# Syntheses and Theoretical and Mechanistic Aspects of 1-Thia-2,4- and 1-Thia-3,4-diphosphole Formed from $CS_2$ and $^t$BuCP and Crystal and Molecular Structure of the First 1-Thia-3,4-diphosphole Complex: cis-[{$PtCl_2(PEt_3)$}$_2$($P_2SC_2{}^tBu_2$)]

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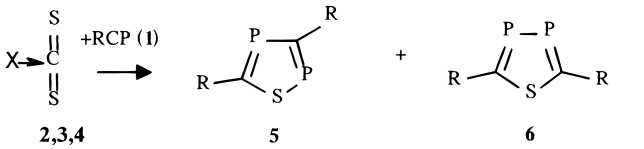
**Abstract:** The reaction of $^t$BuCP with $CS_2$ (or its ylide type complexes such as $R_3PCS_2$ (R = Et, Ph, cyclohexyl), $(C_5H_{10}N)_2CCS_2$, or $(C_4H_8NO)_2CCS_2$) gives a mixture of 3,5-di-*tert*-butyl-1-thia-2,4-diphosphole and 2,5-di-*tert*-butyl-1-thia-3,4-diphosphole, which were characterized by NMR spectroscopy. The latter was also characterized by the single-crystal X-ray structure determination of its bis(platinum(II)) complex [($PtCl_2PEt_3)_2$($\mu$-$P_2SC_2{}^tBu_2$)]. This is the first structural characterization of a 1-thia-3,4-diphosphole ring. The mechanism of these reactions was explored by B3LYP/6-311+G** level quantum chemical calculations. The reaction pathway involves a phosphadithiolediylcarbene and its diphosphatetrathiafulvalene dimer as intermediates. Several other possible reaction pathways were ruled out.

## Introduction

The reactivity of the P≡C triple bond in cycloaddition reactions is well documented,[1] and its similarity to the C≡C bond is remarkable.[2] Phosphaalkyne cycloaddition reactions afford a variety of five-membered heterophospholes.[1,3] Thiaphospholes and thiadiphospholes, obtained previously by various methods,[4−7] have also been considered as possible [3 + 2] cycloaddition products of $^t$BuCP (**1**) and a PC(R)S intermediate.[7]

We now report that **1** readily reacts with $CS_2$ (**2**) or its ylide type $XCS_2$ complexes **3** (X = $Et_3P$, $Ph_3P$, $(cyclohexyl)_3P$), **4a** (X = $(C_5H_{10}N)_2C$), or **4b** (X = $(C_4H_8ON)_2C$) to produce an isomeric mixture of the 1-thia-2,4- and 1-thia-3,4-diphosphole rings **5** (R = $^t$Bu) and **6** (R = $^t$Bu) (see eq I). The symmetric 1-thia-3,4-diphosphole **6** was hitherto unknown. Here we (i)




**2,3,4** **5** **6**

R= $^t$Bu, X: $Et_3P$, $Ph_3P$, $(cyclohexyl)_3P$, $(C_5H_{10}N)_2C$, $(C_4H_8ON)_2C$ (I)

discuss the above reactions, (ii) report the synthesis and NMR study of *cis* and *trans* Pt(II) complexes of **5**, (iii) present the X-ray structure of a bis(platinum((II)) complex of **6**, and (iv) describe the results of a computational mechanistic study of the formation of the rings **5** and **6**.

## Results and Discussion

A large excess of **1** reacts with **4a** and **4b**, affording the isolated and fully characterized [3 + 2] cycloaddition products **7a** and **7b**, respectively, which in the presence of **1** at 100 °C give **5** (R = $^t$Bu) and **6** (R = $^t$Bu).

Interestingly, neither the possible carbene **8** nor its ylide **9** (R = $^t$Bu) has yet been isolated as a primary cycloaddition product from reaction I, utilizing $CS_2$ (**2**) or its tertiary phosphine adducts (**3**), although cycloaddition reactions between acetylenes and $XCS_2$ type dipoles are well-known.[8−10] $CS_2$ itself is known to react with acetylenes.[11,12]

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(1) Regitz, M. Phosphalkynes. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, Germany, 1990.
(2) Dillon, F.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, U.K., 1998.
(3) Regitz, M.; Binger, P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1485. Regitz, M. *Chem. Rev.* **1990**, *90*, 191.
(4) Appel, R.; Moers, R. *Angew. Chem.* **1986**, *98*, 570.
(5) Märkl, G.; Höbel, W.; Kallmünser, H.; Ziegler, U. L.; Nuber, B. *Tetrahedron Lett.* **1991**, *33*, 4421.
(6) Lindner, E.; Schlenker, T.; Haase, C. *J. Organomet. Chem.* **1994**, *464*, C31.
(7) Burghardt, B.; Krill, S.; Okano, Y.; Ando, W.; Regitz, M. *Synlett* **1991**, *5*, 356.
(8) Krasuski, W.; Nikolaus, D.; Regitz, M. *Liebigs Ann. Chem.* **1982**, 1451.
(9) Pittman, C. U., Jr.; Narita, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1996.
(10) Aitken, R. A.; Raut, S. V.; Ferguson, G. *Tetrahedron* **1992**, *48*, 8023.
(11) Krebs, A.; Kimling, H. *Angew. Chem.* **1971**, *83*, 540. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 509.
(12) Hartzler, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 4379.

