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Unexpected Thermal Reactivity of Phosphirano-[1,2]thiaphosphole *P*–$W(CO)_5$ Complexes

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Spiro[fluorene-9,6′-[2]thia[1]phosphabicyclo[3.1.0]hex[3]enes] **7a**–**c** have been obtained in one step from 3,5-diaryl-1,2-thiaphospholes and 9-diazofluorene or its 2,7-dibromo derivative. The bicyclic phosphiranes are stable against water and resist attempts at sulfuration or selenation of the phosphorus atom. However, cleavage of the P–C ring fusion with hydrogen chloride followed by hydrolysis led to the monocyclic 2-(9*H*-fluoren-9-yl)-2,3-dihydro-1,2-thiaphosphole 2-oxides **8a**–**c**. Phosphiranes **7a**–**c** also react to form the hexacarbonyltungsten-(*P*–*W*) complexes **10a**–**c** readily and in high yields. These complexes rearrange in toluene solution at 50–80 °C to form the spiro[fluorene-9,2′-[1]phospha[6]thiabicyclo[3.1.0]hex-3-ene]-$W(CO)_5$-(*P*–*W*) complexes **11a**–**c**, which are the first representatives of ring-fused thiaphosphiranes. Compound **11a** is readily desulfurated with tributylphosphane to form the highly oxygen-sensitive spiro[fluorene-9,2′-[2*H*]phosphole] **13**, which is reconverted into **11a** upon treatment with sulfur. Bicyclic 1,3,2-dithiaphospholanes **12a**–**c** are formed as minor byproducts of the thermal isomerization of phosphiranes **10**. Compound **10a** slowly rearranges in solution to give **12a** as the sole product. Compounds **12** may result from a formal [3+2] cycloaddition reaction of an α,β-unsaturated thione, formed by partial decomposition of **10**, with a dipolar valence isomer of **10** or **11**, featuring a $W(CO)_5$-complexed thiocarbonyl-phospha-ylide dipole ($R_2C{=}S^+{-}P^-R$). $W(CO)_5$ complexation is not a prerequisite for the cycloaddition reaction: the uncomplexed phosphirano-thiaphosphole **7a** reacts with thiobenzophenone in the same way to form the bicyclic 1,3,2-dithiaphospholane **18** in high yield.

Introduction

Phosphiranes are strained three-membered heterocycles, the chemistry of which has been well investigated.[1] They can also be looked at as cyclic phosphanes, and therefore they have attracted attention as potential ligands in catalytically active transition-metal complexes.[2] Owing to the strong pyramidalization at the phosphorus, the ligand properties of phosphiranes are expected to be different to those of common acyclic phosphanes because a rather weak σ-donor character is paired with a significant π-accepting ability.[3–5] However, many phosphiranes appear to be less suited as ligands because they are chemically quite reactive. This problem is solved by the introduction of bulky substituents to reduce the reactivity of the phosphorus atom[3] or by the incorporation of the latter into a rigid polycyclic ring system to suppress the decomposition by a [2+1] cycloreversion. By taking the latter approach, Grützmacher and coworkers have designed the BABAR-Phos class of phosphiranes,[4–7] which were found to form fairly stable Rh^I and Pt^0 complexes that could be used as hydrosilylation[4] and hydroboration[8] catalysts.

Bicyclic [*a*]-fused phosphiranes appear not to have been used so far as ligands in transition-metal-catalyzed reactions, although the existence of a variety of metal carbonyl complexes[1,9] indicates the coordinating ability of the phosphorus atom in this structural environment. Furthermore, the chemistry of this particular type of phosphirane is not yet well developed. A versatile approach to [*a*]-fused phosphiranes is provided by the cyclopropanation of the P=C bond of heterophospholes with diazo compounds through a [3+2] cycloaddition/ring-contraction sequence.[10] As 3,5-diaryl-1,2-thiaphospholes are readily available[11] and the P=C bond of 1,2-thiaphospholes is an excellent cycloaddition partner,[12–14] we followed this route to synthesize a 6,6-diphenyl-2-thia-1-phosphabicyclo[3.1.0]hex-3-ene using diazodiphenylmethane as the cyclopropanation reagent.[15] We found that the thermal stabilities of both the phosphirane and its $W(CO)_5$ and $Fe(CO)_4$ complexes are only moderate, and that the effect of elevated temperatures is different for the free phosphirane and its metal complexes.

In continuation of these studies, we have synthesized spiro[fluorene-9,6′-[2]thia[1]phosphabicyclo[3.1.0]hex[3]enes] and their *P*–$W(CO)_5$ complexes and have found that the thermally induced reactivities of the latter are surprisingly different from the 6,6-diphenyl derivative mentioned above. The results are reported in this paper.

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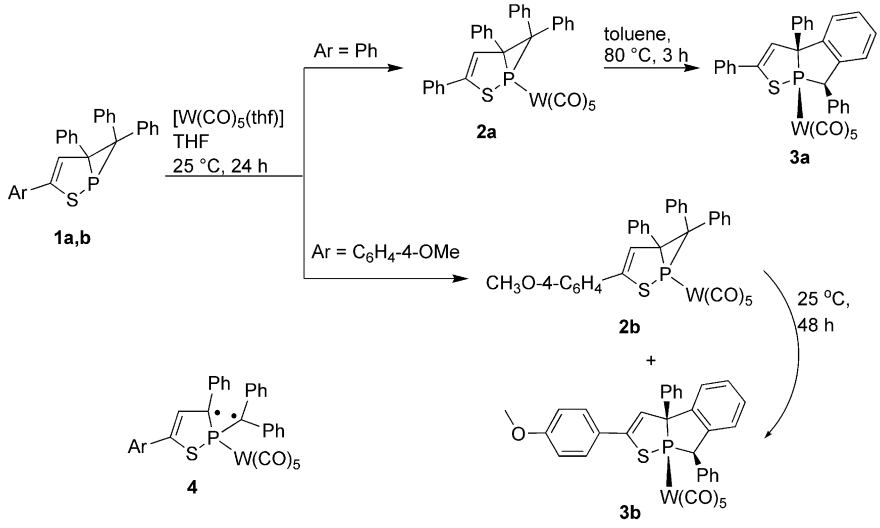
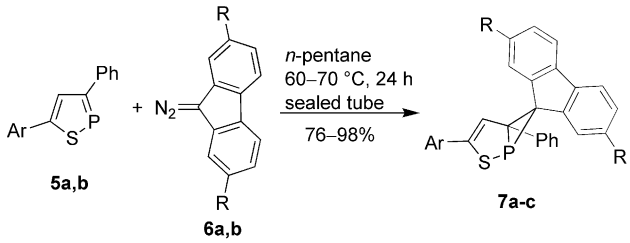


Scheme 1. Formation of thieno[3,2-*a*]isophosphindole derivatives **3**.

Results and Discussion

In our earlier communication,[15] we reported that the 3,5,6,6-tetraphenyl-substituted phosphirano-thiaphosphole **1a** smoothly forms a pentacarbonyltungsten-(*P*–*W*) complex **2a**, which undergoes a skeletal rearrangement to the $W(CO)_5$-complexed dihydroisophosphindole **3a** at elevated temperature (Scheme 1). We have now found that the $W(CO)_5$ complex of the analogous 3-(4-anisyl)-substituted bicyclic phosphirane **1b** can be observed in solution (δ_P = –57.5 ppm) but cannot be isolated in pure form because it is readily transformed into dihydroisophosphindole **3b** under the conditions of its formation from **1b** (25 °C, 24 h). The 2-phenylphosphirane → dihydroisophosphindole ring-expansion pathway is likely to include the strongly resonance-stabilized 1,3-diradical **4** resulting from homolytic cleavage of the C–C bond of the phosphirane ring.

We speculated that replacement of the $Ph_2C^{\cdot}$ unit in diradical **4** by a fluoren-9-yl radical might not allow the radical 1,5-cyclization to take place. Therefore, our attention was drawn to spiro[fluorene-9,6′-[2]thia[1]phosphabicyclo[3.1.0]hex[3]enes] **7**. 1,2-Thiaphospholes **5a**,**b** were found to react with 9-diazofluorene (**6a**) and its 2,7-dibromo derivative **6b** to give the phosphirano-[1,2]thiaphospholes **7a**–**c** in high yields (Scheme 2). The reaction is likely to occur by a [3+2] cycloaddition reaction followed by N_2 extrusion from the resulting pyrazoline and ring contraction.[10a] The progress of the reaction could easily be monitored by ^{31}P NMR spectroscopy: δ_P(**5a**) = 204.2 ppm, δ_P(**7a**) = –51.7 ppm. The loss of aromaticity of the heterophosphole was indicated by the upfield shift of the signal of the ring proton 4-H: δ_H(**5a**) = 8.20 ppm, δ_H(**7a**) = 6.42 ppm. An interesting detail in the ^1H NMR spectra (400 MHz) of compounds **7** is the absence of signals from the 5-phenyl at 25 °C. Clearly, steric hindrance by the fluorene ring reduces the rotation rate of the phenyl ring and leads to signal coalescence; at 227 K the signals of five magnetically nonequivalent ring protons are observed.



