-stereocentre. Terpene-based compounds **1**–**2**, phosphoramidites **9** and **10** with six-membered phosphacycles and diamidophosphites **11a**–**d** possessing a bicyclic framework were characterised as containing small amounts of the minor epimer. In the case of **11a**–**d**, the major stereoisomers have *R*-configuration at the P^*-stereocentre. This was confirmed from the characteristic $^2J_{CH_2N,P}$ values (36.4–38.2 Hz) in the ^{13}C NMR spectra of **11a**–**d**.[2,4] To estimate the steric demands of ligands **1**–**11**, we calculated their Tolman's angles[6] by the reported method using semiempirical quantum mechanical AM1 techniques with full optimisation of geometrical parameters.[2] The results obtained (Table 1) show that the steric demands of **1**–**11** vary over a wide range between 90° and 153°, peaking at compounds **11a**–**d** with the 1,3-diaza-2-phosphabicyclo[3.3.0]octane skeleton.

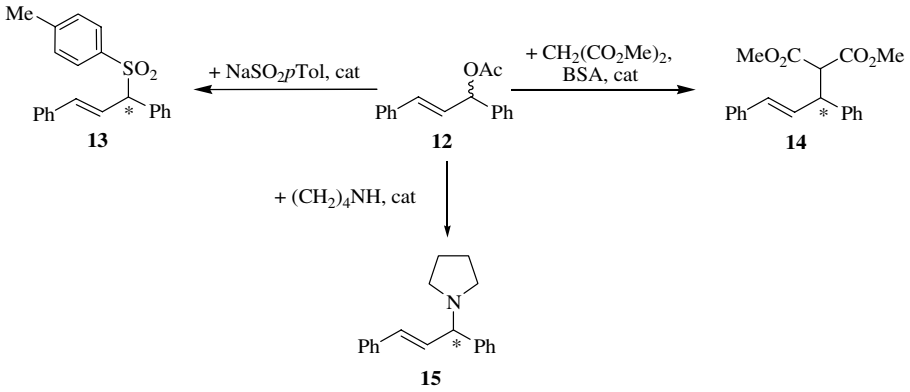
Table 1. ^{31}P NMR chemical shifts ($CDCl_3$) and cone angles θ (deg) of ligands **1**–**11**

Ligand	δ_P	θ[a]
1	141.5 (95%), 151.2 (5%)[b]	97.9
2	141.0 (97%), 147.1 (3%)	90.4
3	152.5	122.3
4	138.7 (66%), 143.9 (34%)	121.5
5	138.5 (62%), 141.7 (38%)	102.3
6	138.8 (36%), 140.1 (64%)	117.6
7	140.1 (67%), 150.7 (33%)	106.4
8	136.1 (78%), 141.5 (22%)	101.4
9	134.6 (96%), 140.4 (4%)	92.6
10	130.6 (98%), 139.3 (2%)	116.0
11a	128.2 (11%), 133.6 (89%)	145.0
11b	125.0 (9%), 131.2 (91%)	153.1
11c	128.0 (8%), 133.7 (92%)	146.2
11d	128.7 (5%), 134.1 (95%)	146.4

[a] Tolman's angles.
[b] Percentage of P^*-epimers.

The library of 14 novel P^*-chiral monodentate phosphite-type ligands was screened in the enantioselective Pd-catalysed allylic substitution of (*E*)-1,3-diphenylallyl acetate **12** as a benchmark test (Scheme 2). The reactions were performed in THF or CH_2Cl_2 at room temperature over 48 h (with $[Pd(allyl)Cl]_2$, L/Pd = 1 or 2) according to the published procedures.[2,7] The results obtained allowed us to divide the ligands into two groups containing different numbers of the ligands. Compounds **1**–**10** demonstrated poor to mediocre enantioselectivity and conversion. The highest enantioselectivites of products **13**, **14** and **15** were 59% (in the case of **8**), 54% and 17% (in the case of **9**), respectively. In general, there was no correlation between the efficiency of **1**–**10** and their Tolman's angles and the ratio of P^*-epimers. For example, practically enantiopure ligands **2** and **3** with different cone angles values (Table 1) gave no enantioselectivity in the synthesis of **13**–**15**. It should be noted that the well-known phosphoramidite $\mathbf{L_b}$ (Z = OMe),[3a] similar to **1**–**10** has shown moderate efficiency: up to 40% ee in the allylic sulfonylation of **12** with $NaSO_2p$Tol and up to 66% ee in the allylic alkylation of **12** with dimethyl malonate.