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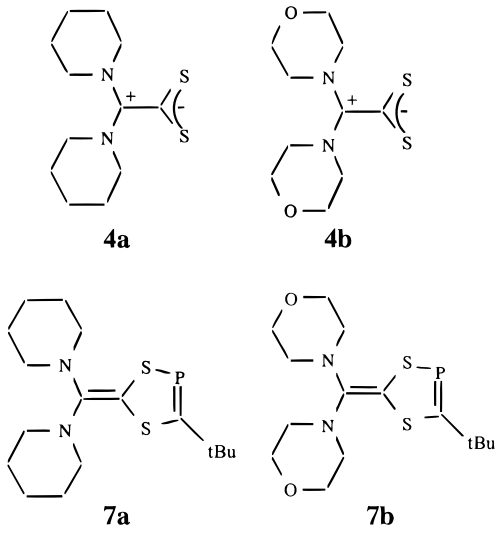
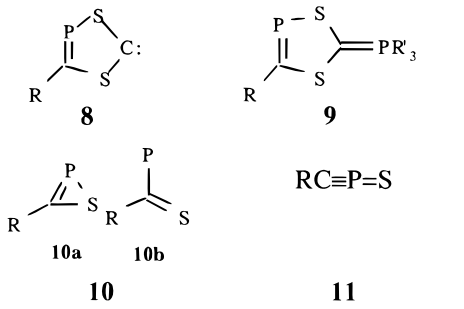
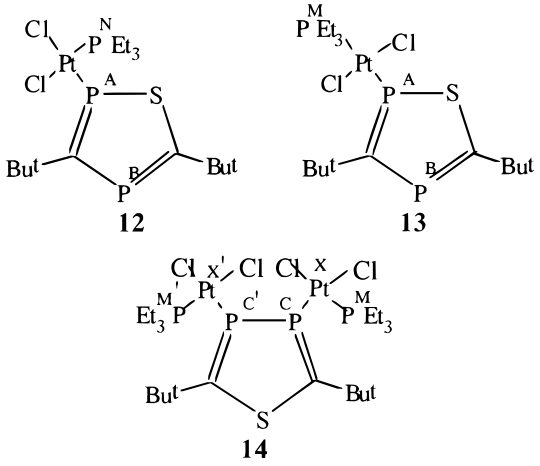



The intermediate carbene **8** can subsequently dimerize or undergo further reactions. A likely possibility would be the




retrocycloaddition step yielding the cyclic **10a** (possibly further rearranging to **11**[13]) or the phosphinidine-like structure **10b** (which can also be formulated as a 1,3-dipole, $P^+-C(R)=S^-$) together with XCS (starting from **3** or **4**) or CS (starting from **2**) as the other product. Compound **10a** (or **10b**) could undergo a second cycloaddition step with **1**, forming the observed regioisomers **5** and **6**. The other possibility is a direct cycloaddition reaction of **7**, **8**, or **9** with $^t$BuCP (**1**), followed by a cycloreversion, furnishing **5**, **6**, and XCS or CS. Before the mechanism is discussed, the characterization of the products will be presented.

The oily nature of the 1-thia-2,4- and 1-thia-3,4-diphosphole products **5** and **6**, synthesized according to the various methods listed in eq I, precluded any single-crystal structural study; however, both rings form Pt(II) complexes, which helped in their structural assignments. It was found that the 1-thia-3,4-diphosphole ring **6** was much more reactive than the corresponding 1-thia-2,4-diphosphole ring **5**. The latter reacts with $[PtCl_2(PEt_3)]_2$, forming both *cis* and *trans* complexes of the type $[PtCl_2(P_2SC_2{}^tBu_2)(PEt_3)]$, **12** and **13**, in which the metal is attached to the ring phosphorus directly bonded to sulfur, as evidenced by their $^{31}P\{^1H\}$ NMR spectra. Of special significance for the structural determination of the 1-thia-3,4-diphosphole **6** is its ready reaction with $[PtCl_2(PEt_3)]_2$ to afford the symmetric *cis* diplatinum complex $[\{PtCl_2(PEt_3)\}_2(P_2SC_2{}^tBu_2)]$ (**14**), in which **both** ring phosphorus atoms are coordinated to the platinum(II) fragments. The $^{31}P\{^1H\}$ NMR spectrum of **14** is particularly informative in confirming the nature of **6**, since it exhibits the characteristic pattern of lines expected for an




$[AMX]_2$ spin system, (A, M = $^{31}$P; X = $^{195}$Pt) shown in Figure 1 (top), which has been successfully simulated by the PANIC program in Figure 1 (bottom) using the chemical shift and coupling constant data listed in the Experimental Section.

Confirmation of the molecular structure of **14** comes from a single-crystal X-ray diffraction study (see Figure 2). The ring is planar, and interestingly the C−P and C−S bond lengths within the ring are almost identical. The P−P bond is rather short (2.074 Å; Table 1) and is comparable to those found in diphosphenes, RP═PR.[2] The X-ray diffraction data match reasonably well those obtained from the calculations (vide infra). All bonds shorten upon complexation; however, the calculated P−P bond length is much shorter for complex **14** than for the free ring **6** (Table 1), while the other bonding parameters show only small changes. It is noteworthy that the calculations were unable to reproduce the P−P bond shortening without using polarization functions on the ring atoms. The structural parameters of the free ring, however, are almost unchanged from the lowest levels and basis set up to MP2/6-311+G(2d). The effect of $\eta^1$ complexation on the P═P bond in diphosphenes is known to have only a small effect on the bond length,[2] whereas $\eta^2$ metal complexation significantly increases the P═P bond length.