7	a	b	c
Ar	Ph	C_6H_4-4-OMe	Ph
R	H	H	Br

Scheme 2. Synthesis of spiro[fluorene-9,6′-[2]thia[1]phosphabicyclo[3.1.0]hex[3]enes] **7a**–**c**.

The structure of **7a** was ascertained by X-ray structure analysis (Figure 1). The P–C bonds of the phosphirane ring (1.904, 1.889 Å) are exceptionally long compared with the hitherto documented range of 1.78–1.89 Å.[1b] On the other hand, the C–C bond length in the three-membered ring (1.540 Å) is in the normal range. The strong pyramidalization of the phosphorus atom is evident from the value of the sum of the bond angles (247.8°).

In the solid state, phosphirano-thiaphospholes **7** are remarkably stable. From a suspension in water, compound **7a** could be recovered unaltered after several days. All attempts to sulfurize (S_8, NEt_3) or selenize (grey or red Se, NEt_3) the phosphorus atom failed. On the other hand, phosphiranes **7a**–**c** turned out to be acid-labile. The products from treatment with a water-containing ethereal HCl solution could be identified as 2-(fluoren-9-yl)-3*H*-1,2-thiaphosphole 2-oxides **8a**–**c** (Scheme 3) by their spectroscopic (e.g., δ_P = 78.3–79.2 ppm) and analytical data and were isolated in 60–76% yields. Complete transformation of **7a** into **8a** was also observed when a $CDCl_3$ solution of **7a** was left in an NMR tube for 12 h. A strong band in the IR spectra of **8** at around 1200 cm^{-1} is in the range expected for the P=O valence vibration of phosphinic acid thioesters.[16] Examina-

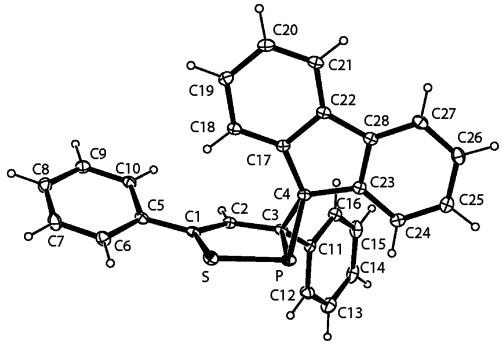
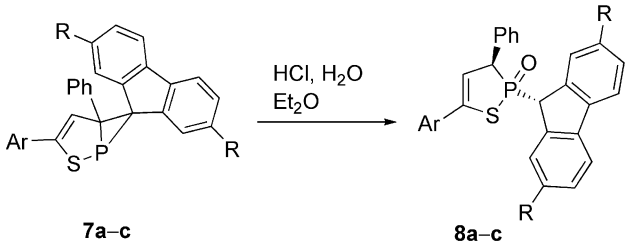


Figure 1. Molecular structure of **7a** in the solid state. Thermal displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: P–C(3) 1.889(2), P–C(4) 1.904(2), C(3)–C(4) 1.540(2), P–S 2.1018(7); C(3)–P–C(4) 47.89(7), C(3)–C(4)–P 65.53(9), C(4)–C(3)–P 66.57(10), C(3)–P–S 94.60(6), C(4)–P–S 105.29(6).



7,8	a	b	c
Ar	Ph	C_6H_4-4-OMe	Ph
R	H	H	Br

Scheme 3. Acid hydrolysis of **7**.

tion of the $^2J_{P,H}$ coupling constants of the protons adjacent to the phosphorus centre (3-H: $J_{P,H}$ = 6.3 Hz; 9′-H: $J_{P,H}$ = 25.5 Hz) suggested a *trans* relationship between 3-H and the P=O bond as well as a *cis* relationship between 9′-H and P=O.[17] The supposed structure was confirmed by an X-ray structure analysis of **8a** (Figure 2). It is evident that the given configuration is the thermodynamically favored diastereoisomer because steric interactions between the fluorene ring system and the *trans*-positioned 3-Ph group are minimized. The fast reactions of **7a**–**c** were unexpected because the 6,6-diphenyl-substituted analogue **1a** proved to be inert against HCl/water over several days.

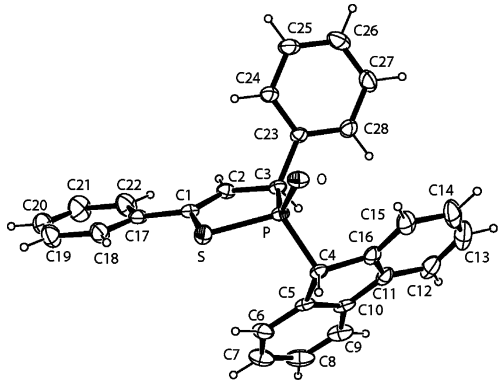
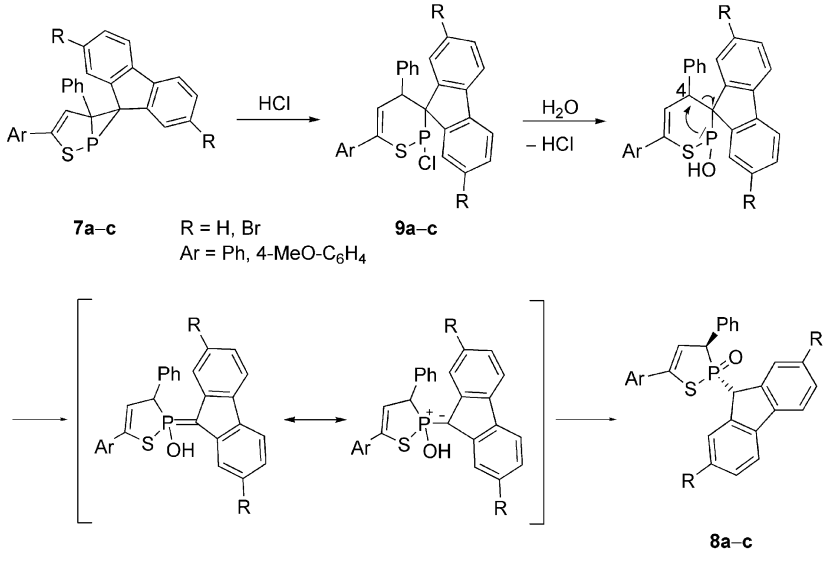


Figure 2. Molecular structure of 3*H*-1,2-thiaphosphole 2-oxide **8a** in the solid state. Thermal displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: P–O 1.466(3), P–C(3) 1.855(3), P–C(4) 1.822(3), S–P 2.094(1); O–P–S 112.97(12), C(3)–P–S 97.77(11), C(4)–P–S 108.95(12), C(4)–P–C(3) 106.23(16), C(23)–C(3)–P 109.7(2).

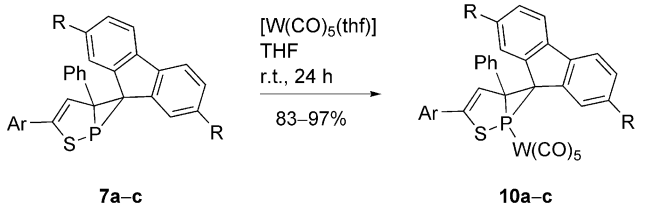
A mechanistic proposal for the formation of the 1,2-thiaphosphole 2-oxides **8** is given in Scheme 4. The transformation is likely to begin with the addition of hydrogen chloride across the internal P–C bond of the phosphirane moiety of **7**, resulting in the formation of the *P*-chloro-3,4-dihydro-1,2-thiaphosphorine **9**. An analogous reaction has been described for phosphirano-[1,2,3]diazaphospholes and the resulting chlorophosphanes were quenched with methanol to



Scheme 4. Suggested mechanism for the formation of 3*H*-1,2-thiaphosphole 2-oxides **8a**–**c**.

give the corresponding methoxyphosphanes.[18] In our case, solvolysis of **9** by the water present in the ethereal HCl solution could generate a hydroxyphosphane; isomerization of this hydroxyphosphane to the phosphane oxide, as shown in Scheme 4, is then conceivable.

