# Regioselective Synthesis of Tricyclic 1,1-Diphosphines

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*Summary: A one-pot regioselective synthesis of tricyclic 1,1-diphosphines involving, first, insertion reaction of 2,3-dihydrophosphole (**3**) into the zirconium−carbon bond of a generated in situ zirconocene benzyne and, then, an exchange reaction between the resulting tricyclic metalated phosphine **4** and various dichlorophosphines is reported. One of these 1,1-diphosphines, **15a** (bis-(sulfide) adduct), is characterized by single-crystal X-ray diffraction studies.*

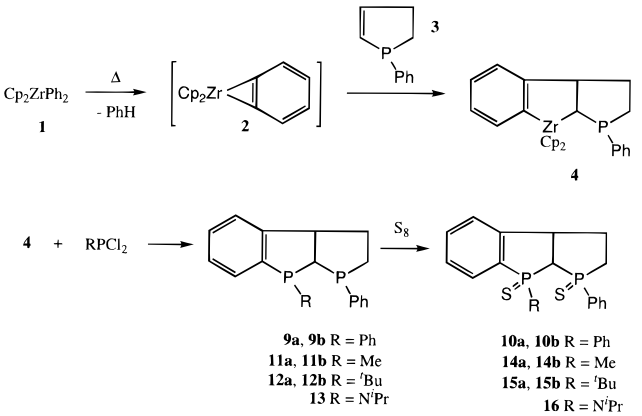


The use of 1,1-diphosphines as ligands is a common feature and is well documented.[1] Although a large number of methods exists for the synthesis of acyclic derivatives of this type, in contrast reports on compounds in which one of the two phosphorus atoms is included in a ring are rare[2,3] and to the best of our knowledge fused cyclic 1,1-diphosphines are even not known. The rigidity or at least the decrease of flexibility introduced by the presence of two (or more) rings should offer new perspectives for example for the formation of transition metal complexes and their use in catalysis.

The present work describes the development of a ring construction methodology from diphenylzirconocene (**1**) and 2,3-dihydrophosphole (**3**) leading to the regiospecific synthesis of the first tricyclic 1,1-diphosphines **9** and **11**−**13** and their corresponding disulfides **10** and **14**−**16**.

A clean insertion reaction of the dihydrophosphole **3** into the zirconium−carbon bond of the transient (benzyne)zirconocene (**2**)[4] occurs when **3** is heated with $Cp_2ZrPh_2$ (**1**) at 80 °C for 6 h (Scheme 1). Only one phosphorus derivative is formed quantitatively and is found to be the tricyclic compound **4** according to NMR data. The regiospecific synthesis of **4** can be regarded as the result of a strong interaction between the phosphorus lone pair and zirconium. Such a phenomenon was already observed when **3** was submitted to hydrozirconation by means of $[Cp_2ZrHCl]_n$ to give exclusively the α-metalated species PhPCH(ZrCp$_2$Cl)-$CH_2CH_2CH_2$ (**5**).[3] It can be noted that, under the same experimental conditions, the corresponding oxide $Ph_2P$-(O)CH=$CHCH_2CH_2$ (**6**) does not react with **1**.

**Scheme 1**




Attempts to obtain crystals of **4** suitable for X-ray structure determination failed up to now. Therefore, the study of the reactivity of **4** was undertaken to confirm the proposed structure.

