$(PPh_3)I$ complex, it was converted to $[CpRu(CO)(PPh_3)(acetone)]SbF_6$ for reuse. The optical purity of the sulfoxide could be determined by the ^1H NMR spectrum of the neomenthylcyclopentadienyl analogue of 1 (Figure 2), which was generated by the reaction between $[NMCpRu(CO)(PPh_3)]SbF_6$ and the sulfoxide. The differentiation of the resonances in (R_{Ru},R_S) and (S_{Ru},S_S) centers arises because they are diastereomeric in the presence of the neomenthyl group. The 490-MHz ^1H spectra in Figure 2 illustrate the improvement possible in a single precipitation. The spectrum in Figure 2a shows the initial ratio of enantiomers, and Figure 2b shows the ratio after the sulfoxide is released from the product remaining in solution after precipitation of the racemates. Minor variations in chemical shift are observed with concentration changes.

$$[CpRu(CO)(PPh_3)(t\text{-}BuMeSO)]^+ + I^- \rightarrow CpRu(CO)(PPh_3)I + t\text{-}BuMeSO \quad (2)$$

Chiroptical Properties. Negative rotations are observed at the Na_D line for both (S_{Ru},S_S)-**1A** and (R_{Ru},S_S)-**1B** owing to an intense negative CD band at 277 nm in both of them. Two much weaker negative CD bands are observed in (–)-(S_{Ru},S_S)-**1A** at 317 and 379 nm.

Conclusion

The efficacy of $[CpRu(CO)(PPh_3)]SbF_6$ as a reagent for the resolution of sulfoxides has been demonstrated. As the racemate of either **1A** or **1B** is less soluble than the pure enantiomer, enhancement of the enantiomeric purities of the soluble enantiomers is readily effected via precipitation of the racemate. The thermodynamic stability of **1A** relative to **1B** effectively provides a route to transform a racemic $CpRu(CO)(PPh_3)X$ complex into a complex with a nearly pure stereogenic Ru center.

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Supplementary Material Available: Tables of bond distances and angles and *U* values (3 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal Structure of $[\{Li(2,4,6\text{-}^tBu_3C_6H_2)\}\{LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)\}]_2$: A Compound with an Unusual $(LiPLiC)_2$ Eight-Membered Ring

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Summary: $[\{Li(2,4,6\text{-}^tBu_3C_6H_2)\}\{LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)\}]_2$ is formed during the synthesis of $LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)$. The X-ray structural analysis shows the presence of four two-coordinate Li atoms, of which two exhibit a short Li–C(aryl) σ-bond. The other two Li atoms exhibit nearly six identical Li–C(aryl) distances ($\overline{Li–C}$ 2.31 Å) and a short lithium to ring center distance (1.83 Å). The latter suggests an η^6 coordination of the aromatic system to the lithium atom.

In addition to being indispensible reagents for preparative organometallic and organic chemistry, lithium compounds often exhibit fascinating structures in the solid state.[1] In the compounds studied up to now, the Li atom exhibits a pronounced tendency to interact with electron-rich ligands or donor molecules. In many cases, the structures cannot be explained in terms of classical bonding theory. Thus the formation of covalent multicenter bonds and σ-bonds as well as interactions with π-systems is observed. We now report the structure of compound **6** in which the two lithium reagents $Li(2,4,6\text{-}^tBu_3C_6H_2)$ (**1**) and $LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)$ (**5**) associate with formation of a central eight-membered $(LiPLiC)_2$ ring.

The reaction of $Li(2,4,6\text{-}^tBu_3C_6H_2)$ (**1**) with PCl_3, followed by reduction with $LiAlH_4$, is reported to give $H_2P(2,4,6\text{-}^tBu_3C_6H_2)$ (**4**) in almost quantitative yield.[2] However, when we reacted **4**, prepared by the literature method, with ^nBuLi in hexane, we obtained $LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)$ (**5**) in only 62% yield. After 3 days, large colorless crystals of $[\{Li(2,4,6\text{-}^tBu_3C_6H_2)\}\{LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)\}]_2$ (**6**) were isolated from the filtrate. We subsequently found, by means of Cl analysis, that the reaction of **1** with PCl_3 followed by $LiAlH_4$ reduction gives a mix-