At the same time, the use of diamidophosphites **11a**–**d** resulted in moderate to good yields and enantioselectivities of the products in most cases (Tables 2 and 3). Hence, for these ligands, cationic palladium catalysts **16a**–**d** were prepared according to known procedures[2] (Scheme 3). In the allylic sulfonylation, employing complex **16b** as the chiral auxiliary, product **13** was obtained in 70% ee (Table 2, entry 6). On the other hand, complex **16a** was found to be the best catalyst in the allylic



Scheme 2. Pd-catalysed allylation.

alkylation. The highest enantioselectivity (84% ee) was obtained in CH_2Cl_2 (Table 2, entry 15). Diamidophosphites **11c,d** with an additional C^*-stereocentre in the N(CH(Ph)Me) moieties were less efficient. They led

Table 2. Pd-catalysed allylic sulfonylation of **12** with $NaSO_2pTol$ (20 °C, 48 h) and allylic alkylation of **12** with dimethyl malonate (BSA, KOAc, 20 °C, 48 h)

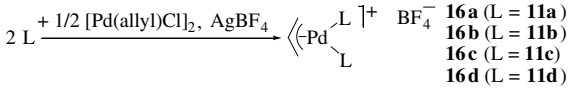
Entry	Catalyst	L/Pd	Solvent	Conv.[a,b] (%)	ee[c,d] (%)
Allylic sulfonylation					
1	[Pd(allyl)Cl]$_2$/**11a**	1/1	THF	48	46 (*S*)
2	[Pd(allyl)Cl]$_2$/**11a**	2/1	THF	52	58 (*S*)
3	**16a**	2/1	THF	50	39 (*S*)
4	[Pd(allyl)Cl]$_2$/**11b**	1/1	THF	80	55 (*S*)
5	[Pd(allyl)Cl]$_2$/**11b**	2/1	THF	60	40 (*S*)
6	**16b**	**2/1**	**THF**	**65**	**70 (*S*)**
7	[Pd(allyl)Cl]$_2$/**11c**	1/1	THF	34	34 (*S*)
8	[Pd(allyl)Cl]$_2$/**11c**	2/1	THF	71	33 (*S*)
9	**16c**	2/1	THF	49	11 (*S*)
10	[Pd(allyl)Cl]$_2$/**11d**	1/1	THF	32	43 (*S*)
11	[Pd(allyl)Cl]$_2$/**11d**	2/1	THF	30	49 (*S*)
12	**16d**	2/1	THF	53	56 (*S*)
Allylic alkylation					
13	[Pd(allyl)Cl]$_2$/**11a**	1/1	CH_2Cl_2	83	47 (*S*)
14	[Pd(allyl)Cl]$_2$/**11**	2/1	CH_2Cl_2	65	30 (*S*)
15	**16a**	**2/1**	**CH_2Cl_2**	**100**	**84 (*S*)**
16	**16a**	2/1	THF	40	19 (*S*)
17	[Pd(allyl)Cl]$_2$/**11b**	1/1	CH_2Cl_2	36	36 (*S*)
18	[Pd(allyl)Cl]$_2$/**11b**	2/1	CH_2Cl_2	80	17 (*S*)
19	[Pd(allyl)Cl]$_2$/**11b**	1/1	THF	21	23 (*S*)
20	[Pd(allyl)Cl]$_2$/**11b**	2/1	THF	40	53 (*S*)
21	**16b**	2/1	CH_2Cl_2	90	30 (*S*)
22	**16b**	2/1	THF	22	26 (*S*)
23	[Pd(allyl)Cl]$_2$/**11c**	1/1	CH_2Cl_2	21	11 (*S*)
24	[Pd(allyl)Cl]$_2$/**11c**	2/1	CH_2Cl_2	95	61 (*S*)
25	[Pd(allyl)Cl]$_2$/**11c**	1/1	THF	16	28 (*S*)
26	[Pd(allyl)Cl]$_2$/**11c**	2/1	THF	12	2 (*S*)
27	**16c**	2/1	CH_2Cl_2	26	45 (*S*)
28	**16c**	2/1	THF	78	3 (*S*)
29	[Pd(allyl)Cl]$_2$/**11d**	1/1	CH_2Cl_2	65	50 (*S*)
30	[Pd(allyl)Cl]$_2$/**11d**	2/1	CH_2Cl_2	90	60 (*S*)
31	[Pd(allyl)Cl]$_2$/**11d**	1/1	THF	50	59 (*S*)
32	[Pd(allyl)Cl]$_2$/**11d**	2/1	THF	30	65 (*S*)
33	**16d**	2/1	CH_2Cl_2	74	65 (*S*)
34	**16d**	2/1	THF	55	72 (*S*)