Indeed, a clean reaction takes place when phenyldichlorophosphine is reacted with **4** in benzene at room temperature for 1 h (Scheme 1). The $^{31}$P NMR spectrum of the resulting mixture exhibits two sets of doublets of doublets at $\delta$ 5.5 and −4.9 ($J_{PP}$ = 38.1 Hz) and at $\delta$ −20.4 and −24.8 ($J_{PP}$ = 37.6 Hz) ppm, respectively. The phosphorus−phosphorus coupling constants are perfectly consistent with the formation of 1,1-diphosphines and not 1,2-diphosphines for which a smaller phosphorus−phosphorus coupling constant should be observed. This is exemplified by the values found for diphosphines **7** ($^2J_{PP}$ = 31.5 Hz) and **8** (trans, $^3J_{PP}$ = 8.9 Hz; cis, $^3J_{PP}$ = 0 Hz).[3b] Therefore structures **9a,b** can be attributed to these phosphorus derivatives which were isolated by chromatography as their disulfide adducts **10a,b** in a 1/1 ratio. Mass spectrometry corroborates such an assignment, and $^1$H and $^{13}$C NMR data confirm the construction of the tricyclic skeleton for the two isomers

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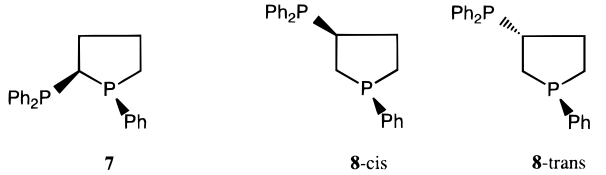



7 8-cis 8-trans

**10a,b**. One might assume that phosphorus in **4** has the Ph group on the convex face of the tricycle and that it retains its configuration in **10a,b**, so that **10a,b** differ in the configuration of phosphorus in the central ring.

Similar exchange reactions are performed with **4** and several dichlorophosphines such as $MePCl_2$, $^tBuPCl_2$, or $^iPr_2NPCl_2$. Two isomers in a 1/1 ratio are formed starting from $MePCl_2$[5] [$\delta(^{31}P)$: **11a**, −34.7, −25.1 ($^2J_{PP}$ = 37.2 Hz) ppm; **11b**, −34.2, −26.0 ($^2J_{PP}$ = 7.2 Hz) ppm] or from $^tBuPCl_2$ [$\delta(^{31}P)$: **12a**, −25.8, 15.8 ($^2J_{PP}$ = 128.9 Hz); **12b**, −9.1, 31.1 ($^2J_{PP}$ = 4.7 Hz) ppm] while only one is obtained from the reaction between **4** and $^iPr_2NPCl_2$ [$\delta(^{31}P)$: **13**, 61.5, −0.5 ($^2J_{PP}$ = 271.3 Hz) ppm] (Scheme 1). All these 1,1-diphosphines are isolated as their corresponding disulfide adducts, **14**−**16**, by chromatography, and their structures are clearly established by $^1H$ and $^{13}C$ NMR as well as by elemental analysis.

Somewhat unusual are the $^2J_{PP}$ values detected for **12a** ($^2J_{PP}$ = 128.9 Hz) and **13** ($^2J_{PP}$ = 271 Hz). However definite proof of the structure of the bis(sulfide) adduct of **12a**, i.e. **15a**, is provided by a single-crystal X-ray analysis showing a trans arrangement for the two P=S bonds (Figure 1). Since it is well established that sulfuration of phosphines takes place with retention of configuration,[6] a trans arrangement of the lone pair of the two phosphorus atoms can be proposed for **12a**. Such a conclusion can also reasonably be done for **13**.

These preliminary results point out the usefulness of the 2,3-dihydrophosphole **3** as a starting reagent for the formation of new tricyclic 1,1-diphosphines. In marked contrast the reaction of 3,4-dihydrophosphole (**17**) with $Cp_2ZrPh_2$ followed by addition of a dichlorophosphine does not afford the expected 1,2-diphosphine **18** (Scheme 2).

Extension of this methodology to the synthesis of various main group element containing polycylic systems is underway.

## Experimental Section

All manipulations were carried out under an argon atmosphere, either on a high-vacuum line using standard Schlenk techniques or in a glovebox. Benzene, pentane, hexane, and dichloromethane were treated with $LiAlH_4$, distilled, and stored under argon. NMR chemical shifts are expressed in ppm upfield from $Me_4Si$ ($^1H$ and $^{13}C$) and 85% $H_3PO_4$ ($^{31}P$). The $^{13}C$ NMR assignments were confirmed by proton-decoupled and/or selective heteronuclear-decoupled spectra.