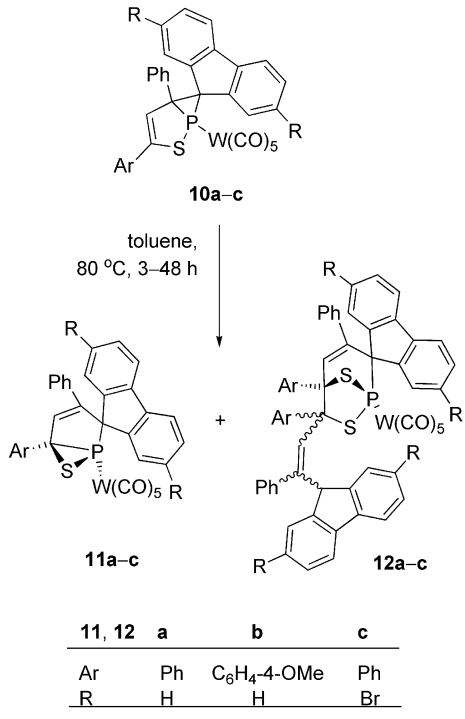
When exposed to $[W(CO)_5(thf)]$, the phosphiranes **7a**–**c** were readily converted into the pentacarbonyltungsten complexes **10a**–**c** in high yields (Scheme 5). The ^{31}P NMR signals of the complexes are shifted downfield relative to the parent phosphiranes **7** [e.g., δ_P(**10b**) = –37.0 ppm; δ_P(**7b**) = –54.2 ppm] and show a $J_{P,W}$ coupling constant typical of η^1-$W(CO)_5$ complexes (e.g., **10b**: $J_{P,W}$ = 275.6 Hz). Other NMR changes occurring after complexation are also characteristic of phosphiranes (an increase in $^3J_{P,H}$ and a decrease in $^1J_{P,C}$ in the phosphirane ring). Owing to the increase in steric hindrance after addition of the $W(CO)_5$ fragment, the rotation of the phenyl group directly attached to the phosphirane ring is hindered on the NMR timescale even at ambient temperature. In contrast to the parent phosphiranes **7** (see above), the signals of the individual 5-Ph protons are observable in the ^1H NMR spectra under standard conditions.



10	a	b	c
Ar	Ph	C_6H_4-4-OMe	Ph
R	H	H	Br

Scheme 5. Synthesis of the $W(CO)_5$–phosphirane complexes **10a**–**c**.

In solution, the bicyclic phosphiranes **7** as well as their $W(CO)_5$ complexes **10** undergo further thermal transformations, which proceed slowly even at room temperature and with an appreciable rate at 50–80 °C. However, only the *P*-complexed compounds react cleanly, whereas the free bicyclic phosphiranes produce an inseparable mixture of undefined products, as indicated by a multitude of ^{31}P NMR signals. The products obtained differ significantly from the tricyclic thieno[3,2-*a*]isophosphindole derivatives **3** observed upon heating of the analogous 6,6-diphenyl-1,2-phosphirano-thiaphosphole complexes **2** (see Scheme 1).[15] For the spiro-connected complexes **10**, heating at 80 °C in toluene led to the thiaphosphirane complexes **11** [δ_P = –6.4 (**11a**), –6.2 (**11b**), –6.9 (**11c**) ppm] in yields of up to 80% (Scheme 6 and Table 1). Bicyclic dithiaphospholanes **12** were obtained as minor byproducts as a mixture of two stereoisomers (e.g., **12a**: δ_P = 54.3 and 53.1 ppm, 7:1 ratio; repeated chromatographic purification shifted this ratio to 10:1). When a solution of **10a**,**b** in $[D_1]$chloroform or $[D_8]$-toluene was allowed to stand at ambient temperature for 4 weeks, dithiaphospholanes **12a**,**b** (ratio of isomers for **12a**: 2.3:1) were formed almost exclusively (isolated yield of **12a**: 68%) with traces (about 2%) of **11a**,**b**. In $[D_3]$acetonitrile, the transformation of **10a** was 2–3 times faster than in toluene: after 24 h at 22 °C, a conversion of 22% (yield of **11a**: 4%; **12a**: 16%) was observed compared with 8.7% in toluene solution (almost exclusive formation of **12a**). As **10a** is only sparingly soluble in acetonitrile at room temperature, the higher ratio of **11a/12a** compared with the situation in toluene solution may reflect the influence of concentration on the different kinetics of the formation of **11a** and **12a** (monomolecular vs. bimolecular, see the discussion on the mechanism). In acetonitrile solution at 80 °C, on the other hand, the dominating transformation of the bicyclic phosphiranes **10** is the decomplexation reaction which reconstitutes the metal-free phosphiranes **7**.



11, 12	a	b	c
Ar	Ph	C_6H_4-4-OMe	Ph
R	H	H	Br

Scheme 6. Thermally induced transformation of phosphirano-thiaphosphole–$W(CO)_5$ complexes **10a**–**c**. See Table 1 for conditions and yields.

Table 1. Results of the thermal reactions of **10a**–**c** in toluene solution.

	Conditions	% Conversion	% Yield of **11**, **12**	δ_P(**12**)[a] [ppm]
10a	80 °C, 48 h	100	80, 7	54.3, 53.1
10b	80 °C, 3 h	100	70, 0	53.6, 52.2
	50 °C, 24 h	79	61, 20[b]	
10c	80 °C, 8 h	88	70, 15[b,c]	58.0, 53.2
	50 °C, 72 h	44	24, 20[b,c]	

[a] Two isomers, values refer to the major/minor isomer. [b] Yield determined by ^{31}P NMR spectroscopy. [c] Purification and separation not possible.

The structures of **11a** and **12a** were clarified by X-ray structure analysis (Figure 3 and Figure 4). The ^1H NMR spectra of **12a** displayed two signals for the fluorenyl proton

9-H with the same intensity ratio as observed in the ^{31}P NMR spectra [δ_H(9-H) = 5.07 (major isomer) and 4.90 ppm]. The two isomers are either the *E* and *Z* isomers of the exocyclic double bond or the two C-6 epimers. As the signal(s) of the exocyclic olefinic proton appears amid the many aromatic protons and therefore could not be observed separately, neither of the two possibilities can be excluded.

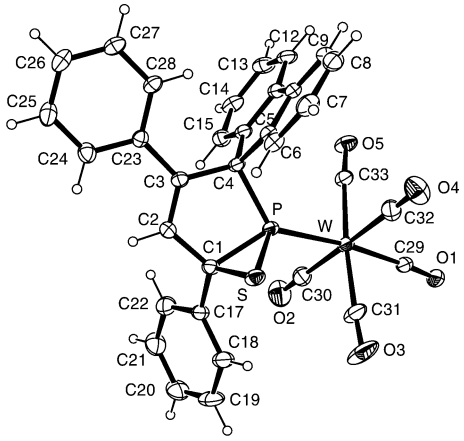


Figure 3. Molecular structure of thiaphosphirane **11a** in the solid state. Thermal displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: P–C(1) 1.833(3), P–S 2.085(1), S–C(1) 1.883(4), P–C(4) 1.895(3), P–W 2.4457(9); P–C(1)–S 68.23(12), C(1)–P–S 57.01(11), C(1)–S–P 54.75(10), C(2)–C(3)–C(23) 123.6(3).

Heterocycles **11** are the first ring-fused thiaphosphiranes and also the first 1,2λ^3-thiaphosphirane complexes reported so far. Only a few examples of monocyclic 1,2λ^3- and 1,2λ^5-thiaphosphiranes have been reported.[19] All the bond lengths in the three-membered ring of **11a** are shorter than in 2-mesityl-3,3-diphenyl-1,2-thiaphosphirane,[19e] an effect that is associated with the diminished electron density at the phosphorus due to complexation.

Similar to simple thiiranes,[20] 1,2-thiaphosphiranes should be amenable to desulfuration by appropriate tertiary phosphanes. This transformation has so far been successful with 1,2λ^5-phosphiranes,[19d,19e] and in one case also with 1,2λ^3-phosphiranes.[21] We found that **11a** could be desulfurated with tributylphosphane within 1 min to furnish the W(CO)$_5$-containing complex **13** quantitatively (Scheme 7). Owing to its high sensitivity toward oxygen (see below), this phosphole, which displays a ^{31}P NMR resonance (δ_P = 233.5 ppm) in the expected[22] range, could not be separated from the byproducts. When polymer-supported PPh_3 was used for the desulfuration, incomplete conversion was observed even after 24 hours. On the other hand, phosphole **13** reacted immediately with an excess of elemental sulfur and was reconverted quantitatively into **11a**.