Scheme I

$Li(2,4,6\text{-}^tBu_3C_6H_2)$ (1)

$\downarrow + PCl_3$

$Cl_2P(2,4,6\text{-}^tBu_3C_6H_2)$ (2) + $Cl(2,4,6\text{-}^tBu_3C_6H_2)$ (3)

$\downarrow + LiAlH_4$

$H_2P(2,4,6\text{-}^tBu_3C_6H_2)$ (4) + $Cl(2,4,6\text{-}^tBu_3C_6H_2)$ (3)

$\downarrow + {}^nBuLi$

$LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)$ (5) (FAST) +

$[\{Li(2,4,6\text{-}^tBu_3C_6H_2)\}\{LiP(H)(2,4,6\text{-}^tBu_3C_6H_2)\}]_2$ (6) (SLOW)

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[1] Setzer, W. N.; v. Ragué-Schleyer, P. *Adv. Organomet. Chem.* **1985**, *24*, 353 and literature cited therein.

[2] Cowley, A. H.; Norman, N. C.; Pakulski, M. *Inorg. Synth.* **1990**, *27*, 235.

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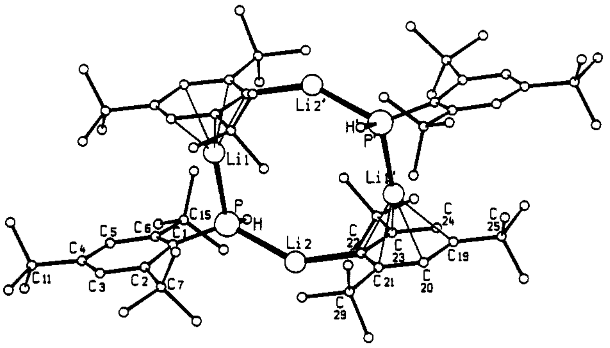

Figure 1. Molecular structure of 6 [{Li(2,4,6-$^tBu_3C_6H_2$)}{LiP(H)(2,4,6-$^tBu_3C_6H_2$)}]$_2$ (SCHAKAL plot). Selected bond lengths (Å) and angles (deg): P–C1 = 1.863 (7), P–Li1 = 2.47 (1), P–Li2 = 2.47 (1), P–H = 1.59 (8), Li1′–C19 = 2.35 (1), Li1–C20 = 2.33 (1), Li1′–C21 = 2.29 (1), Li1′–C22 = 2.31 (1), Li1′–C23 = 2.28 (1), Li1′–C24 = 2.31 (1), Li2–C22 = 2.09 (1), Li2–P–C1 = 132.5 (4), Li2–P–Li1 = 114.4 (4), Li1–P–C1 = 106.9 (4), P–Li2–C22 = 144.3 (6). Hydrogen atoms are omitted for clarity.

ture of 4 and Cl(2,4,6-$^tBu_3C_6H_2$) (3) in the approximate ratio 2:1, suggesting that in addition to the expected nucleophilic substitution to give Cl_2P(2,4,6-$^tBu_3C_6H_2$) (2), Li/Cl exchange to give 3 also occurs (see Scheme I). Lithium/chlorine exchange has also been observed in the reaction of $POCl_3$ with Li(2,4,6-$^tBu_3C_6H_2$) (1).[3]

The crystal structure of 6 is shown in Figure 1.[4] Atomic coordinates and thermal parameters of 6 are listed in Table I. The compound is made up of two molecules of the lithium aryl 1 and two molecules of the lithium phosphide 5. The association of 1 and 5 to give 6 initially results from an Li–P interaction, which has also been observed for other lithium phosphides.[5] The coordination sphere of the lithium atom Li1 is completed through association of two 1/5 units, whereby Li1 and Li1′ interact with the aromatic system of the lithium aryls 1′ and 1, respectively. The resulting centrosymmetric eight-membered ring [Li1, P, Li2, C22, and inverse atoms (′)] is slightly puckered, the maximum deviation from the best plane being 0.26 Å (Li2). A general principle for the dimerization of lithium reagents has been described in the literature:[6] The compound α-lithio-2,6-dimethylpyridinetetramethylethylenediamine also forms centrosymmetric dimeric molecules, which exhibit a central eight-membered $(LiCCN)_2$ ring.[6] The P(H)(2,4,6-$^tBu_3C_6H_2$)$^-$ anion has two alternative sites for interaction with the Li^+ ion—the P atom and the aromatic ring. The formation of dimers allows both sites to be used simultaneously.