**Zirconaindene−Phospholane 4.** To a solution of $Cp_2ZrPh_2$ (0.375 g, 1 mmol) in 3 mL of $C_6D_6$ was added phospholene **3** (0.162 g, 1 mmol) at room temperature. The resulting mixture was refluxed for 6 h and used as it was.

**4** (98% yield): $^{31}P\{^1H\}$ NMR ($C_6D_6$) $\delta$ −4.7; $^1H$ NMR ($C_6D_6$) $\delta$ 2.05−2.80 (m, 4H, $CH_2$), 3.12 (dd, $^3J$(HH) = 7.4, $^2J$(HP) = 0.8, 1H, PCHZr), 4.56 (dd, $^3J$(HH) = 7.4, $^3J$(HH) = 7.4, 1H, PCHC*H*), 5.62 (s, Cp), 5.83 (s, Cp), 7.07−7.22, 7.47−7.57 (m, 9H, Ph); $^{13}C$ NMR ($C_6D_6$) $\delta$ 32.7 (dd, $^3J$(CP) = 4.1, $PCH_2$), 37.1 (s, $PCH_2CH_2$), 49.1 (d, $^1J$(CP) = 37.0, PCHZr), 57.6 (s, PCH*C*H), 110.2 (s, Cp), 112.6 (s, Cp), 124.5, 125.2, 125.9 (s, $C_6H_4$), 129.2 (s, *p*-Ph), 129.6 (d, $J$(CP) = 6.6, $C_6H_4$), 132.3 (d, $J$(CP) = 15.8, *m*-Ph), 139.8 (d, $J$(CP) = 20.3, *o*-Ph), 143.9 (d, $^1J$(CP) = 34.3, *i*-Ph), 160.3 (d, $^3J$(CP) = 15.3, *C*CZr), 182.1 (d, $^3J$(CP) = 5.1, CZr).

**1,1-Diphosphine Disulfides 10a,b.** To a crude solution of the zirconaindene−phospholane **4** (0.459 g, 1 mmol) in 5 mL of benzene was added dichlorophenylphosphine (136 $\mu$L, 1 mmol) at 0 °C. After the mixture was stirred for 1 h at room temperature, sulfur (0.096 g, 3 mmol) was added and stirring was maintained for an additional 12 h. **10a,b** were further isolated by chromatography eluting with 9/1 dichloromethane/pentane solution (**10a**, $R_f$ = 0.25; **10b**, $R_f$ = 0.38).

**10a**: 40% yield; $^{31}P\{^1H\}$ NMR (THF) $\delta$ 45.3 (d, $J$(PP) = 3.2, PPh), 38.3 (d, $J$(PP) = 3.2, PPh); $^1H$ NMR ($CDCl_3$) $\delta$ 2.45 (m, 1H, $CH_2$), 2.74 (m, 1H, $CH_2$), 2.97 (m, 1H, $CH_2$), 3.20 (m, 1H, $CH_2$), 3.29 (ddd, $^3J$(HH) = 13.4, $^2J$(HP) = 17.9, $^2J$(HP) = 11.3, 1H, PCHP), 4.33 (m, 1H, PCHC*H*), 7.31−7.35, 7.50−7.58, 7.92−8.08 (m, 14H, Ph); $^{13}C$ NMR ($CDCl_3$) $\delta$ 26.2 (dd, $^2J$(CP) = 13.7, $^3J$(CP) = 2.7, $PCH_2CH_2$), 37.5 (dd, $^1J$(CP) = 55.9, $^3J$(CP) = 4.6, $PCH_2$), 50.9 (dd, $^2J$(CP) = 12.9, $^2J$(CP) = 7.5, PCH*C*H), 58.4 (dd, $^1J$(CP) = 56.5, $^1J$(CP) = 50.9, PCHP), 123.2 (d, $J$(CP) = 9.2, $C_6H_4$), 128.1 (d, $J$(CP) = 12.7, Ph), 128.2 (d, $J$(CP) = 9.5, $C_6H_4$), 128.5 (d, $J$(CP) = 10.8, $C_6H_4$), 128.6 (d, $J$(CP) = 13.4, Ph), 129.4 (d, $^1J$(CP) = 36.2, *i*-Ph), 131.4 (d, $J$(CP) = 12.0, Ph), 131.6 (d, $J$(CP) = 2.4, Ph), 132.2 (d, $J$(CP) = 1.3, $C_6H_4$), 132.3 (d, $J$(CP) = 1.4, *p*-Ph), 132.6 (d, $J$(CP) = 10.9, Ph), 133.5 (d, $^1J$(CP) = 21.3, *i*-$C_6H_4$), 144.3 (dd, $^2J$(CP) = 18.2, $^3J$(CP) = 14.5, $C_6H_4$). Anal. Calcd for $C_{22}H_{20}P_2S_2$: C, 64.38; H, 4.91. Found: C, 64.23; H, 4.78.