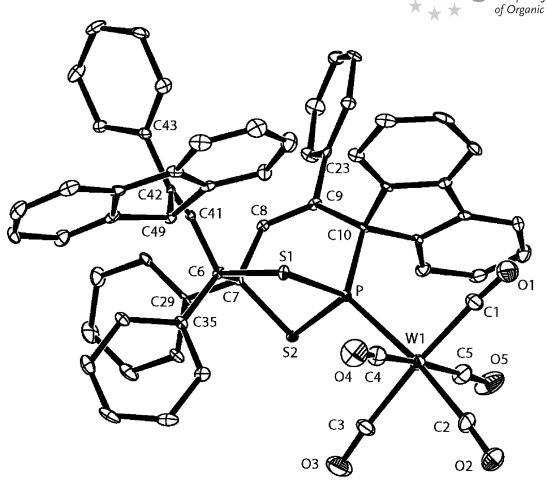
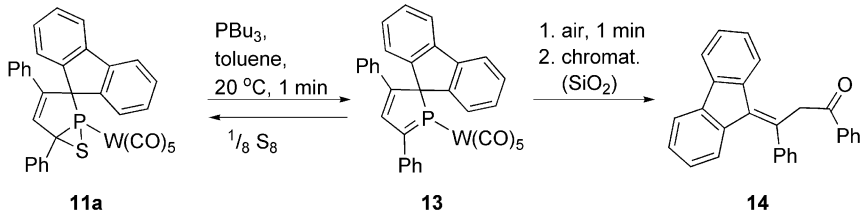


Figure 4. Molecular structure of bicyclic 1,3,2-dithiaphospholane **12a** in the solid state. Thermal displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: S(1)–P 2.086(2), S(1)–C(6) 1.856(5), S(2)–P 2.069(2), S(2)–C(7) 1.849(5), C(6)–C(7) 1.620(7), C(8)–C(9) 1.324(8), P–C(10) 1.892(6), P–W(1) 2.5244(14); S(2)–P–S(1) 96.46(8), S(1)–C(6)–C(7) 107.5(3), S(2)–C(7)–C(6) 109.0(3), P–S(1)–C(6) 102.2(2), P–S(2)–C(7) 92.9(2), C(10)–P–W(1) 125.4(2).

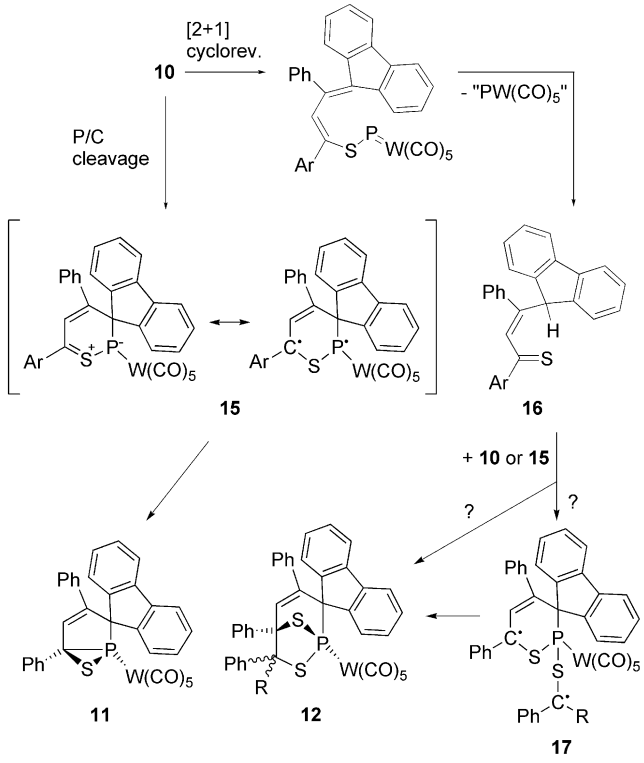
The fate of 2*H*-phosphole **13** upon exposure to air can be clarified. When a solution of freshly prepared **13** was in contact with air, it was consumed quantitatively within 1 min (^{31}P NMR control). Column chromatography allowed the separation of fluorenylidenepropanone **14** (80% yield) from tributylphosphane sulfide and a fraction, which according to the ^{31}P chemical shifts, was a mixture of the known[23] tungsten complexes *trans*- and *cis*-[W(CO)$_4$(PBu$_3$)$_2$] and [W(CO)$_5$(PBu$_3$)] (δ_P = –2.23, –9.25 and –5.88 ppm, respectively). The mode of formation of **14** is not yet fully clear. Similarly to the behavior of phosphaalkenes,[24] however, it may be assumed that **13** initially reacts with oxygen to undergo an oxidative cleavage via a 1,2,3-dioxaphosphetane. The details of the loss of the [P(=O)W(CO)$_5$] fragment from the ring-opened intermediate are unknown.

A mechanism for the formation of compounds **11** and **12** from the phosphirano-thiaphosphole–W(CO)$_5$ com-



Scheme 7. Synthesis and reactions of 2*H*-phosphole **13**.

plexes **10** is proposed in Scheme 8. The conversion **10** → **11** at elevated temperature corresponds to a valence isomerization, for which a stepwise pathway is proposed. A concerted 4e electrocyclic process would have to take a conrotatory course, which cannot be realized by the bicyclic structure of **10**. A six-membered phosphorus heterocycle **15**, which can be considered as a thiocarbonyl-phosphaylide dipole or the corresponding 1,3-diradical, could be generated by cleavage of the ring-connecting P–C bond and could form phospholo-thiaphosphirane **11** by 1,3-cyclization. The observed rate acceleration for the isomerization of **10b** (Ar = 4-anisyl) compared with **10a** (Ar = Ph) is reasonable as the anisyl substituent can stabilize both a positive charge and a radical centre on the thiocarbonyl carbon atom of the intermediate **15**. On the other hand, the formation of **12**, which occurs slowly at room temperature, is likely to begin with the cleavage of the phosphirane ring by a [2+1] cycloreversion. This generates a tungsten-complexed phosphinidene unit, R–S–P=$W(CO)_5$, which after loss of the $PW(CO)_5$ fragment and hydrogen abstraction (from the solvent) yields the ene-thione **16**. A formal [3+2] cycloaddition of the latter to **10**, **11** or **15** provides the bicyclic 1,3,2-dithiaphospholane **12**. The postulated cycloreversion step has analogies in the chemistry of phosphiranes. Thus, it has been reported that $Fe(CO)_4$-complexed bicyclic *P*-aminophosphiranes (2-aza-1-phosphabicyclo[*n*.1.0]alkanes) undergo a slow [2+1] cycloreversion at room temperature and that the formed R–P=$Fe(CO)_4$ intermediates can be trapped by intra- and intermolecular [2+1] cycloaddition at C=C and C≡C bonds, respectively.[9]

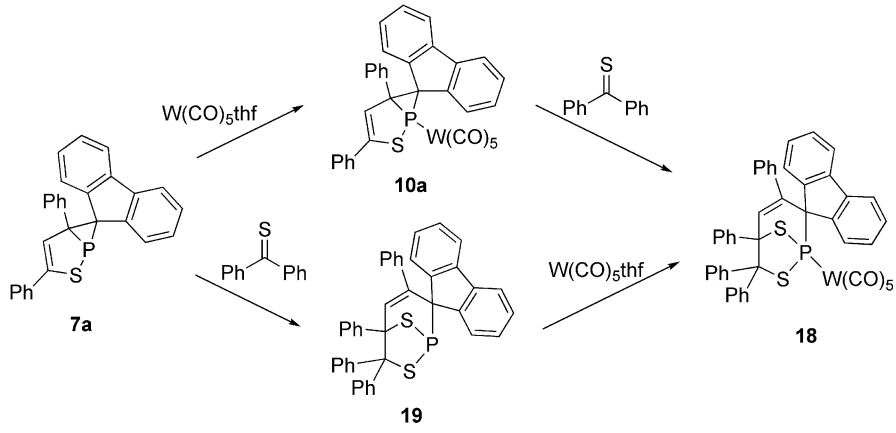


Scheme 8. Suggested mechanism for the formation of **11a** and **12a** [R = CH=C(Ar)(9-fluorenyl)].

At this point, it is appropriate to recall the thermal behavior of the 6,6-diphenyl-substituted 2-thia-1-phosphabicyclo[3.1.0]hex-3-enes **1a**,**b** and their $W(CO)_5$ complexes **2**.[15] The uncomplexed phosphirane **1a** undergoes a thermal fragmentation to yield a butadienyl sulfide (i.e., a tautomer of an alkenyl thione that is structurally analogous to **16** in Scheme 8), for which a phosphinidene cycloreversion, analogous to the one proposed above for the $W(CO)_5$-complexed phosphiranes **10**, has been suggested. The $W(CO)_5$ complexes **2**, on the other hand, undergo a skeletal rearrangement (see Scheme 1) beginning with a homolytic cleavage of the phosphirane C–C bond, which is in contrast to the suggested P–C bond cleavage of **10** at elevated temperature. It would be interesting to know whether the different reaction pathways are related to the bond lengths in the phosphirane rings of **1**, **2** and **10**. However, all our efforts to obtain suitable crystals of **10a** for structure determination failed and therefore comparison with **2a**[15] was not possible.