The Li atoms Li1 and Li2 in 6 have a formal coordination number of 2, which in contrast to the coordination numbers 3 and 4, is only observed in the presence of sterically demanding ligands.[7] The P–Li distances are identical [2.47 (1) Å] and lie at the lower end of the range of values observed for lithium phosphides (2.44–2.67 Å).[5] The coordination of the P atom by the two Li atoms Li1 and Li2 and the C atom C1 of the 2,4,6-$^tBu_3C_6H_2$ ligand is almost trigonal planar (sum of angles (Li1, Li2, C1)–P 353.8°, deviation of P from the Li1, Li2, C1 plane −0.31 Å). Accordingly, the average element–P–H angle is 99° (Li2–P–H 90 (2), Li1–P–H 113 (3), C1–P–H 95 (2)°).

Table I. Atomic Coordinates and Thermal Parameters U_{eq} (Å^2) for 6 (Standard Deviations in Parentheses)[a]

atom	x/a	y/b	z/c	U_{eq}/U_{iso}
P	0.7730 (2)	0.0372 (1)	0.6015 (1)	0.0340 (6)
C1	0.9019 (5)	0.0747 (3)	0.6792 (4)	0.027 (3)
C2	0.9101 (6)	0.1443 (3)	0.6865 (4)	0.030 (3)
C3	0.9887 (6)	0.1716 (3)	0.7583 (4)	0.034 (3)
C4	1.0637 (6)	0.1356 (3)	0.8210 (4)	0.033 (3)
C5	1.0645 (6)	0.0685 (3)	0.8085 (4)	0.036 (3)
C6	0.9910 (5)	0.0368 (3)	0.7383 (4)	0.030 (2)
C7	0.8400 (6)	0.1926 (3)	0.6170 (5)	0.035 (3)
C8	0.7061 (6)	0.1897 (3)	0.6120 (5)	0.049 (3)
C9	0.8724 (6)	0.1803 (3)	0.5277 (4)	0.047 (3)
C10	0.8736 (6)	0.2652 (3)	0.6390 (5)	0.060 (3)
C11	1.1440 (7)	0.1675 (4)	0.9027 (5)	0.042 (3)
C12	1.145 (1)	0.2382 (5)	0.8982 (7)	0.196 (8)
C13	1.2665 (7)	0.1471 (6)	0.9117 (7)	0.198 (8)
C14	1.1069 (8)	0.1482 (6)	0.9840 (5)	0.166 (8)
C15	1.0095 (6)	−0.0338 (3)	0.7289 (5)	0.036 (3)
C16	1.1265 (6)	−0.0611 (3)	0.7889 (5)	0.072 (4)
C17	0.9113 (6)	−0.0777 (3)	0.7602 (5)	0.051 (3)
C18	1.0269 (6)	−0.0559 (3)	0.6366 (4)	0.050 (3)
C19	0.4285 (6)	−0.0569 (3)	0.1804 (5)	0.037 (3)
C20	0.4406 (6)	0.0099 (3)	0.1935 (4)	0.034 (3)
C21	0.5193 (6)	0.0374 (4)	0.2685 (4)	0.032 (3)
C22	0.5935 (6)	−0.0026 (3)	0.3320 (4)	0.030 (3)
C23	0.5821 (6)	−0.0717 (3)	0.3171 (4)	0.033 (3)
C24	0.5028 (6)	−0.0972 (3)	0.2427 (4)	0.035 (3)
C25	0.3432 (7)	−0.0857 (4)	0.1006 (5)	0.045 (3)
C26	0.2239 (7)	−0.0553 (5)	0.0916 (6)	0.141 (6)
C27	0.3858 (7)	−0.0719 (6)	0.0208 (5)	0.162 (8)
C28	0.323 (1)	−0.1551 (5)	0.1090 (7)	0.229 (8)
C29	0.5236 (6)	0.1135 (3)	0.2731 (4)	0.035 (3)
C30	0.5590 (6)	0.1413 (3)	0.1903 (4)	0.046 (3)
C31	0.4023 (5)	0.1395 (3)	0.2810 (4)	0.045 (3)
C32	0.6157 (6)	0.1377 (3)	0.3532 (4)	0.050 (3)
C33	0.6608 (6)	−0.1200 (3)	0.3830 (4)	0.029 (3)
C34	0.7909 (5)	−0.1022 (3)	0.3936 (4)	0.045 (3)
C35	0.6195 (5)	−0.1134 (3)	0.4717 (4)	0.045 (3)
C36	0.6452 (6)	−0.1905 (3)	0.3536 (5)	0.054 (3)
Li1	0.604 (1)	0.0333 (6)	0.6783 (7)	0.042 (4)
Li2	0.713 (1)	0.0372 (7)	0.4392 (8)	0.045 (5)