**10b**: 40% yield; $^{31}P\{^1H\}$ NMR (THF) $\delta$ 59.8 (d, $^2J$(PP) = 4.7, PPh), 55.9 (d, $^2J$(PP) = 4.5, PPh); $^1H$ NMR ($CDCl_3$) $\delta$ 2.13 (m, 1H, $CH_2$), 2.38 (m, 1H, $CH_2$), 2.63 (m, 1H, $CH_2$), 2.74 (m, 1H, $CH_2$), 3.74 (ddd, $^3J$(HH) = 8.9, $^2J$(HP) = 8.9, $^2J$(HP) = 17.8, 1H, PCHP), 4.31 (m, 1H, PCHC*H*), 7.26−7.55, 7.61−7.81 (m, 14H, Ph); $^{13}C$ NMR ($CDCl_3$) $\delta$ 30.4 (d, $^2J$(CP) = 3.6, $PCH_2CH_2$), 36.2 (d, $^1J$(CP) = 54.3, $PCH_2$), 49.8 (dd, $^2J$(CP) = 10.4, $^2J$(CP) = 4.7, PCH*C*H), 53.8 (dd, $^1J$(CP) = 48.2, $^1J$(CP)

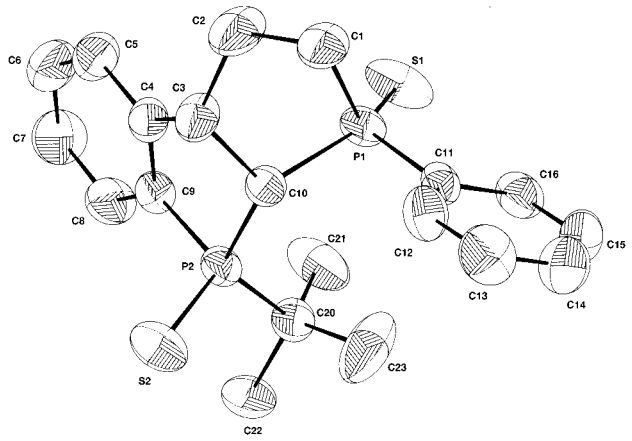
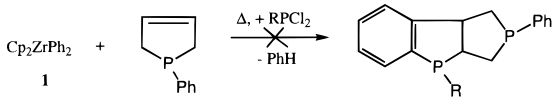



**Figure 1.** Molecular structure of **15a** in the crystal. Selected distances (Å) and angles (deg): P(1)−S(1) 1.944(2), P(2)−S(2) 1.957(1), P(1)−C(1) 1.813(4), P(2)−C(9) 1.801(4), P(1)−C(10) 1.848(3), P(2)−C(10) 1.852(3), P(1)−C(11) 1.800(4), P(2)−C(20) 1.850(4); C(1)−P(1)−C(10) 91.3(2), C(10)−P(2)−C(9) 93.1(2).