Ylides of the type $R_2C{=}S^+{-}P^-{-}R$, as embedded in intermediate **15**, have not yet been described in the literature. However, two related types of phosphaylides have been described recently. Streubel and co-workers[25] proposed a carbonyl phosphaylide [$R_2C{=}O^+{-}P^-(R')$–$W(CO)_5$] as an intermediate in the reaction of a (2*H*-azaphosphirene)pentacarbonyltungsten complex with 2 equiv. of an aldehyde furnishing a 1,4,2-dioxaphospholane. Lammertsma and co-workers[26] discussed the role of dipolar azomethine phosphaylides [$R_2C{=}N^+(R){-}P^-(R')$–$W(CO)_5$] in the reaction of diimines with phosphinidene–$W(CO)_5$ complexes giving bicyclic 1,4,2-diazaphospholanes. Quantum chemical calculations for an uncomplexed model system suggested that the products resulted from an intramolecular [3+2] cycloaddition of the 1,3-dipole at an imine C=N bond rather than from an insertion of the latter in the C–P bond of the azaphosphiridine valence isomer of the dipole. The analogy to these two reports, as well as the highly dipolarophilic character of the C=S bond of thiones,[27] suggests that 1,3,2-dithiaphospholanes **12** result from a [3+2] cycloaddition reaction of thiocarbonyl-phosphaylide **15** and thione **16** (Scheme 8). It is not clear, however, whether such a cycloaddition would take a concerted or a stepwise (via diradical **17**) pathway. Computational studies[28] of the closely related cycloaddition reaction of thiobenzophenone *S*-methylide ($Ph_2C{=}S^+{-}CH_2^-$) and thiobenzophenone yielding 4,4,5,5-tetraphenyl-1,3-dithiolane have revealed that the stepwise biradical process has a lower activation energy than the concerted one, which would lead to the regioisomeric and thermodynamically favoured 2,2,4,4-tetraphenyl-1,3-dithiolane. We note that the regiochemistry of the formation of 1,3,2-dithiaphospholanes **12** corresponds to the regiochemistry that leads to 4,4,5,5-tetraphenyl-1,3-dithiolane and may hint toward the stepwise diradical process.

Is thiocarbonyl-phospha-ylide **15** the only possible cycloaddition partner to trap thioketone **16** or are the bicyclic valence isomers **10** and **11** likely candidates, too? To answer this question, we investigated the reaction of **10a** with thiobenzophenone (Scheme 9) and were pleased to find that



Scheme 9. Synthesis of dithiaphospholane **19** and its metal complex **18**.

1,3,2-dithiaphospholane **18** (δ_P = 52.3 ppm, $^1J_{P,W}$ = 271.0 Hz) was formed readily (3 h, 22 °C) and in 93% yield. Notably, even the uncomplexed phosphirane **7a** reacted with thiobenzophenone under identical conditions to give in 93% yield the uncomplexed 1,3,2-dithiaphospholane **19** (δ_P = 26.9 ppm), which in turn could be converted quantitatively into the W(CO)$_5$ complex **18**. In contrast to **7a**, the corresponding 6,6-diphenyl derivative **1a** did not react cleanly with thiobenzophenone. The reaction of phospholothiaphosphirane **11a** with Ph_2C=S (toluene, 22 °C, 4 h), on the other hand, did not furnish **18** but gave a so-far unknown product (δ_P = 101.9 ppm), which was of limited stability under the conditions of column chromatography. These results suggest that phosphirano-thiaphospholes **7** and **10** react with thioketones, either directly or via ring-opened intermediates such as **15** (Scheme 8), in a formal [3+2] cycloaddition, whereas phospholothiaphosphiranes **11** do not react in the same manner.

Based on these results, phospholo-thiaphosphiranes **11** can be excluded as the precursors of 1,3,2-dithiaphospholanes **12**. The Diels–Alder-like [2π+2σ+2π] cycloaddition reaction of **10** and a thioketone remains a possibility, also in view of the highly dienophilic character of thiocarbonyl compounds.[29] This cycloaddition could be highly asynchronous, proceeding via 1,5-diradical **17** as an intermediate in the extreme case. Because the reaction of **10a** with Ph_2C=S takes place at room temperature, the alternative mechanistic proposal discussed above, namely the [3+2] cycloaddition pathway involving phosphaylide **15**, would require **15** to be in equilibrium with **10a** already at room temperature, but not to undergo the 1,3-cyclization to yield thiaphosphirane **11** at this temperature.[30]

Conclusions

Spiro[fluorene-9,6′-[2]thia[1]phosphabicyclo[3.1.0]hex[3]-enes] **7** can be prepared conveniently and in high yields from 1,2-thiaphosphole and 9-diazofluorenes. We have studied three different reactions of **7**, namely acidic hydrolysis, leading to cleavage of the P–C ring-fusion bond and the formation of monocyclic 3*H*-1,2-thiaphosphole 2-oxides **8**, the formation of *P*–W(CO)$_5$ complexes **10** and the smooth cycloaddition reaction with thiobenzophenone, which yields the bicyclic 1,3,2-dithiaphospholane **19**. Neither the uncomplexed phosphirano-thiaphospholes **7** nor their *P*–W(CO)$_5$ complexes **10** are thermally robust. Whereas the former seem to undergo unspecific decomposition, the latter can enter different reaction channels depending on the solvent and the temperature. In toluene solution at room temperature, the major pathway includes an α,β-unsaturated thione, which likely results from a slow [2+1] cycloreversion followed by fragmentation of the so-formed W(CO)$_5$-complexed thiophosphinidene moiety. This thione undergoes a rather fast cycloaddition reaction with the precursor molecule **10** or a monocyclic valence isomer thereof, which may result from the cleavage of the P–C ring-fusion bond of **10** and can be considered as a so-far unknown thiocarbonyl-phosphaylide dipole, $R_2C=S^+–P^–R$, or the corresponding 1,3-diradical form. Although the analogy, in terms of reactivity and regiochemistry, with the well-known [3+2] cycloaddition reaction of the thiocarbonyl ylide dipole $Ph_2C=S^+–CH_2^–$ and thiobenzophenone is striking, the available data do not allow the mechanistic proposals to be distinguished. At elevated temperatures in toluene solution, a valence isomerization transforms the bicyclic phosphiranes **10** into phospholo-thiaphosphiranes **11**. Again, the $R_2C=S^+–P^–R$ dipole is a likely intermediate. In acetonitrile solution at 80 °C, on the other hand, decomplexation of **10** becomes the major pathway. Although the chemistry of phosphiranes **10** is remarkable, not least by comparison with the different thermal reactivities of the related 6,6-diphenyl-2-thia-1-phosphabicyclo[3.1.0]hex-3-enes **1** and **2**, their considerable reactivity and low thermal stability do not suggest that these bicyclic phosphiranes are potential ligands for catalytically active transition metals.

Experimental Section

General Information: All reactions were carried out under argon by using standard Schlenk techniques. Rigorously dried solvents were used. Melting points were measured in open capillaries and are not corrected. Infrared spectra (IR) were recorded with a Bruker Vector

22 FTIR spectrometer using KBr disks. ^{1}H (400.13 MHz) and ^{13}C NMR (100.62 MHz) spectra were measured with a Bruker DRX 400 spectrometer. All NMR spectra were recorded in $CDCl_3$ at 298 K. NMR chemical shifts were referenced to the solvent peak for ^{1}H ($CHCl_3$: δ = 7.26 ppm) and ^{13}C ($CDCl_3$: δ = 77.00 ppm) spectra, and for ^{31}P to external 85% H_3PO_4. When necessary, signal assignments were made on the basis of COSY, HMBC, TOCSY, HSQC and NOESY experiments. Mass spectra were recorded with Finnigan MAT SSQ 7000 and Micromass ZMD (with formic acid) spectrometers. CI refers to chemical ionization, ESI to electrospray ionization (ESI).

Starting Materials: 9-Diazofluorene,[31] 2,7-dibromo-9-diazofluorene,[32] and diphenyldiazomethane[33] were prepared by dehydrogenation of the corresponding hydrazones using a six-fold excess of activated MnO_2 rather than yellow mercuric oxide. 1,2-Thiaphospholes **5a**,**b**[11] and thiobenzophenone[34] were prepared by following published procedures.