[a] $U_{eq} = {}^1/_3(U_{ij}a^*(i)a^*(j)a(i)a(j))$.

The planar six-membered rings deviate considerably from ideal D_{6h} symmetry (C23–C22–C21 115.7°, C2–C1–C6 117.2°), which has also been found for other metalated phenyl derivatives (in Li(tmpn)P(H)(2,4,6-$^tBu_3C_6H_2$), tmpn = $Me_2NCH(Me)CH_2NMe_2$, this angle is 113.6°;[8] cf. also ref 9).

The bond length Li2–C22 [2.09 (1) Å] lies at the lower end of the range of Li–C distances observed for organolithium compounds that formally contain an Li–C σ-bond [cf. $LiCH(SiMe_3)_2$, Li–C 2.03 (6) Å,[10] $Li(Et_2O)_2$(2,4,6-$Ph_3C_6H_2$), Li–C 2.07 (2) Å,[11] Li(pmdeta){$C(SiMe_3)_2H$}, Li–C 2.13 Å,[12] Li(tmpn)P(H)(2,4,6-$^tBu_3C_6H_2$), Li–C 2.117 (9) Å[8]

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or a multicenter bond [e.g., $\{Li(tmeda)(\mu\text{-}Ph)\}_2$, Li–C 2.208, 2.278 Å[13]], indicating strong bonding between the Li atom and the C atom of the aromatic ring. In addition to this σ-bond, there is also interaction of the planar aromatic system C19–C24 with Li1′.

Whereas the η^5 coordination predicted theoretically for cyclopentadienyllithium[14] has been confirmed experimentally,[15] the η^6 coordination with C_{6v} symmetry expected for the interaction of lithium fragments (Li^+, LiH) with benzene[14,16] has so far only been observed in the gas phase[17] and in the double-sandwich compound lithium indenofluorenide.[18] Thus the widely differing Li–C distances in those organolithium compounds in which solvated Li centers are coordinated to opposite sides of neighboring six-membered rings of mesomerically stabilized anions such as lithium naphthalenide [2.26 (1)–2.66 (1) Å[19]] and lithium anthracenide [2.273 (7)–2.671 (5) Å[20]] indicate unsymmetrical coordination of the aromatic system. In contrast, the almost equal Li1′–C(aryl) distances [2.28 (1)–2.35 (1) Å, $\overline{\text{Li–C}}$ 2.31 (1) Å] and short Li1′–Cen (Cen = center of aromatic ring) distance [1.83 (1) Å] in **6** indicate an arene-like η^6 coordination of the aromatic ring of the neutral compound **1** to Li1′, a coordination that has also been observed for lithium indenofluorenide [Li–C(aryl) 2.343 (4)–2.453 (5) Å[18]], $[\{Li(2,4,6\text{-}Me_3C_6H_2)N\}_2SiMe_2]_2$ [Li–C(aryl) 2.347 (8)–2.43 (1) Å[21]], and some other main-group elements[22] as well as for potassium[23] and sodium compounds[24] in the solid state.