**Scheme 2**




(5) In this case the formation of a minor third compound ($\delta(^{31}P)$: −38.8 and −27.6, $J_{PP}$ = 0 Hz) was detected but attempts to isolate it failed till now.

(6) See for example: (a) Young, D. P.; McEwen, W. E.; Velez, D. C.; Johnson, J. W.; Van der Werf, C. A. *Tetrahedron Lett.* **1964**, 359. (b) Horner, L.; Winkler, H. *Tetrahedron Lett.* **1964**, 175.

= 44.6, PCHP), 125.2 (d, $J$(CP) = 11.1, $C_6H_4$), 127.7 (d, $J$(CP) = 13.3, Ph), 128.9 (d, $J$(CP) = 12.3, Ph), 129.3 (d, $J$(CP) = 10.0, $C_6H_4$), 129.4 (d, $J$(CP) = 10.9, $C_6H_4$), 130.0 (d, $J$(CP) = 10.7, Ph), 129.9 (d, $^1J$(CP) = 79.8, *i*-Ph), 131.9 (d, $J$(CP) = 3.1, Ph), 132.3 (d, $J$(CP) = 3.2, Ph), 133.1 (d, $J$(CP) = 2.5, $C_6H_4$), 133.5 (d, $^1J$(CP) = 73.4, *i*-Ph), 133.8 (dd, $^1J$(CP) = 89.4, $^3J$(CP) = 2.4, *i*-$C_6H_4$), 134.0 (d, $J$(CP) = 12.2, Ph), 148.4 (dd, $^2J$(CP) = 22.8, $^3J$(CP) = 6.2, $C_6H_4$). Anal. Calcd for $C_{22}H_{20}P_2S_2$: C, 64.38; H, 4.91. Found: C, 64.25; H, 4.83.

**1,1-Diphosphine Disulfides 14a,b.** The same experimental procedure as above was followed with dichloromethylphosphine (90 $\mu$L, 1 mmol) instead of dichlorophenylphosphine. **14a,b** were isolated by chromatography eluting with dichloromethane (**14a**, $R_f$ = 0.30; **14b**, $R_f$ = 0.24).

**14a**: 20% yield; $^{31}P\{^1H\}$ NMR (THF) $\delta$ 41.2 (d, $^2J$(PP) = 7.5), 34.1 (d, $^2J$(PP) = 7.5); $^1H$ NMR ($CDCl_3$) $\delta$ 2.22 (s, $^2J$(HP) = 13.8, 3H, $PCH_3$), 2.64−3.22 (m, 4H, $CH_2$), 2.91 (m, 1H, PCHP), 4.19 (m, 1H, PCHC*H*), 7.25−7.57, 8.00−8.12 (m, 9H, Ph); $^{13}C$ NMR ($CDCl_3$) $\delta$ 22.4 (s, $^1J$(CP) = 56.7, $PCH_3$), 26.3 (dd, $^2J$(CP) = 13.7, $^3J$(CP) = 2.4, $PCH_2CH_2$), 37.5 (dd, $^1J$(CP) = 55.6, $^3J$(CP) = 4.4, $PCH_2$), 50.7 (dd, $^2J$(CP) = 12.8, $^2J$(CP) = 6.8, PCH*C*H), 58.5 (dd, $^1J$(CP) = 52.3, $^1J$(CP) = 54.6, PCHP), 123.2 (d, $J$(CP) = 8.9, $C_6H_4$), 126.9 (d, $J$(CP) = 9.8, $C_6H_4$), 128.2 (d, $J$(CP) = 12.8, $C_6H_4$), 128.2 (d, $J$(CP) = 11.8, Ph), 131.6 (s, *p*-Ph), 132.3 (d, $J$(CP) = 3.1, $C_6H_4$), 132.6 (d, $J$(CP) = 10.8, Ph), 143.7 (dd, $^2J$(CP) = 12.0, $^3J$(CP) = 14.9, $C_6H_4$), *i*-Ph and *i*-$C_6H_4$ not detected. Anal. Calcd for $C_{17}H_{18}P_2S_2$: C, 58.61; H, 5.21. Found: C, 58.47; H, 5.13.