The NICS values[14] for **5** and **6** (R = H) at the ring center are −12.4 and −12.7 ppm, respectively, compared to −13.2 ppm for thiophene, indicating significant aromaticity of the phosphorus-containing rings, in full agreement with the results from previous studies on related thiaphospholes and thiadiphospholes.[15]

To better understand the mechanism of the reactions leading to the formation of thiadiphospholes **5** and **6** from $^t$BuCP, we have investigated computationally the energetics of the hypothetical reaction between $CS_2$ (**2**) and HCP (**1**; R = H) and the possible involvement of HCPS (**10** and **11**; R = H). We find that both **10** and **11** are minima, the former having the **10a** type structure (no **10b** type structure has been found as a minimum) with a quite elongated P−S bond (2.343 Å), in accord with the four-$\pi$-electron antiaromatic character of the ring. **11** (R = H) is less stable than **10** (R = H) by 36.0 kcal/mol. **10** (R = H) + CS lies 54.4 kcal/mol above the reactants (see Figure 3). Thus a reaction pathway involving the high-energy intermediate **10** (formed either via direct sulfuration of **1** or following a retrocycloaddition step from intermediates **7**−**9**) is very unlikely.

Formation of the cyclic carbene intermediate **8** (R = H) (which lies 15.14 kcal/mol above the reactants **2** + **1**) proceeds

(13) Formation of $^t$BuCPS (**11**) can also be considered as a result of direct sulfuration of $^t$BuCP.

(14) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(15) Nyulászi, L.; Várnai, P.; Veszprémi, T. *THEOCHEM* **1995**, *358*, 55. Nyulászi, L.; Várnai, P.; Krill, S.; Regitz, M. *J. Chem. Soc., Perkin Trans 2* **1995**, 315.