3-(4-Methoxyphenyl)-5,6,6-triphenyl-1-phospha-2-thiabicyclo[3.1.0]-hex-3-ene (1b): A solution of 3-(4-methoxyphenyl)-5-phenyl-1,2-thiaphosphole (**5b**; 0.600 g, 2.10 mmol) and diazodiphenylmethane (0.490 g, 2.50 mmol) in toluene (18 mL) was heated at 70 °C until the red color of the diazo compound had disappeared (24 h). The solvent was removed in vacuo and the residue was washed twice with *n*-pentane. The product was obtained as a pale-yellow solid (0.898 mg, 94%); m.p. 181 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1603 (s), 1507 (s), 1491 (s), 1443 (s), 1251 (s), 1176 (s), 1031 (m), 831 (m), 763 (m), 697 (vs) cm^{-1}. ^{1}H NMR: δ = 3.75 (s, 3 H, CH_3), 6.45 (d, $^3J_{P,H}$ = 4.6 Hz, 1 H, 4-H), 6.72 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, H_{Ph}), 6.78 (m, 2 H, H_{Ph}), 6.94 (m, 4 H, H_{Ph}), 7.09–7.29 (m, 9 H, H_{Ph}), 7.47 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, H_{Ph}) ppm. ^{13}C NMR: δ = 42.2 (d, $^1J_{P,C}$ = 49.0 Hz, C-5), 55.3 (s, CH_3) 72.8 (d, $^1J_{P,C}$ = 41.0 Hz, C-6), 113.5, 125.4, 125.5, 126.5, 126.7, 127.4, 127.7, 127.8, 128.2, 128.3, 128.4, 129.0, 129.3, 129.6, 130.1, 130.7, 131.2, 131.7, 132.0, 133.6, 135.1, 137.6, 137.9, 141.6, 141.8, 143.4, 143.8, 158.5 (s, *p*-3-Ph) ppm. ^{31}P NMR: δ = –78.3 ppm. MS (CI, 100 eV): *m*/*z* (%) = 451 (100) $[MH]^+$, 450 (51) $[M]^+$, 285 (46) $[MH - CPh_2]^+$. $C_{29}H_{23}OPS$ (450.5): calcd. C 77.31, H 5.15; found C 77.37, H 5.44.

1,2-Thiaphospholo[2,3-*a*]phosphirane–W(CO)$_5$ Complex 2b and Pentacarbonyl[(3a*S,8*R**)-2-(4-methoxyphenyl)-3a,8-diphenyl-3a,8-dihydroisophosphindolo[2,1-*b*][1,2]thiaphosphole-κP]tungsten (3b):** A solution of hexacarbonyltungsten (0.500 g, 1.40 mmol) in tetrahydrofuran (100 mL) was placed in a photolysis apparatus and irradiated for 60 min using a 150-W medium-pressure mercury lamp. The yellow solution of the [W(CO)$_5$(thf)] complex formed was added to a solution of phosphirane **1b** (0.200 g, 0.440 mmol) in THF (10 mL) and the solution was stirred for 8 h. At this point, a mixture of **2b** and **3b** was present (approximately 2:1 ratio), from which pure **2b** could not be isolated due to continuous rearrangement into **3b**. [Column chromatography with toluene/pentane (1:6) as eluent gave a fraction containing at best a 74:26 mixture of **2b** and **3b**.] The solution was stirred for a further 16 h, the solvent was removed in vacuo and the residue was purified by chromatography over silica gel with toluene/cyclohexane (1:1) to give **3b** as an off-white solid (0.270 g, 80%).

Data for **2b** (in admixture with **3b**): ^{1}H NMR: δ = 3.73 (s, 3 H, OCH_3), 6.09 (d, $^3J_{P,H}$ = 17.2 Hz, 1 H, 4-H), 6.48 (d, *J* = 8.6 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 6.91 (m, 5 H), 7.49–7.60 (m, 10 H) ppm. ^{31}P NMR: δ = –57.5 ppm ($^1J_{P,W}$ = 268.8 Hz).

Data for **3b**: M.p. 189 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2077 (s), 1939 (vs, br), 1604 (m), 1508 (m), 1444 (m), 1254 (m), 1176 (m), 1031 (m), 700 (m), 592 (m), 571 (m) cm^{-1}. ^{1}H NMR: δ = 3.86 (s, 3 H, CH_3), 5.29 (d, $^2J_{P,H}$ = 13.9 Hz, 1 H, 8-H), 6.20 (d, $^3J_{P,H}$ = 18.4 Hz, 1 H, 3-H), 6.94 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *o*-2-Ph*H*), 7.28–7.60 (m, 14 H, H_{Ph}), 7.61 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *m*-2-Ph*H*) ppm. ^{13}C NMR: δ = 55.4 (s, CH_3), 62.6 (d, $^1J_{P,C}$ = 3.7 Hz, C-8), 75.2 (d, $^1J_{P,C}$ = 11.0 Hz, C-3), 114.0, 126.6, 127.0, 127.5, 127.7, 128.2, 128.4, 129.0, 129.1, 129.3, 129.4, 130.5, 137.8, 138.0, 139.3, 141.1, 141.9, 142.8, 160.4 (s, *p*-2-Ph), 194.3 (d, $^2J_{P,C}$ = 6.6 Hz, CO_{eq}), 197.9 (d, $^2J_{P,C}$ = 30.7 Hz, CO_{ax}) ppm. ^{31}P NMR: δ = 124.6 ($^1J_{P,W}$ = 261.9 Hz) ppm. MS (CI, 100 eV): *m*/*z* (%) = 775 (72) $[MH]^+$, 774 (59) $[M]^+$, 746 (12) $[M - CO]^+$, 451 (43) $[MH - W(CO)_5]^+$, 388 (100). $C_{34}H_{23}O_6PSW$ (774.5 + 0.15 toluene): calcd. C 52.30, H 3.10; found C 52.27, H 3.24.

General Procedure for the Preparation of Spiro[fluorene-9,6′-phosphirano[1,2]thiaphospholes] 7a–c: A mixture of 1,2-thiaphosphole **5a**,**b** (8.10 mmol) and 9-diazofluorene **6a**,**b** (9.58 mmol) in *n*-pentane (25 mL) was heated at 60 °C for 1 day in a closed thick-walled tube. The solvent was evaporated at 0.05 mbar/20 °C. The residue was recrystallized from chloroform/*n*-pentane at ambient temperature.

3′,5′-Diphenylspiro[fluorene-9,6′-[2]thia[1]phosphabicyclo[3.1.0]hex-[3]ene] (7a): Synthesis by the general procedure from 1,2-thiaphosphole **5a** (2.06 g, 8.10 mmol) and 9-diazofluorene (**6a**; 1.84 g, 9.58 mmol) provided **7a** as a colourless crystalline solid (2.81 g, 83%); m.p. 191 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1596 (w), 1573 (w), 1491 (m), 1447 (w), 1442 (s), 937 (m), 775 (s), 761 (s), 732 (vs), 703 (s), 690 (m) cm^{-1}. ^{1}H NMR: δ = 6.00 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, 1-H_{Fluo}), 6.54 (d, $^3J_{P,H}$ = 4.5 Hz, 1 H, 4′-H), 6.88 (dt, $^3J_{H,H}$ = 7.6, 1.0 Hz, 1 H, 2-H_{Fluo}), 7.25–7.27 (m, 3 H, 3-H_{Fluo}, 7-H_{Fluo}, 8-H_{Fluo}), 7.40 (m, 4 H, 6-H_{Fluo}, *m*/*p*-3′-Ph*H*), 7.62 (m, 2 H, *o*-3′-Ph*H*), 7.84 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 4-H_{Fluo}), 7.95 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, 5-H_{Fluo}) ppm. ^{13}C NMR: δ = 34.4 (d, $^1J_{P,C}$ = 49.8 Hz, C-5′), 72.8 (d, $^1J_{P,C}$ = 47.6 Hz, C-6′), 119.6 (s, C_{Fluo}-5), 119.9 (s, C_{Fluo}-4), 122.8 (d, $^3J_{P,C}$ = 11.7 Hz, C_{Fluo}-8), 124.3 (s, C_{Fluo}-6), 125.5 (s, C_{Fluo}-2), 125.9 (s, C_{Fluo}-7), 126.2 (s, C_{Fluo}-3), 126.8 (s, *o*-3′-Ph), 126.9 (s, C_{Fluo}-1), 127.9 (s, *m*-3′-Ph), 128.9 (s, *p*-3′-Ph), 129.2 (d, $^2J_{P,C}$ = 3.7 Hz, C-4), 134.2, 138.6, 138.8, 140.5, 141.2, 144.6, 145.8 ppm. ^{31}P NMR: δ = –51.7 ppm. MS (CI, 100 eV): *m*/*z* (%) = 420 (15) $[MH]^+$, 419 (49) $[M]^+$, 387 (20) $[MH - S]^+$, 255 (100) $[M - C_{13}H_8]^+$. $C_{28}H_{19}PS$ (418.5): calcd. C 80.36, H 4.58; found C 80.45, H 4.66.