**14b**: 20% yield; $^{31}P\{^1H\}$ NMR (THF) $\delta$ 56.2 (d, $^2J$(PP) = 4.7), 54.4 (d, $^2J$(PP) = 4.7); $^1H$ NMR ($CDCl_3$) $\delta$ 2.53 (s, $^2J$(HP) = 13.9, 3H, $PCH_3$), 2.45 (m, 1H, $CH_2$), 2.60−3.00 (m, 3H, $CH_2$), 3.57 (ddd, $^2J$(HP) = 17.2, $^2J$(HP) = 8.6, $^3J$(HH) = 8.6, 1H, PCHP), 4.38 (m, 1H, PCHC*H*), 7.32−7.58, 7.93−8.02 (m, 9H, Ph); $^{13}C$ NMR ($CDCl_3$) $\delta$ 23.6 (s, $^1J$(CP) = 52.4, $PCH_3$), 30.7 (dd, $^2J$(CP) = 3.0, $^3J$(CP) = 3.0, $PCH_2CH_2$), 38.0 (d, $^1J$(CP) = 54.0, $PCH_2$), 50.7 (dd, $^2J$(CP) = 9.5, $^2J$(CP) = 4.8, PCH*C*H), 53.1 (dd, $^1J$(CP) = 42.0, $^1J$(CP) = 48.5, PCHP), 124.8 (d, $J$(CP) = 10.8, $C_6H_4$), 127.6 (d, $J$(CP) = 11.3, $C_6H_4$), 129.1 (d, $J$(CP) = 10.0, $C_6H_4$), 129.3 (d, $J$(CP) = 8.7, Ph), 130.3 (d, $J$(CP) = 10.9, Ph), 130.3 (d, $J$(CP) = 2.7, *p*-Ph), 132.7 (d, $J$(CP) = 2.1, $C_6H_4$), *i*-Ph and *i*-$C_6H_4$ not detected. Anal. Calcd for $C_{17}H_{18}P_2S_2$: C, 58.61; H, 5.21. Found: C, 58.50; H, 5.13.

**1,1-Diphosphine Disulfides 15a,b.** The same experimental procedure as above was followed with dichloro-*tert*-butylphosphine (0.160 g, 1 mmol) instead of dichlorophenylphosphine. **15a,b** were isolated by chromatography eluting with 4/1 dichloromethane/pentane (**15a**, $R_f$ = 0.30; **15b**, $R_f$ = 0.20).