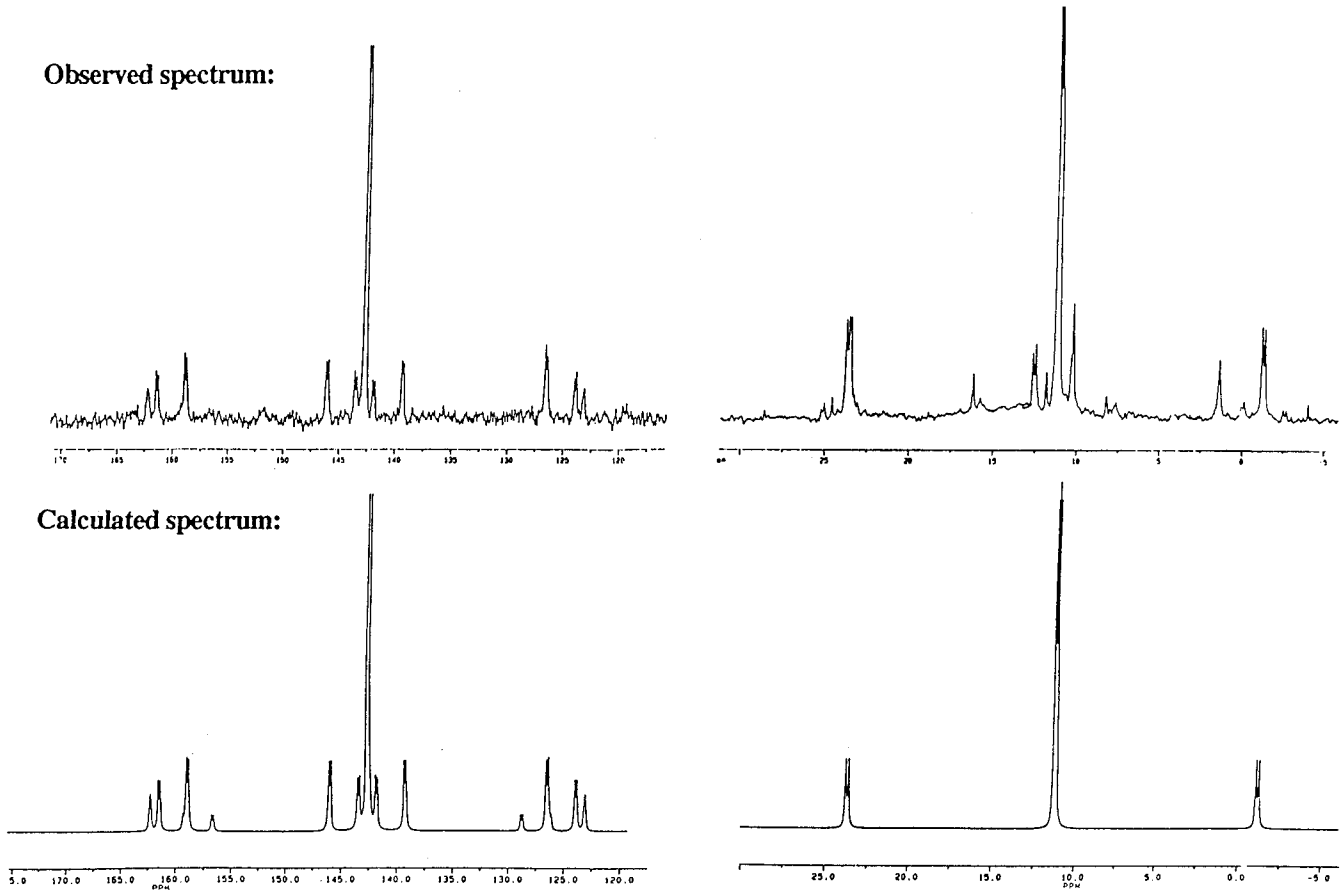



**Figure 1.** Calculated and observed $^{31}P\{^{1}H\}$ NMR spectra of **14**.

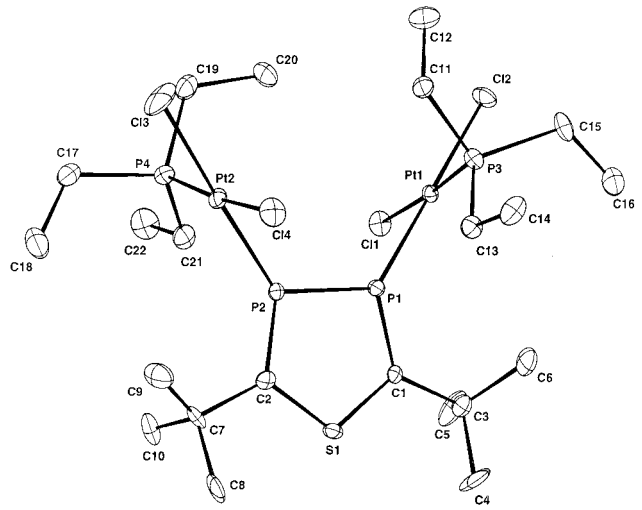
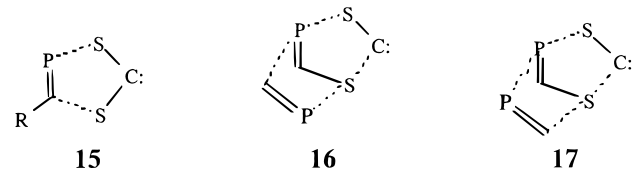



**Figure 2.** Molecular structure of **14**.

via the transition state **15** (R = H) (29.2 kcal/mol). A similar



**15** **16** **17**

transition structure has been found by Sauers[16] in the reaction of $CO_2$ and $CH_2{=}CH_2$. Intermediate **8** might be stabilized by the typical carbene dimerization[17] or alternatively could react directly with a second molecule of **1**.

**Table 1.** Important Measured and Calculated[a] Bond Lengths (Å) for **14**

| | X-ray | calcd[a] | calcd for uncomplexed ring[a] |
|---|---|---|---|
| S1C2 | 1.695 | 1.695 | 1.712 |
| C2P2 | 1.708 | 1.676 | 1.722 |
| P2P1 | 2.074 | 2.107 | 2.179 |
| P1C1 | 1.694 | 1.682 | 1.722 |
| C1S1 | 1.701 | 1.688 | 1.712 |

[a] Calculations were carried out at the B3LYP level, using the LANL2DZ pseudopotentials for Pt, P, S, and Cl atoms as employed in the G94 suite of programs. d polarization functions with exponents of 0.8 for C and Cl, 0.65 for S, 0.55 for P, and 0.2 for Pt were added to the basis set. $^{t}$Bu groups were replaced by H and $PEt_3$ groups were replaced by $PH_3$ in the calculations.

In the reaction of **8** (R = H) with **1** (R = H), two transition structures, **16** and **17** (54.7 and 62.8 kcal/mol relative to the reactants, respectively), were found, each of which leads directly to CS and the thiadiphosphole rings **5** and **6** (R = H)), respectively (Figure 3),[18] but their high energy rules out these as possible reaction pathways. The products **5** (R = H) + CS and **6** (R = H) + CS are more stable than the reactants (**2** and 2 **1** (R = H)) by 8.3 and 1.7 kcal/mol, respectively. It is noteworthy that structure **18** has also been found as a possible transition state, connecting the most stable isomer 1-thia-2,5-diphosphole **19** (R = H) + CS (20.6 kcal/mol relative to the reactants) with $CS_2$ + P−CH=HC−P, **20** (R = H). However, since P−C($^{t}$Bu)=($^{t}$Bu)C−P has never been observed as a dimerization product of **1** (R = $^{t}$Bu), and also since **19** (R =

(16) Sauers, R. R. *Tetrahedron Lett.* **1994**, *35*, 7213.
(17) Regitz, M. *Angew. Chem.* **1996**, *35*, 725.

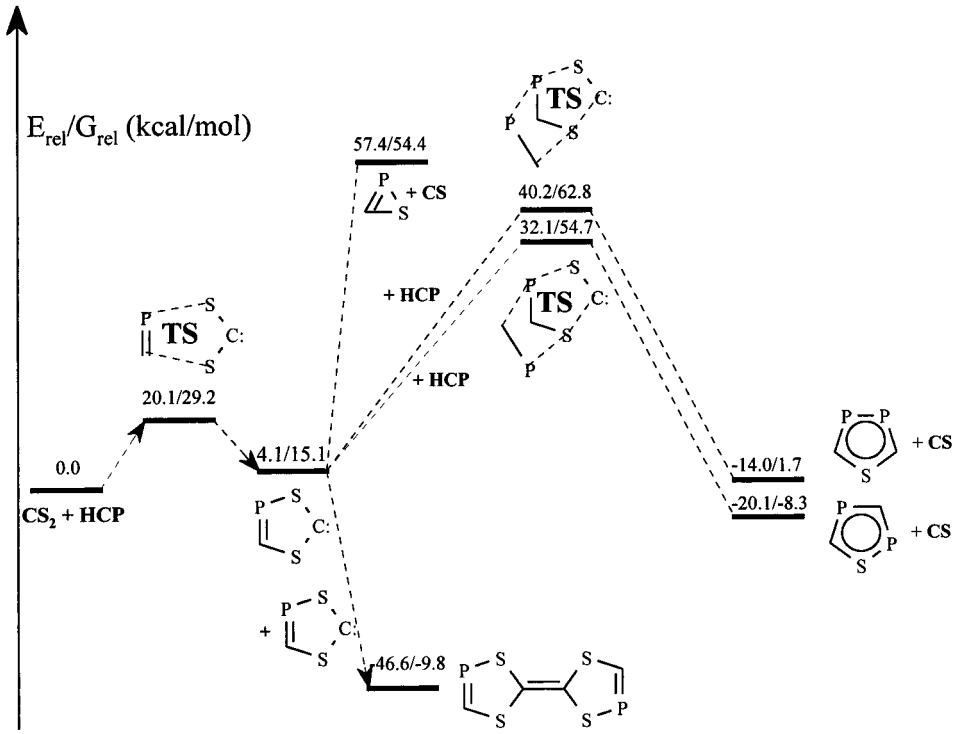
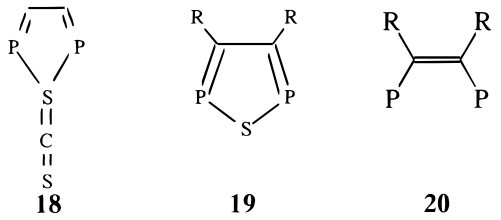