3′-(4-Methoxyphenyl)-5′-phenylspiro[fluorene-9,6′-[2]thia[1]phosphabicyclo[3.1.0]hex[3]ene] (7b): Synthesis by the general procedure from 1,2-thiaphosphole **5b** (2.30 g, 8.10 mmol) and 9-diazofluorene (**6a**; 1.84 g, 9.58 mmol) gave **7b** as a colorless crystalline solid (2.76 g, 76%); m.p. 180 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1605 (s), 1507 (s), 1443 (s), 1431 (m), 1297 (m), 1217 (vs), 1176 (s), 1036 (m), 810 (s), 734 (s), 700 (s) cm^{-1}. ^{1}H NMR: δ = 3.85 (s, 3 H, CH_3), 6.00 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, 1-H_{Fluo}), 6.41 (d, $^3J_{P,H}$ = 4.3 Hz, 1 H, 4′-H), 6.88 (t, $^3J_{H,H}$ = 7.1 Hz, 1 H, 2-H_{Fluo}), 6.93 (d, $^2J_{P,H}$ = 8.8 Hz, 2 H, *m*-3′-Ph*H*), 7.25–7.27 (m, 3 H, 3-H_{Fluo}, 7-H_{Fluo}, 8-H_{Fluo}), 7.40 (t, $^3J_{H,H}$ = 6.9 Hz, 1 H, 6-H_{Fluo}), 7.55 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *o*-3′-Ph*H*), 7.84 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 4-H_{Fluo}), 7.93 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, 5-H_{Fluo}) ppm. ^{13}C NMR: δ = 34.8 (d, $^1J_{P,C}$ = 49.0 Hz, C-5′), 55.4 (s, CH_3), 72.9 (d, $^1J_{P,C}$ = 48.3 Hz, C-6′), 114.2, 119.5, 119.9, 122.8, 124.3, 125.4, 125.9, 126.1, 126.9, 127.4 (d, $^2J_{P,C}$ = 3.7 Hz, C-4′), 127.8, 128.3, 138.8, 140.5, 141.1, 144.6, 145.4, 160.3 (s, *p*-3′-Ph) ppm. ^{31}P NMR: δ = –54.2 ppm. MS (CI, 100 eV): *m*/*z* (%) = 449 (21) $[M]^+$, 285 (100) $[M - C_{13}H_8]^+$. $C_{29}H_{21}OPS$ (448.5): calcd. C 77.66, H 4.72; found C 77.40, H 4.74.

2,7-Dibromo-3′,5′-diphenylspiro[fluorene-9,6′-[2]thia[1]phosphabicyclo[3.1.0]hex[3]ene] (7c): Synthesis by the general procedure from 1,2-thiaphosphole **5a** (2.06 g, 8.10 mmol) and 2,7-dibromo-9-diazofluorene (**6b**; 3.35 g, 9.58 mmol) at 70 °C. The crude product was dissolved in dichloromethane, the residue was filtered off and the solvent was evaporated at 0.05 mbar/20 °C to furnish **7c** as a yellow

solid (4.57 g, 98%); m.p. 189 °C (dec.). IR (KBr): ṽ = 2064 (w), 1595 (m), 1566 (m), 1445 (s), 1396 (s), 1259 (w), 1070 (m), 920 (m), 805 (s), 759 (s), 696 (s) cm^{-1}. ^{1}H NMR: δ = 6.06 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H, 1-H$_{Fluo}$), 6.51 (d, $^3J_{P,H}$ = 4.5 Hz, 1 H, 4′-H), 7.26–7.45 (m, 5 H, 3′-Ph*H*), 7.52 (dd, $^3J_{H,H}$ = 8.2, 1.6 Hz, 1 H, 3-H$_{Fluo}$), 7.63 (m, 3 H, 4-H$_{Fluo}$, 6-H$_{Fluo}$, 8-H$_{Fluo}$), 7.74 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, 5-H$_{Fluo}$) ppm. ^{13}C NMR: δ = 34.0 (d, $^1J_{P,C}$ = 50.5 Hz, C-5′), 73.3 (d, $^1J_{P,C}$ = 48.3 Hz, C-6′), 112.0, 120.7, 121.0, 122.1, 125.9, 127.1, 127.6, 128.3, 128.6, 129.1, 129.4, 133.7, 136.7, 137.5, 138.9, 141.9, 146.5, 146.6 ppm. ^{31}P NMR: δ = –47.8 ppm. MS (CI, 100 eV): *m*/*z* (%) = 579/577/575 (1.3/2.6/1.6) [M]$^+$, 255 (100) [M – $C_{13}H_6Br_2$]$^+$. $C_{28}H_{17}Br_2PS$ (576.3): calcd. C 58.36, H 2.97; found C 58.35, H 3.50.

General Procedure for the Preparation of 3*H*-1,2λ^5-Thiaphosphole 2-Oxides 8a–c: A 2 M ethereal HCl solution (2.1 mL) containing a small amount of water was added to the vigorously stirred solution of phosphirano-thiaphosphole **7** (95.2 μmol) in dichloromethane (20 mL) at 20 °C. Within minutes, the solution had turned yellow. After 1 h, the solvent was removed at 0.05 mbar/20 °C. The crude product was purified by recrystallization from dichloromethane/*n*-pentane at 0 °C.

2-(9*H*-Fluoren-9-yl)-3,5-diphenyl-2,3-dihydro-1,2-thiaphosphole 2-Oxide (8a): Synthesis by the general procedure from **7a** (40.0 mg, 95.2 μmol). Pale-yellow crystalline solid (29.2 mg, 70%), m.p. 229 °C (dec.). IR (KBr): ṽ = 1598 (w), 1490 (m), 1445 (s), 1203 (vs, P=O), 917 (m), 809 (m), 756 (s), 734 (vs), 693 (s) cm^{-1}. ^{1}H NMR: δ = 3.40 (dd, $^2J_{P,H}$ = 6.3, $^3J_{H,H}$ = 3.3 Hz, 1 H, 3-H), 5.17 (d, $^2J_{P,H}$ = 25.5 Hz, 1 H, 9-H$_{Fluo}$), 5.73 (dd, $^3J_{P,H}$ = 34.9, $^3J_{H,H}$ = 3.3 Hz, 1 H, 4-H), 6.53 (dd, $^3J_{H,H}$ = 7.6, 2.0 Hz, 2 H, *o*-3-Ph*H*), 7.14 (m, 3 H, *m*/*p*-3-Ph*H*), 7.25 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, 2-H$_{Fluo}$), 7.33 (t, $^3J_{H,H}$ = 8.2 Hz, 1 H, 6-H$_{Fluo}$), 7.36 (m, 3 H, *m*/*p*-3-Ph*H*), 7.41 (m, 2 H, *o*-5-Ph*H*), 7.45 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, 3-H$_{Fluo}$), 7.55 (t, $^3J_{H,H}$ = 7.6 Hz, 1 H, 7-H$_{Fluo}$), 7.90 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 4-H$_{Fluo}$), 7.94 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, 5-H$_{Fluo}$, 8-H$_{Fluo}$), 8.01 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, 1-H$_{Fluo}$) ppm. ^{13}C NMR: δ = 51.8 (d, $^1J_{P,C}$ = 53.4 Hz, C-3), 53.0 (d, $^1J_{P,C}$ = 55.6 Hz, C$_{Fluo}$-9), 120.0 (s, C$_{Fluo}$-5), 120.4 (d, $^4J_{P,C}$ = 1.5 Hz, C$_{Fluo}$-4), 121.5 (d, $^2J_{P,C}$ = 4.4 Hz, C-4), 126.6 (s, *o*-5-Ph), 127.0 (d, $^3J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-1), 127.5 (d, $^4J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-2), 127.6 (d, $^4J_{P,C}$ = 3.7 Hz, *m*-3-Ph), 127.7 (d, $^5J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-6), 128.2 (d, $^3J_{P,C}$ = 3.7 Hz, C$_{Fluo}$-8), 128.4 (d, $^5J_{P,C}$ = 2.2 Hz, C$_{Fluo}$-3), 128.6 (m, *o*/*m*-3-Ph), 128.7 (s, *m*-5-Ph), 128.7 (d, $^4J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-7), 129.2 (s, *p*-5-Ph), 132.4 (d, $^2J_{P,C}$ = 8.1 Hz, *ipso*-3-Ph), 135.0 (d, $^3J_{P,C}$ = 4.4 Hz, C-5), 137.2 (d, $^3J_{P,C}$ = 4.4 Hz, C$_{Fluo}$-4a), 137.6 (d, $^3J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-4b), 138.8 (s, *ipso*-5-Ph), 141.78/141.84 (d, $^2J_{P,C}$ = 5.9 Hz, C$_{Fluo}$-8a, C$_{Fluo}$-9a) ppm. ^{31}P NMR: δ = 79.2 ppm. MS (CI, 100 eV): *m*/*z* (%) = 437 (100) [MH]$^+$, 271 (12) [M – fluorenyl]$^+$, 165 (7) [fluorenyl]$^+$. $C_{28}H_{21}OPS$ (436.5): calcd. C 77.04, H 4.85; found C 77.18, H 4.73.