**15a**: 45% yield; $^{31}P\{^1H\}$ NMR ($C_6D_6$) $\delta$ 62.6 (s, P$^t$Bu), 40.5 (s, PPh); $^1H$ NMR ($C_6D_6$) $\delta$ 1.04 (d, $^3J$(HP) = 17.8, 9H, $CH_3$), 2.00 (m, 1H, $CH_2$), 2.56 (m, 1H, PCHP), 3.12−2.82 (m, 3H, $CH_2$), 4.56 (m, 1H, PCHC*H*), 7.28−7.53, 7.93−8.02 (m, 9H, Ph); $^{13}C$ NMR ($C_6D_6$) $\delta$ 25.4 (d, $^2J$(CP) = 2.1, C*C*H$_3$), 28.5 (dd, $^1J$(CP) = 12.4, $^3J$(CP) = 2.7, *C*CH$_3$), 35.2 (d, $^2J$(CP) = 50.4, $PCH_2CH_2$), 41.9 (dd, $^1J$(CP) = 56.5, $^3J$(CP) = 3.6, $PCH_2$), 46.7 (dd, $^1J$(CP) = 53.6, $^1J$(CP) = 50.0, PCHP), 50.7 (dd, $^2J$(CP) = 14.0, $^2J$(CP) = 5.6, PCH*C*H), 124.0 (d, $J$(CP) = 8.1, $C_6H_4$), 127.7 (d, $J$(CP) = 8.7, $C_6H_4$), 128.3 (d, $J$(CP) = 10.7, $C_6H_4$), 128.9 (d, $J$(CP) = 12.2, Ph), 131.2 (d, $J$(CP) = 10.6, Ph), 131.3 (s, *p*-Ph), 132.1 (d, $J$(CP) = 3.0, $C_6H_4$), 132.9 (d, $^1J$(CP) = 75.6, *i*-Ph), 140.1 (dd, $^1J$(CP) = 74.8, $^3J$(CP) = 4.5, *i*-$C_6H_4$), 145.2 (dd, $^2J$(CP) = 15.5, $^3J$(CP) = 10.3, $C_6H_4$). Anal. Calcd for $C_{20}H_{24}P_2S_2$: C, 61.52; H, 6.19. Found: C, 61.36; H, 6.05.

**15b**: 45% yield; $^{31}P\{^1H\}$ NMR ($C_6D_6$) $\delta$ 85.0 (d, $^2J$(PP) = 12.1, P$^t$Bu), 53.4 (d, $^2J$(PP) = 12.1, PPh); $^1H$ NMR ($C_6D_6$) $\delta$ 1.46 (d, $^3J$(HP) = 18.6, 9H, $CH_3$), 2.18−2.94 (m, 4H, $CH_2$), 3.95 (m, 1H, PCHP), 4.41 (m, 1H, PCHC*H*), 7.32−7.58, 7.96−8.06 (m, 9H, Ph); $^{13}C$ NMR ($C_6D_6$) $\delta$ 27.3 (d, $^2J$(CP) = 3.5, C*C*H$_3$), 28.9 (dd, $^1J$(CP) = 3.0, $^3J$(CP) = 3.0, *C*CH$_3$), 37.6 (d, $^2J$(CP) = 44.0, $PCH_2CH_2$), 38.8 (dd, $^1J$(CP) = 55.6, $^3J$(CP) = 2.5, $PCH_2$), 50.3 (dd, $^2J$(CP) = 10.5, $^2J$(CP) = 4.1, PCH*C*H), 59.0 (dd, $^1J$(CP) = 37.5, $^1J$(CP) = 37.6, PCHP), 124.9 (d, $J$(CP) = 10.2, $C_6H_4$), 128.2 (d, $J$(CP) = 10.5, $C_6H_4$), 129.0 (d, $J$(CP) = 12.2, Ph), 129.1 (d, $J$(CP) = 9.7, $C_6H_4$), 130.6 (d, $J$(CP) = 10.5, Ph), 132.1 (d, $J$(CP) = 3.0, *p*-Ph), 132.3 (d, $J$(CP) = 2.3, $C_6H_4$), 132.4 (d, $^1J$(CP) = 80.8, *i*-Ph), 134.1 (dd, $^1J$(CP) = 77.9, $^3J$(CP) = 3.2, *i*-$C_6H_4$), 147.8 (dd, $^2J$(CP) = 18.7, $^3J$(CP) = 4.9, $C_6H_4$). Anal. Calcd for $C_{20}H_{24}P_2S_2$: C, 61.52; H, 6.19. Found: C, 61.46; H, 6.14.

**1,1-Diphosphine Disulfide 16.** The same experimental procedure as above was followed with dichloro(diisopropylamino)phosphine (0.202 g, 1 mmol) instead of dichlorophenylphosphine. **16** was purified by chromatography eluting with 9/1 dichloromethane/hexane solution ($R_f$ = 0.1).