The theoretically calculated values for the lithium–benzene complex $HLi(C_6H_6)$ ($\overline{\text{Li–C}}$ 2.303 Å, Li–Cen 1.829 Å)[14] are in good agreement with the distances found for **6**. The lithium/aromatic ring system has six interstitial electrons and thus fulfills the requirements for a nido cluster,[14] whereby the aromatic system forms the base and the lithium atom the vertex of a hexagonal pyramid. The almost linear arrangement of P–Li1–Cen′ (174.9 (7)°, Li1–Cen′–(ring plane)′ 87.4 (5)°) suggests sp hybridization of the two-coordinate Li atoms. The bonding of Li1 with the aromatic system C19′–C24′ can then be described in terms of the interaction of two empty p-orbitals and an sp hybrid orbital of Li1 with the a- and e-orbitals of the ring, which have the appropriate symmetry for orbital overlap. This interaction should lead to formation of three stabilized molecular orbitals.[14] The short Li1–ring distance of 1.83 Å (Li^+ radius 0.68 Å, half van der Waals radius of benzene ring 1.70 Å, sum of radii 2.38 Å) and the location of the Li atom almost exactly above the center of the ring also suggest that, in addition to the electrostatic interaction usually regarded as dominant in organolithium compounds, covalent bonding may also play a role here. It is nevertheless surprising that almost perfect η^6 coordination with the aromatic ring is possible in spite of the strong interaction between Li2 and C22. A possible reason is that the sterically demanding ${}^tBu$ groups cause displacement of the Li atom toward the center of the ring. We hope to obtain more exact information about the nature of the interaction from theoretical calculations.

Experimental Section

$H_2P(2,4,6\text{-}{}^tBu_3C_6H_2)$ (**4**) was prepared according to the literature procedure.[2]

$1,3,5\text{-}{}^tBu_3C_6H_3$ (Fluka). ^1H NMR (C_6D_6, 25 °C, δ/ppm): 1.43 (s, ${}^tBu$), 7.47 (s, ${}^tBu_3C_6H_3$).

$Br(2,4,6\text{-}{}^tBu_3C_6H_2)$ was prepared according to ref 2. ^1H NMR (C_6D_6, 25 °C, δ/ppm): 1.36 (s, p-${}^tBu$), 1.64 (s, o-${}^tBu$), 7.58 (s, m-H).

$Cl_2P(2,4,6\text{-}{}^tBu_3C_6H_2)$ (2) was prepared according to ref 2. Whereas an almost quantitative yield of **2** is reported in the literature, we observe formation of **2** in 69% yield and **3** in 31% yield (elemental analysis). ^{31}P NMR (C_6D_6, 25 °C, δ/ppm) data for this mixture of **2** and **3**: 153.1, s (lit. 155 ppm, THF).

$H_2P(2,4,6\text{-}{}^tBu_3C_6H_2)$. A mixture of 26 g (75 mmol) $Cl_2P(2,4,6\text{-}{}^tBu_3C_6H_2)$ (**2**) and 9.7 g (34 mmol) $Cl(2,4,6\text{-}{}^tBu_3C_6H_2)$ (**3**) in THF is treated with 8.2 g (210 mmol) of $LiAlH_4$ according to ref 2. The product consists of 16.6 g (60 mmol) of $H_2P(2,4,6\text{-}{}^tBu_3C_6H_2)$ (**4**) and 9.7 g (34 mmol) of unreacted $Cl(2,4,6\text{-}{}^tBu_3C_6H_2)$ (**3**) (elemental analysis). ^1H NMR (C_6D_6, 25 °C, δ/ppm): 1.37 (s, p-${}^tBu$), 1.65 (s, o-${}^tBu$), 4.33 (d, P–H, ^1J(PH) 207 Hz), 7.60 (d, m-H, ^3J(PH) 3 Hz). ^{31}P NMR (C_6D_6, 25 °C, δ/ppm): −129.7 (t, ^1J(PH) 207 Hz).

There is no evidence of the presence of **3** in the NMR spectrum. Apparently, the chemical shifts of the protons of the $2,4,6\text{-}{}^tBu_3C_6H_2$ ligands are identical for **3** and **4** (cf. also chemical shifts for $Br(2,4,6\text{-}{}^tBu_3C_6H_2)$).

$LiP(H)(2,4,6\text{-}{}^tBu_3C_6H_2)$ (5) and $[\{Li(2,4,6\text{-}{}^tBu_3C_6H_2)\}\{LiP(H)(2,4,6\text{-}{}^tBu_3C_6H_2)\}]_2$ (6). To a solution of 10.5 g (38 mmol) of **4** and 6.05 g (21 mmol) of **3** in 400 mL of hexane is added at 0 °C 45 mL (65 mmol) of ${}^nBuLi$ (1.48 m solution in hexane). After 1 h at 0 °C and 2 h at room temperature, nearly quantitative precipitation of **5** has occurred. The slightly yellow precipitate of **5** is isolated by filtration and washed several times with hexane (250 mL). Yield: 9.9 g (35 mmol), 92% based on **4**.