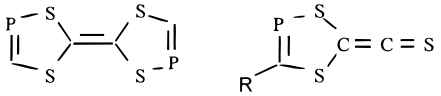

**Figure 3.** Relative energies/Gibbs free energies of the reactants, transition structures, intermediates, and products of the HCP + $CS_2$ reaction, leading to **21** (in kcal/mol).



**18** **19** **20**

$^t$Bu) is not obtained as a reaction product in eq I, we do not consider this as a viable pathway.

While the high energy of transition structures **16** and **17** prevents the reaction of **8** (R = H) with HCP, the dimerization of carbene **8** to **21** is an exothermic process, the latter being

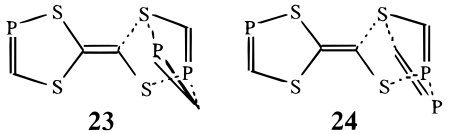


**21** **22**

more stable than the reactants by 9.8 kcal/mol. **21** has a structure similar to that of the isolated **7**, and also to that of **9**, all containing the −S−C(R)=P fragment within a five-membered ring. Since **5** and **6** as sole products of all three reactions shown in eq I, can be formed from this fragment and RCP (**1**), species **7**, **9**, and **21** should be key intermediates in the reaction. The isolation of **7** provides experimental evidence for the proposed reaction mechanism.

(18) It is interesting to note that cycloaddition reactions followed by a retroreaction are well-known. Phosphinine and triphosphabenzene react with phosphaalkynes, forming the corresponding phosphabarrelenes; however, the retroreaction is not known: Märkl, G.; Lieb, F. *Angew. Chem.* **1968**, *80*, 702; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 733. 1,3,2-Diazaphosphinine reacts with acetylenes, giving the stable diazadiphosphabarrelene, which undergoes a retroreaction in boiling toluene, to form 1-aza-2,4-diphosphinine: Avarvari, N.; Ricard, L.; Mathey, F.; Le Floch, P.; Löber, O.; Regitz, M. *Eur. J. Org. Chem.*, in press. Some five-membered ring transition states similar to **16** and **17** have been postulated: Bastide, J.; Henri-Russeau, O. Cycloadditions and cyclizations involving triple bonds. In *Chemistry of the carbon-carbon triple bond*; Patai, S., Ed.; Wiley: Chichester, U.K., 1978.

**21** (like **8**) can provide, after a retrocycloaddition step, species **10** (and also **22**). **10** can then react with an additional molecule of **1** (R = H). The other possibility is a direct reaction of **21** and **1** via transition states **23** and **24** (note their similarity to **16**



**23** **24**

and **17**, respectively). The Gibbs free energies of transition structures **23** and **24** are higher by 15.5 and 19.8 kcal/mol, respectively, than those of the original reactants (2 **2** + 3 **1**). It is worth noting that, in these transition structures, two new bonds are forming and two further bonds are breaking simultaneously (see Figure 4). The final products **22** and **5** or **6** (R = H) are 31.1 or 24.5 kcal/mol more stable than the original reactants, thereby providing the thermodynamic driving force for the entire reaction. Compound **22** (R = $^t$Bu) has not yet been observed in our experimental studies, but in any case it is likely to polymerize. Figure 5 shows both the energies and Gibbs free energies of the structures investigated.

The effect of $^t$Bu substitution on the reaction pathways was also considered theoretically and proved to be important because the energies of the transition states are increased with respect to those of the reactants by 8.5 kcal/mol for **15** and by 15 kcal/mol for **16** and **17**. The energy difference of the two transition structures **16** and **17**, which lead to the two regioisomers **5** and **6**, is lowered by 3.2 kcal/mol as a result of the $^t$Bu substitution. A similar effect operating on **23** and **24** would make their energies differ by less than 1 kcal/mol, which is therefore entirely consistent with the observed formation of **both** thiadiphospholes **5** and **6**.

## Experimental Section

All compounds were handled in an inert atmosphere or with the use of high-vacuum line and Schlenk tube techniques. Solvents were rigorously dried and redistilled before use.

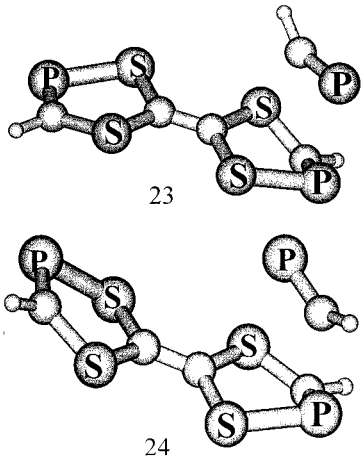



**Figure 4.** Transition structures **23** and **24**.

**Syntheses of 5-(Diaminomethylidene)-1,4,2-dithiaphospholes 7a and 7b. 1** (300 mg, 30 mmol) was reacted with a $CH_2Cl_2$ (5 mL) solution of **4a** and **4b** (10 mmol, 224 and 228 mg, respectively). During the course of the reaction, the deep red solution of **4** became pale red. The reaction mixture was stirred for 3−4 h, and excess **1** was evaporated in vacuo. To extract the rest of the phosphaalkyne, the resulting oil was mixed with hexane (10 mL). **7a** and **7b** were obtained as thermolabile oils after decanting the hexane phase. Yield: 60%.