[a] Isolated yield of **13** from the allylic sulfonylation.
[b] Conversion of **12** in allylic alkylation was determined by HPLC (Daicel Chiralcel OD-H).
[c] Enantiomeric excess of **13** was determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 4:1, 1 ml/min, 254 nm).
[d] Enantiomeric excess of product **14** was determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH = 99:1, 0.6 ml/min, 254 nm).

Table 3. Pd-catalysed allylic amination of **12** with pyrrolidine (20 °C, 48 h)

Entry	Catalyst	L/Pd	Solvent	Conv.[a] (%)	ee[b] (%)
1	[Pd(allyl)Cl]$_2$/**11c**	1/1	CH_2Cl_2	85	11 (*S*)
2	[Pd(allyl)Cl]$_2$/**11c**	2/1	CH_2Cl_2	94	20 (*S*)
3	[Pd(allyl)Cl]$_2$/**11c**	1/1	THF	10	25 (*S*)
4	[Pd(allyl)Cl]$_2$/**11c**	2/1	THF	21	5 (*S*)
5	**16c**	2/1	CH_2Cl_2	24	20 (*S*)
6	**16c**	2/1	THF	95	45 (*S*)
7	[Pd(allyl)Cl]$_2$/**11d**	1/1	CH_2Cl_2	85	58 (*R*)
8	[Pd(allyl)Cl]$_2$/**11d**	2/1	CH_2Cl_2	97	62 (*R*)
9	[Pd(allyl)Cl]$_2$/**11d**	1/1	THF	100	66 (*R*)
10	[Pd(allyl)Cl]$_2$/**11d**	2/1	THF	100	63 (*R*)
11	**16d**	2/1	CH_2Cl_2	68	47 (*R*)
12	**16d**	2/1	THF	62	26 (*R*)
13	[Pd(allyl)Cl]$_2$/**17**	1/1	CH_2Cl_2	43	89 (*R*)
14	**[Pd(allyl)Cl]$_2$/17**	**2/1**	**CH_2Cl_2**	**100**	**91 (*R*)**
15	**18**	2/1	CH_2Cl_2	67	90 (*R*)
16	**18**	2/1	THF	48	88 (*R*)

[a] Conversion of **12** in allylic amination was determined by HPLC (Daicel Chiralcel OD-H).
[b] Enantiomeric excess of product **15** was determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*PrOH/Et_2NH = 200:1:0.1, 0.9 ml/min, 254 nm).



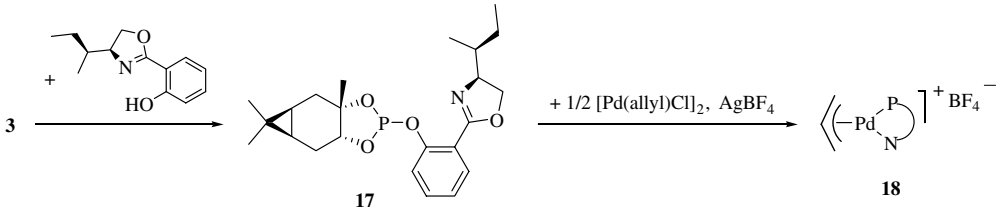
Scheme 3.