5: pyrophoric, only slightly soluble in benzene, toluene, and hexane (solubility: 170 mg in 100 mL of hexane), soluble in donor solvents (THF, Et_2O, etc.). Mp: 127–130 °C, dec. ^{31}P NMR: (THF/1 drop of C_6D_6, 25 °C, δ/ppm) −107.7 (d, ^1J(PH) 172 Hz); (C_6D_6/1 drop of THF, 25 °C, δ/ppm): −121.1 (this shows that the chemical shift of lithium phosphides is solvent-dependent). ^7Li NMR (THF/C_6D_6, 25 °C, δ/ppm): 1.46 (s).

The filtrate consists of 650 mL of hexane, in which 1.1 g (4 mmol) of **5**, 6.05 g (21 mmol) of **3**, and 35 mmol of ${}^nBuLi$ are present. After 3 days at room temperature, colorless crystals of **6** precipitated from the red-orange filtrate. Yield: 1.4 g (1.2 mmol), 64% based on **5**, 12% based on **3**. Mp: 128 °C, dec, turns brown, melts at 228–230 °C.

6 is nearly insoluble in noncoordinating solvents. It is soluble in donor solvents, but the eight-membered ring is cleaved and $Li(2,4,6\text{-}{}^tBu_3C_6H_2)$ (**1**) decomposes at room temperature due to ether cleavage. ^{31}P NMR (C_7D_8/1 drop of THF, 25 °C, δ/ppm): −124.8 ($\Delta_{1/2}$ ca. 300 Hz). ^7Li NMR (C_7D_8/1 drop of THF, 25 °C, δ/ppm): 2.3 (t?, $\Delta_{1/2}$ ca. 120 Hz), 0.6 ($\Delta_{1/2}$ ca. 80 Hz). A sample of **6** was made up in THF/1 drop of C_7D_8 at −190 °C and kept at this temperature prior to NMR spectroscopic investigation. ^7Li NMR spectra were recorded from −80 to 20 °C in 20-deg intervals, and recording parameters were unchanged: (−80 °C) 2.2 (broad, $\Delta_{1/2}$ ca. 80 Hz), 0.1 (s); (−80 to −20 °C) no apparent change; (−20 °C) 2.0 ($\Delta_{1/2}$ ca. 25 Hz), 0.1 (s); (0 °C) both signals broaden; (20 °C) one broad signal at 0.5 ppm, $\Delta_{1/2}$ ca. 170 Hz.

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Supplementary Material Available: Tables of crystal data and details of intensity collection, positional parameters, anisotropic thermal parameters, least-squares planes, and bond lengths and angles and the molecular structure of $[\{Li(2,4,6\text{-}{}^tBu_3C_6H_2)\}\{LiP(H)(2,4,6\text{-}{}^tBu_3C_6H_2)\}]_2$ with complete atom labeling (11 pages). Ordering information is given on any current masthead page.

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Palladium(0)-Catalyzed Hydroboration of 1-Buten-3-ynes: Preparation of Allenylboranes

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Summary: Reaction of 2-substituted 1-buten-3-ynes ($CH_2{=}CR{-}C{\equiv}CH$) with catecholborane in the presence of a palladium catalyst bearing a monodentate phosphine ligand such as PPh_3 or $PPh_2(C_6F_5)$ proceeded in a 1,4-fashion to give (3-substituted 1,2-butadienyl)-1,3,2-benzodioxaboroles ($CH_3(R)C{=}C{=}CH(BO_2C_6H_4)$). Reaction of the allenylboranes with benzaldehyde gave the corresponding homopropargyl alcohols.

Recently, much attention has been paid to catalytic hydroboration of unsaturated compounds for its great potential in organic synthesis.[1-4] We have previously reported the asymmetric hydroboration of styrenes[2] and 1,3-dienes[3] catalyzed by rhodium–phosphine complexes, which proceeds with unusual regioselectivity and with high enantioselectivity. Here we report the palladium-catalyzed hydroboration of 1,3-enynes giving allenylboranes selectively and the effects of phosphine ligands on the selectivity in this reaction.