Anal. Calcd for **7a**, $C_{17}H_{29}N_2PS_2$: C, 57.27; H, 8.20; N, 7.86. Found: C, 56.9; H, 7.9; N, 7.5. $^1$H NMR ($CDCl_3$): $\delta$ 1.45 ppm (s, 9H, $C(CH_3)_3$), $\delta$ 1.50−2.60 ppm (m, 12H, $\beta/\beta'/\gamma$-$CH_2$), $\delta$ 2.90−3.85 ppm (m, 8H, $\alpha/\alpha'$-$CH_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 22.8 ppm ($\gamma$-$CH_2$), $\delta$ 26.0 ppm ($\beta/\beta'$-$CH_2$), $\delta$ 32.6 ppm (d, $C(CH_3)_3$, $^3J_{PC}$ = 10.9 Hz), $\delta$ 40.1 ppm (d, $C(CH_3)_3$, $^2J_{PC}$ = 15.4 Hz), $\delta$ 50.5 ppm ($N(CH_2)_2$), $\delta$ 100.6 ppm (C-5), $\delta$ 146.2 ppm (d, C(pip)$_2$, $^3J_{PC}$ = 3.0 Hz), $\delta$ 200.0 ppm (d, C-3, $^1J_{PC}$ = 71.5 Hz). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 203.7 ppm (s).

Anal. Calcd for **7b**, $C_{15}H_{25}O_2N_2S_2P$: C, 49.9; H, 7.0; N, 7.8. Found: C, 50.1; H, 7.2; N, 8.0. $^1$H NMR ($CDCl_3$): $\delta$ 1.50 ppm (s, 9H, $C(CH_3)_3$), $\delta$ 2.90−3.30 ppm (m, 8H, $N(CH_2)_2$), $\delta$ 3.50−3.85 ppm (m, 8H, $O(CH_2)_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 31.9 ppm (d, $C(CH_3)_3$), $^3J_{PC}$ = 12.2 Hz), $\delta$ 39.7 ppm (d, $C(CH_3)_3$, $^2J_{PC}$ = 16.7 Hz), $\delta$ 49.9 ppm ($N(CH_2)_2$), $\delta$ 66.7 ppm ($O(CH_2)_2$), $\delta$ 101.6 ppm (C-5), $\delta$ 144.8 ppm (d, C(morph)$_2$, $\delta$ 200.5 ppm (d, C-3, $^1J_{PC}$ = 70.0 Hz). $^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 205.4 ppm (s).

**Reaction of 7a or 7b with $^t$BuCP (1). 7a** or **7b** (5 mmol), 162 or 164 mg, respectively) dissolved in $CH_2Cl_2$ (20 mL) was reacted with **1** (30 mmol) in a sealed tube at 100 °C. After the reaction mixture was cooled, solvent and excess phosphaalkyne were removed in vacuo. The residue was distilled at 150 °C/$10^{-3}$ mbar, resulting in a 3:2 mixture of **5** and **6** (R = $^t$Bu). Yield: 50%. The NMR data for **5** are identical to those published in ref 7. NMR data for **6** are as follows. $^1$H NMR ($C_6D_6$): $\delta$ 1.67 ppm (d, $C(CH_3)_3$, $^4J_{PH}$ = 1.5 Hz). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 35.6 ppm (d, $C(CH_3)_3$), $^3J_{PC}$ = 4.6 Hz), $\delta$ 41.3 ppm (d, $C(CH_3)_3$, $^2J_{PC}$ = 18.8 Hz), $\delta$ 206.4 ppm (pt, C-2/C-5, $^1J_{PC}$ = $^2J_{PC}$ = 48.1 Hz). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 283.2 ppm (s). MS (70 eV): *m*/*z* 232.2 (95.3, $M^+$). Anal. Calcd for $C_{10}H_{18}SP_2$: C, 51.7; H, 7.8. Found: C, 51.9; H, 7.8.

**Reaction of 4a or 4b with $^t$BuCP (1).** The mixture of **5** and **6** can be obtained directly from **4a** or **4b** on treatment with $^t$BuCP (**1**) by heating the mixture at 100 °C for 1 h. The workup procedure is the same as described above.

**Reaction of $CS_2$ with $^t$BuCP (1).** $^t$BuCP (3.942 g, 39.42 mmol) was added to a solution of $CS_2$ (1 g, 13.15 mmol) in diethyl ether (8 mL), and the reaction mixture was allowed to stir for 36 h. The solvents were removed in vacuo, and the dark yellow residue was purified by column chromatography (silica/hexane) to give a colorless oil (1.409 g, 46.1%), which was identified as a 4:1 mixture of **5** and **6** (R = $^t$Bu). The NMR data are identical to those given above.