**16**: 90% yield; $^{31}P\{^1H\}$ NMR (THF) $\delta$ 69.8 (d, $^2J$(PP) = 4.5, PN$^i$Pr), 56.4 (d, $^2J$(PP) = 4.5, PPh); $^1H$ NMR ($CDCl_3$) $\delta$ 1.32 (d, $^3J$(HH) = 6.9, 6H, $CH_3$), 1.43 (d, $^3J$(HH) = 6.9, 6H, $CH_3$), 2.45 (m, 2H, $CH_2$), 2.72 (m, 1H, PCHP), 3.10 (m, 2H, $CH_2$), 3.53 (d sept, $^3J$(HH) = 6.9, $^3J$(HP) = 18.6, 2H, NCH), 3.74 (m, 1H, PCHC*H*), 7.12−7.53, 7.84−7.95 (m, 9H, Ph); $^{13}C$ NMR ($CDCl_3$) $\delta$ 23.5 (s, $CH_3$), 30.3 (s, $PCH_2CH_2$), 32.2 (d, $^1J$(CP) = 53.7, $PCH_2$), 46.1 (dd, $^2J$(CP) = 14.6, $^2J$(CP) = 7.2, PCH*C*H), 48.2 (dd, $^1J$(CP) = 58.6, $^1J$(CP) = 53.7, PCHP), 125.3 (d, $J$(CP) = 11.8, $C_6H_4$), 126.4 (d, $J$(CP) = 10.3, $C_6H_4$), 128.6 (d, $J$(CP) = 13.1, $C_6H_4$), 128.9 (d, $J$(CP) = 11.7, Ph), 129.4 (d, $J$(CP) = 9.9, Ph), 131.2 (d, $J$(CP) = 2.3, *p*-Ph), 131.8 (d, $J$(CP) = 1.9, $C_6H_4$), 135.6 (dd, $^1J$(CP) = 21.2, $^3J$(CP) = 4.1, *i*-Ph), 137.5 (dd, $^1J$(CP) = 57.1, $^3J$(CP) = 4.2, *i*-$C_6H_4$), 145.1 (dd, $^2J$(CP) = 26.9, $^3J$(CP) = 9.7, $C_6H_4$). Anal. Calcd for $C_{22}H_{29}NP_2S_2$: C, 60.95; H, 6.74. Found: C, 60.86; H, 6.81

**Crystal Data for 15a.** Crystal data for $C_{20}H_{24}P_2S_2$ (**15a**): monoclinic, $P2_1/c$, $a$ = 11.371(2) Å, $b$ = 10.663(2) Å, $c$ = 16.842 Å, $\beta$ = 90.15(2)°, $V$ = 2042.1 Å$^3$, $Z$ = 4, $\mu$ = 4.04 cm$^{-1}$, Mo K$\alpha$ radiation used ($\lambda$ = 0.710 73 Å), $\rho_{calcd}$ = 1.27 g·cm$^{-3}$, $T$ = 293 K, 0.2 × 0.4 × 0.3 mm. A selected crystal of $C_{20}H_{24}P_2S_2$ was mounted on a goniometer head and transferred on a STOE IPDS diffractometer; 15 975 reflections were collected ($3 \le 2\theta \le 48°$), with 15 497 merged and 3211 independent reflections ($R_m$ = 0.041), and 2412 reflections were observed with a criterion of $I > 3\sigma(I)$. Corrections for Lorentz and polarization effects were applied. The structure was solved by direct methods using the package SIR92; refinement was performed on C, P, and S atoms, while H atoms were included in the processes of refinement as fixed contributors with C−H = 0.96 Å, and $U$(iso) values were fixed 20% higher than those of the carbons atom to which they were connected. $R$ = 0.0475, $R_w$ = 0.0485, and GOF = 1.03, with a ponderation unit, $N_o/N_v$ = 11.

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**Supporting Information Available:** Text describing X-ray procedures and tables of positional parameters and isotropic and anisotropic thermal parameters and bond length and bond angle values for **15a** (7 pages). Ordering information is given on any current masthead page.

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