Suzuki and co-workers have briefly described[4] the formation of an allenylborane in the reaction of 2-methyl-1-buten-3-yne (**1a**) with catecholborane in the presence of $Pd(PPh_3)_4$. We examined the palladium-catalyzed hydroboration of **1a** (Scheme I), focusing our attention on the selectivity forming the allenylborane. Table I summarizes the results obtained for the reaction in the presence of several phosphine–palladium catalysts. Reaction of **1a** with 1.3 equiv of catecholborane in chloroform in the presence of 2 mol % of the palladium catalyst, generated in situ by mixing $Pd_2(dba)_3{\cdot}CHCl_3$ and triphenylphosphine (5 equiv per Pd), was completed in 30 min at 25 °C. The products, which were isolated by bulb-to-bulb distillation in 86% yield, consisted of allenylborane **2a**, (*Z*)-dienylborane **3a**, and (*E*)-dienylborane **4a** in a ratio of 38:37:25 (entry 2). Allenylborane **2a** is the product formed by

Scheme I

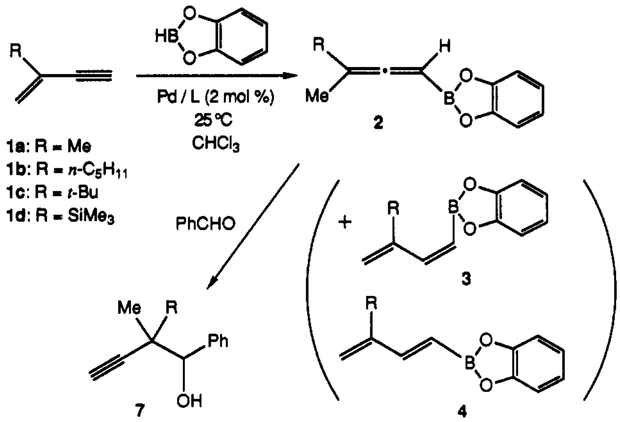

Table I. Hydroboration of 1-Buten-3-ynes 1 with Catecholborane Catalyzed by Palladium–Phosphine Complexes[a]

entry	substrate (R)	catalyst[b]	time (h)	yield[c] (%)	2/3/4[d]
1	**1a** (Me)	$Pd(PPh_3)_4$[e]	0.5	75	60/34/6
2	**1a** (Me)	$[Pd]/5PPh_3$	0.5	86	38/37/25
3	**1a** (Me)	$[Pd]/4PPh_3$	0.5	75	41/53/6
4	**1a** (Me)	$[Pd]/2PPh_3$	0.5	70	62/38/0
5	**1a** (Me)	$[Pd]/1.5PPh_3$	0.5	63	84/16/0
6	**1a** (Me)	$[Pd]/1PPh_3$	0.5	22	92/8/0
7	**1a** (Me)	[Pd]	5	0	
8	**1a** (Me)	[Pd]/dppe	2	39	0/0/100
9	**1a** (Me)	[Pd]/dppb	2	61	0/0/100
10	**1a** (Me)	[Pd]/dppf	0.5	89	0/0/100
11	**1a** (Me)	$[Pd]/2PPh_2(C_6F_5)$	0.5	73	83/17/0
12	**1b** (n-C_5H_{11})	$[Pd]/2PPh_2(C_6F_5)$	0.5	74	88/12/0
13	**1c** (t-Bu)	$[Pd]/2PPh_2(C_6F_5)$	2.5	89	83/4/13
14	**1d** ($SiMe_3$)	$[Pd]/2PPh_2(C_6F_5)$	0.5	46	*f*

[a] Carried out in chloroform at 25 °C with 1.2–1.5 equiv of catecholborane in the presence of 2 mol % of catalyst prepared from $Pd_2(dba)_3{\cdot}CHCl_3$ and a phosphine ligand. [b] $[Pd] = {}^1/_2Pd_2(dba)_3{\cdot}CHCl_3$. [c] Isolated yield by distillation. [d] Determined by ^1H NMR spectra. [e] 1 mol %. [f] The ratio was not determined.

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