**Reaction of $Et_3PCS_2$ with $^t$BuCP (1).** To a solution of $Et_3PCS_2$ (0.6 g, 3.09 mmol)[19] in diethyl ether (10 mL) was added $^t$BuCP (1.237 g, 12.37 mmol). The pink solution turned dark orange, and this reaction

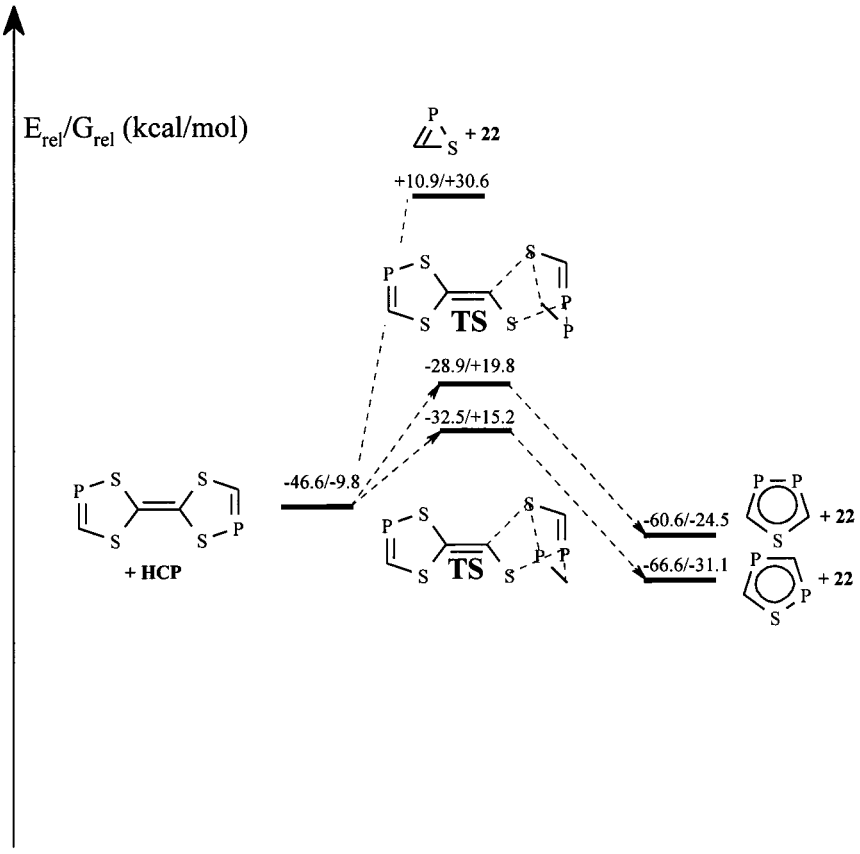



**Figure 5.** Relative energies/Gibbs free energies of the reactants, transition structures, intermediates, and products of the reaction of **21** with HCP (in kcal/mol).

mixture was stirred for 24 h, resulting in an orange solution and a yellow precipitate. The solution was removed by filtration, solvents were removed in vacuo, and the yellow residue was purified by column chromatography (silica/hexane) to give a pale yellow oil (0.526 g, 73.3%), which was identified as a 1:1 mixture of **5** and **6**. NMR data are identical to those above.

**Reaction of $(C_6H_{11})_3PCS_2$ with $^t$BuCP (1).** To a solution of $(C_6H_{11})_3PCS_2$ (1.2 g, 3.37 mmol)[20] in diethyl ether (10 mL) was added $^t$BuCP (1.179 g, 11.79 mmol), and the reaction mixture was allowed to stir for 48 h. The solution was removed by filtration, solvents were removed in vacuo, and the pale red residue was purified by column chromatography (silica/hexane) to give a pale yellow oil (0.325 g, 41.6%), which was identified as a 2:1 mixture of **5** and **6**. NMR data are identical to those given above.

**Synthesis of *cis*- and *trans*-$[PtCl_2(P_2SC_2{}^tBu_2)(PEt_3)]$ (12 and 13).** To a solution of pure $P_2SC_2{}^tBu_2$ (**5**) (200 mg, 0.86 mmol) in THF (5 mL) (prepared by a synthetic route[21] different from that described in this paper) was added solid $[\{Pt(PEt_3)Cl_2\}_2]$ (330 mg, 0.43 mmol). The pale yellow solution was stirred for 24 h, and the volatile components were removed in vacuo. The yellow residue was purified by column chromatography (silica/hexane) to give a yellow solid (176 mg, 67.6%), which was identified as a 1:2 mixture of *cis*- and *trans*-$[PtCl_2(P_2SC_2{}^tBu_2)(PEt_3)]$ by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^1H$ NMR spectroscopy. $^{31}P\{^1H\}$ NMR for **12** (101.3 MHz, $C_6D_6$, $H_3PO_4$ external standard, 25 °C): $\delta$ 243.2 ppm (d, P(B), $^2J_{P(B)P(A)} = 63.8$ Hz), $\delta$ 181.4 ppm (dd, P(A), $^2J_{P(A)P(N)} = 23.1$ Hz, $^2J_{P(A)P(B)} = 64.0$ Hz, $^1J_{P(A)Pt} = 4156.4$ Hz), $\delta$ 22.3 ppm (d, P(N), $2J_{P(N)P(A)} = 22.9$ Hz, $^1J_{P(N)Pt} = 3048.1$ Hz). $^{31}P\{^1H\}$ NMR for **13** (101.3 MHz, $C_6D_6$, $H_3PO_4$ external standard, 25 °C): $\delta$ 254.6 ppm (d, P(B), $^2J_{P(B)P(A)} = 60.2$ Hz), $\delta$ 210.5 ppm (dd, P(A), $^2J_{P(A)P(M)} = 529.1$ Hz, $^2J_{P(A)P(B)} = 60.0$ Hz, $^1J_{P(A)Pt} = 2408.2$ Hz), $\delta$ 13.4 ppm (d, P(M), $^2J_{P(M)P(A)} = 528.8$ Hz, $^1J_{P(M)Pt} = 3021.6$ Hz).