to the formation of products **13** and **14** with *S*-configuration and with higher optical yields for **11d** due to a matched combination of the (2*R*,5*S*)-phosphocentre with the N[(*R*)-CH(Ph)Me] fragment. In contrast, only poor stereoselectivity was obtained in the Pd-catalysed allylic amination of **12** with pyrrolidine using ligands **11a** (up to 35% ee) and **11b** (up to 12% ee). Compounds **11c** and **11d** were found to be more efficient catalysts, enantioselectivities up to 45% and 66% ee, respectively, were obtained in THF as the optimal solvent (Table 3, entries 6 and 9). Opposite enantiomers of the amine were formed when using **11c** and **11d** (Table 3, entries 1–6 and 7–12). It can be assumed that ligands **11a**–**d** lead to a better chiral induction than compounds **1**–**10** due to their high steric demands (Table 1, $\theta = 145$–$153°$) and the presence of a rigid 1,3-diaza-2-phosphabicyclo[3.3.0]octane framework.

Another approach to enhance the asymmetrising activity of *P**-chiral phosphite-type compounds is the synthesis of the respective P,N-bidentate ligands with additional *C**-stereocentres in the peripheral N-containing group. In particular, we have prepared oxazolinophosphite **17** using phosphoramidite **3** as a phosphorylating reagent (Scheme 4).[8] Compound **17** acts as a typical P,N-bidentate ligand to form chelate cationic complex **18** by reaction with [Pd(allyl)Cl]$_2$ according to the published procedure (Scheme 4).[9,10] Using the allylic amination of (*E*)-1,3-diphenylallyl acetate **12** with pyrrolidine as an example (Scheme 2), it was shown that the use of Pd-catalysts with oxazolinophosphite **17** leads to a dramatic improvement in enantioselectivity. Starting compound **3** as well as ligand **2** produced reaction product **15** as an almost racemic mixture, whereas up to 91% ee was achieved using **17** (Table 3, entries 13–16).

A new family of ligands with *P**-stereocentres has been prepared from inexpensive optically active precursors. These novel ligands were tested in Pd-catalysed asymmetric allylic amination. The catalytic performance is affected greatly by the structure of the phosphocentre of the ligand.

In summary, new modular *P**-chiral phosphite-type ligands require a systematic search for adequate catalytic transformations. As stated above, ligand $\mathbf{L_b}$ results in only moderate enantioselectivity in Pd-catalysed allylations, but is excellent in Rh-catalysed hydrogenation. Further testing of ligands **1**–**11** and **17** in other benchmark reactions is in progress in our laboratory.



Scheme 4.

Acknowledgements

The authors gratefully acknowledge receiving the chiral HPLC columns (*R*,*R*)-WHELK-01 from Regis Technologies (USA) and Chiralcel OD-H from Daicel Chemical Industries, Ltd (Japan). This work was supported by the INTAS Open Call 2005–2006 Grant (INTAS Ref. No. 05-1000008-8064) and RFBR Grant No. 06-03-90898-Mol-a. Eduard B. Benetsky thanks the Russian Science Support Foundation for a research fellowship.