**Synthesis of *cis*-$[\{PtCl_2(PEt_3)\}_2(P_2SC_2{}^tBu_2)]$ (14).** In preliminary experiments, it was ascertained that symmetric $P_2SC_2{}^tBu_2$ ring **6** reacts much more rapidly with $[\{Pt(PEt_3)Cl_2\}_2]$ than its corresponding isomer **5**, permitting selective complexation of **6** to be achieved. Thus a sample of $[\{Pt(PEt_3)Cl_2\}_2]$ (500 mg, 0.65 mmol) was added as a solid to a THF solution of the two rings containing an equimolar amount of **6** (150 mg, 0.64 mmol), and the reaction mixture allowed to stir for 24 h. The presence of unreacted **5** was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. Solvent was removed in vacuo, and the residue was purified by column chromatography (silica/hexane) to give **14** as a yellow solid. Recrystallization from hexane afforded yellow crystals (460 mg, 70.7%) suitable for the X-ray diffraction study. Anal. Calcd for $C_{22}H_{48}C_{14}P_4SPt_2$: C, 26.41; H, 4.84; P, 12.4. Found: C, 26.2; H, 4.7; P, 12.3. $^{31}P\{^1H\}$ NMR for **14** (101.3 MHz, $C_6D_6$, $H_3PO_4$ ext. standard, 25 °C): $\delta$ 142.5 ppm (P(C), $^1J_{P(C)P(C')}$ 312.3 Hz, $^2J_{P(C)P(M)}$ 21.5 Hz, $^1J_{P(C)Pt(X)}$ 4213.6 Hz, $^2J_{P(C)Pt(X')}$ 21.5 Hz); $\delta$ 11.2 ppm (P(M), $^2J_{P(M)P(C)}$ 21.6 Hz, $^1J_{P(M)Pt(X)}$ 3022.0 Hz).

**Crystallography of 14 (as Its 2.5-Toluene Solvate).** Crystal data: $C_{22}H_{48}Cl_4P_4Pt_2 \cdot 2.5C_7H_8$, $M = 1230.9$, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.791(4)$ Å, $b = 13.293(4)$ Å, $c = 15.210(6)$ Å, $\alpha = 108.61(3)°$, $\beta = 94.85(3)°$, $\gamma = 90.92(2)°$, $V = 2440(1)$ Å$^3$, $Z = 2$. $D_c = 1.68$ g cm$^{-3}$. $F(000) = 1210$. Monochromated Mo K$\alpha$ radiation was used; $\lambda = 0.710\,73$ Å. $T = 173(2)$ K. Data were collected on a $0.3 \times 0.2 \times 0.2$ mm crystal using an Enraf-Nonius CAD 4 diffractometer. A total of 6763 unique reflections were measured for $2 < \theta < 25°$, of which 5195 had $I > 2\sigma(I)$. The structure was solved by direct methods using SHELX86 and refined on $F^2$ with all non-H atoms anisotropic. H atoms were included in the riding mode with $U_{iso} = 1.2U_{eq}$(C). Final residuals were R1 = 0.048 for $I > 2\sigma(I)$ and wR2 = 0.119 (for all data).

## Theoretical Calculations

Calculations were carried out with the Gaussian 94 package[22] at the B3LYP/3-21G(*) and B3LYP/6-311+G** levels of theory. For the smaller systems, MP2/6-31+G* calculations were also carried out to determine whether the choice of the method used had an impact on the relative energies of the transition states and the products. Since the changes at the MP2 level relative to the B3LYP results were less than 5 kcal/mol and on the competing reaction pathways (leading to different stereoisomers) were even much smaller, only the B3LYP/6-311+G** results are discussed. When other data are considered, the level of theory employed is mentioned. The reactants, intermediates and products were confirmed as minima on the potential energy hypersurface by second-derivative calculations. Transition structures were characterized by a single imaginary frequency. Subsequent IRC runs showed the minima corresponding to the transition structures. The Gibbs free energies used were uncorrected for internal rotations; however, it is likely that, if corrected, they would have similar contributions for the competing pathways leading to the different isomers. In the Results and Discussion, the Gibbs free energy values are given; the relative energies are given only in Figures 3 and 5.

## Conclusions

The reaction of $CS_2$ and its complexes with $^t$BuCP furnished an isomeric mixture of the aromatic compounds 3,5-di-*tert*-butyl-1-thia-2,4-diphosphole and 2,5-di-*tert*-butyl-1-thia-3,4-diphosphole, the latter not having been characterized before. The formation of these unexpected products could be rationalized by a combined theoretical−experimental approach. The reaction mechanism proposed accounts for all the observed products and intermediates and is—according to the calculations carried out at different levels—energetically feasible. The reaction proceeds via a nucleophilic carbene intermediate, which forms via cycloaddition. During the course of the reaction, transition structures are found where two $\sigma$ bonds are breaking and a delocalized $\pi$ system is dispersing while simultaneously two new $\sigma$ bonds and an aromatic $\pi$ system are forming. Such intermediates are likely to occur in other five-membered systems with second- and third-row elements, which form hypervalent systems relative easily.

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**Supporting Information Available:** Crystal data, structure refinement details, positional and thermal parameters, bond distances and angles, and least-squares-plane data for **14** (Tables S1−S5) and total energies and B31YP/6-311+G** optimized geometries in Cartesian coordinates for the most important minima and transition structures (Tables S6 and S7) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Margulis, T. N.; Templeton, D. H. *J. Am. Chem. Soc*. **1961**, *83*, 995.
(20) Vittal, J. J.; Dean, P. A. W. *Acta Crystallogr*. **1997**, *C53*, 1879.
(21) d'Arbeloff, S. E.; Hitchcock, P. B.; Nixon, J. F.; Nagasawa, T.; Kawaguchi, H.; Tatsumi, K. *J. Organomet. Chem*. **1998**, *564*, 189.
(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.