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4. (a) *General procedure for the preparation of ligands* **1**, **2** and **4**–**11a**–**d**: A solution of the appropriate diol, aminoalcohol or diamine (5 mmol) in benzene (15 ml) was added dropwise at 0 °C over 20 min to a vigorously stirred solution of PCl_2OMe (0.66 g, 5 mmol) and Et_3N (1.45 ml, 10.4 mmol) in benzene (25 ml). The mixture was then briefly heated to the boiling point and cooled to 20 °C. Solid $Et_3N{\cdot}HCl$ was filtered off, and the filtrate concentrated in vacuo (40 Torr). The residue was dried for 30 min at 10 Torr and distilled in vacuo (1 Torr) to give the desired product. Yields: 65–81%. Spectral data of **11d**: ^{13}C NMR (100.6 MHz, $CDCl_3$): 23.3 (d, $^3J = 15.9$ Hz, CH_3), 26.0 (s, CH_2), 31.8 (s, CH_2), 48.6 (d, $^2J = 36.4$ Hz, CH_2N), 49.8 [s, CH(Ph)], 54.1 (d, $^2J = 8.7$ Hz, $CHCH_2N$), 56.7 (d, $^2J = 12.1$ Hz, CH_3OP), 63.6 (d, $^2J = 10.6$ Hz, CHN); 126.3 (d, $^3J = 20.9$ Hz), 126.6 (s), 128.1 (s), 144.8 (s) (C_{Ar}). MS (EI), *m*/*z* (*I*, %): 264 (42) $[M]^+$. Anal. Calcd for $C_{14}H_{21}N_2OP$: C, 63.62; H, 8.01; N, 10.60. Found: C, 63.85; H, 8.18; N, 10.36. (b) *Procedure for the preparation of ligand* **3**: A mixture of (1*S*,3*S*,4*R*,6*R*)-3,7,7-trimethylbicyclo[4.1.0]heptane-3,4-diol (1.70 g, 10 mmol) and $P(NEt_2)_3$ (2.47 g, 10 mmol) was stirred at 120 °C for 40 min. Then, the mixture was stirred in vacuo (10 Torr, 80 °C) for 30 min in order to remove $HNEt_2$ and distilled. Yield: 72%. Colourless oil, bp 81–82 °C (1 Torr). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.9 (s, CH), 15.3 (d, $^3J = 2.2$ Hz, CH_3CH_2N), 16.8 (d, $^4J = 1.5$ Hz, CH), 17.7 (d, $^3J = 3.7$ Hz, CH_3), 18.3 (s, C), 24.8 (d, $^3J = 5.8$ Hz, CH_2), 27.9 (s, CH_3), 28.2 (s, CH_3), 31.8 (d, $^3J = 3.6$ Hz, CH_2), 37.3 (d, $^2J = 21.2$ Hz, CH_2N), 80.0 (d, $^2J = 8.0$ Hz, CHOP), 81.1 (s, COP). MS (EI), *m*/*z* (*I*, %): 271 (5) $[M]^+$, 119 (100). Anal. Calcd for $C_{14}H_{26}NO_2P$: C, 61.97; H, 9.66; N, 5.16. Found: C, 62.24; H, 9.78; N, 4.95.
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8. *Procedure for the preparation of ligand* **17**: A mixture of 2-((*S*)-4-*sec*-butyl-4,5-dihydrooxazol-2-yl)phenol (1.10 g, 5 mmol) and compound **3** (1.36 g, 5 mmol) was stirred at 120 °C for 40 min. Then the mixture was stirred in vacuo (10 Torr, 80 °C) for 30 min in order to remove $HNEt_2$. Yield: 91%. Colourless oil. ^{31}P NMR (162.0 MHz, $CDCl_3$): 125.7 (s, 7%) and 133.0 (s, 93%). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 11.4 [s, CH_3 (*sec*-Bu)], 14.4 [s, CH_3 (*sec*-Bu)],14.7 (s, CH), 15.6 (s, CH), 16.9 (s, CH_3), 17.8 (s, C), 23.6 (d, $^3J = 5.1$ Hz, CH_2), 25.9 [s, CH_2 (*sec*-Bu)], 28.1 (s, CH_3), 28.6 (s, CH_3), 31.0 (d, $^3J = 3.7$ Hz, CH_2), 39.1 [s, CH (*sec*-Bu)], 69.4 (s, CH_2O), 71.3 (s, CHN), 80.6 (d, $^2J = 8.0$ Hz, CHOP), 83.3 (d, $^2J = 8.8$ Hz, COP); 121.0, 123.1, 127.8, 131.7, 133.1, 151.1 (d, $^2J = 4.4$ Hz), all C_{Ar}; 161.9 (s, C=N). MS (EI), *m*/*z* (*I*, %): 417 (3) $[M]^+$, 200 (100). Anal. Calcd for $C_{23}H_{32}NO_4P$: C, 66.17; H, 7.73; N, 3.36. Found: C, 66.37; H, 7.82; N, 3.55.
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10. *Spectral data of* **18**: ^{31}P NMR (162.0 MHz, $CDCl_3$): δ_P 140.1 (s). MS (MALDI TOF/TOF), *m*/*z* (*I*, %): 565 (100) $[M-BF_4]^+$. Anal. Calcd for $C_{26}H_{37}BF_4NO_4PPd$: C, 47.91; H, 5.72; N, 2.15. Found: C, 48.17; H, 5.52; N, 2.26.