2-(9*H*-Fluoren-9-yl)-5-(4-methoxyphenyl)-3-phenyl-2,3-dihydro-1,2-thiaphosphole 2-Oxide (8b): Synthesis by the general procedure from **7b** (42.9 mg, 95.2 μmol). Yellow crystalline solid (33.9 mg, 76%), m.p. 180 °C (dec.). IR (KBr): ṽ = 1605 (s), 1508 (s), 1447 (m), 1300 (w), 1258 (s), 1205 (vs, P=O), 1179 (s), 1027 (m), 833 (m), 808 (m), 739 (s), 519 (m) cm^{-1}. ^{1}H NMR: δ = 3.42 (dd, $^2J_{P,H}$ = 6.3, $^3J_{H,H}$ = 3.3 Hz, 1 H, 3-H), 5.16 (d, $^2J_{P,H}$ = 25.5 Hz, 1 H, 9-H$_{Fluo}$), 5.62 (dd, $^3J_{P,H}$ = 35.0, $^3J_{H,H}$ = 3.4 Hz, 1 H, 4-H), 6.53 (dd, $^3J_{H,H}$ = 5.4, 1.6 Hz, 2 H, *o*-3-Ph*H*), 6.89 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *m*-5-Ph*H*), 7.14 (m, 3 H, *m*/*p*-3-Ph*H*), 7.24 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, 2-H$_{Fluo}$), 7.33 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, 6-H$_{Fluo}$), 7.35 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, *o*-5-Ph*H*), 7.45 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, 3-H$_{Fluo}$), 7.55 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, 7-H$_{Fluo}$), 7.89 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 4-H$_{Fluo}$), 7.93 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, 5-H$_{Fluo}$, 8-H$_{Fluo}$), 8.00 (d, $^3J_{H,H}$ = 7.1 Hz, 1 H, 1-H$_{Fluo}$) ppm. ^{13}C NMR: δ = 51.7 (d, $^1J_{P,C}$ = 52.7 Hz, C-3), 52.9 (d, $^1J_{P,C}$ = 55.6 Hz, C$_{Fluo}$-9), 55.4 (s, CH$_3$), 114.0 (s, *m*-5-Ph), 119.7 (d, $^2J_{P,C}$ = 3.7 Hz, C-4), 120.0 (d, $^4J_{P,C}$ = 1.5 Hz, C$_{Fluo}$-5), 120.3 (s, C$_{Fluo}$-4), 127.0 (d, $^3J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-1), 127.4 (d, $^4J_{P,C}$ = 2.2 Hz, C$_{Fluo}$-2), 127.4 (s, *ipso*-5-Ph), 127.5 (d, $J_{P,C}$ = 3.6 Hz, C-3-Ph), 127.7 (d, $^5J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-6), 127.9 (s, *o*-5-Ph), 128.1 (d, $^3J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-8), 128.3 (d, $^5J_{P,C}$ = 2.2 Hz, C$_{Fluo}$-3), 128.5 (m, C-3-Ph), 128.6 (d, $^4J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-7), 132.6 (d, $^2J_{P,C}$ = 8.1 Hz, *ipso*-3-Ph), 137.2 (d, $^3J_{P,C}$ = 3.7 Hz, C$_{Fluo}$-4a or C$_{Fluo}$-4b), 137.6 (d, $^3J_{P,C}$ = 4.4 Hz, C$_{Fluo}$-4a or C$_{Fluo}$-4b), 138.2 (s, C-5), 141.7 (d, $^2J_{P,C}$ = 3.7 Hz, C$_{Fluo}$-8a or C$_{Fluo}$-9a), 141.8 (d, $^2J_{P,C}$ = 3.7 Hz, C$_{Fluo}$-8a or C$_{Fluo}$-9a), 160.3 (s, *p*-5-Ph) ppm. ^{31}P NMR: δ = 79.2 ppm. MS (CI, 100 eV): *m*/*z* (%) = 467 (100) [MH]$^+$, 301 (8) [M – fluorenyl]$^+$, 165 (4) [fluorenyl]$^+$.

2-(2,7-Dibromo-9*H*-fluoren-9-yl)-3,5-diphenyl-2,3-dihydro-1,2-thiaphosphole 2-Oxide (8c): Synthesis by the general procedure from **7c** (29.9 mg, 95.2 μmol). Yellow crystalline solid (18.1 mg, 60%), m.p. 222 °C (dec.). IR (KBr): ṽ = 1595 (m), 1568 (m), 1489 (m), 1448 (s), 1394 (m), 1261 (m), 1200 (vs, P=O), 1062 (s, C–Br), 907 (m), 888 (m), 813 (s), 753 (s), 725 (s), 694 (s) cm^{-1}. ^{1}H NMR: δ = 3.37 (dd, $^2J_{P,H}$ = 6.6, $^3J_{H,H}$ = 3.3 Hz, 1 H, 3-H), 5.12 (d, $^2J_{P,H}$ = 25.5 Hz, 1 H, 9-H$_{Fluo}$), 5.79 (dd, $^3J_{P,H}$ = 35.6, $^3J_{H,H}$ = 3.5 Hz, 1 H, 4-H), 6.62 (dd, $^3J_{H,H}$ = 5.4, 1.6 Hz, 2 H, *o*-3-Ph*H*), 7.22 (m, 3 H, *m*/*p*-3-Ph*H*), 7.36 (m, 3 H, *m*/*p*-5-Ph*H*), 7.43 (m, 2 H, *o*-5-Ph*H*), 7.57 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, 3-H$_{Fluo}$), 7.69 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, 6-H$_{Fluo}$), 7.70 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 4-H$_{Fluo}$), 7.75 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, 5-H$_{Fluo}$), 8.07 (s, 1 H, 8-H$_{Fluo}$), 8.14 (s, 1 H, 1-H$_{Fluo}$) ppm. ^{13}C NMR: δ = 52.0 (d, $^1J_{P,C}$ = 54.2 Hz, C-3), 52.9 (d, $^1J_{P,C}$ = 54.2 Hz, C$_{Fluo}$-9), 121.1 (d, $^4J_{P,C}$ = 5.1 Hz, C-4), 121.3 (d, $^4J_{P,C}$ = 1.5 Hz, C$_{Fluo}$-5), 121.6 (d, $^4J_{P,C}$ = 1.5 Hz, C$_{Fluo}$-4), 121.7 (d, $^4J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-Br), 121.9 (d, $^4J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-Br), 126.7 (s, *o*-5-Ph), 128.0 (d, $^2J_{P,C}$ = 2.9 Hz, *m*/*p*-3-Ph), 128.4 (d, $^3J_{P,C}$ = 5.1 Hz, *o*-3-Ph), 128.8 (s, *m*-5-Ph), 129.4 (s, *p*-5-Ph), 130.0 (d, $^3J_{P,C}$ = 2.9 Hz, C$_{Fluo}$-1), 130.8 (d, $^3J_{P,C}$ = 2.2 Hz, C$_{Fluo}$-8), 131.7 (d, $^2J_{P,C}$ = 8.1 Hz, *ipso*-3-Ph), 131.8 (d, $^5J_{P,C}$ = 2.2 Hz, C$_{Fluo}$-3), 132.2 (d, $^4J_{P,C}$ = 2.2 Hz, C$_{Fluo}$-6), 134.4, 139.0 (d, $^3J_{P,C}$ = 4.4 Hz, C$_{Fluo}$-4a or C$_{Fluo}$-4b), 139.3 (d, $^3J_{P,C}$ = 2.2 Hz, C$_{Fluo}$-4a or C$_{Fluo}$-4b), 139.4 (s, *ipso*-5-Ph), 139.6/139.7 (each d, $^2J_{P,C}$ = 5.9 Hz, C$_{Fluo}$-8a, C$_{Fluo}$-9a) ppm. ^{31}P NMR: δ = 78.3 ppm. MS (CI, 100 eV): *m*/*z* (%) = 597/595/593 (46/100/43) [MH]$^+$. $C_{28}H_{19}Br_2OPS$ (594.3): calcd. C 56.59, H 3.22; found C 56.61, H 3.04.

General Procedure for the Preparation of Complexes 10a–c: A solution of hexacarbonyltungsten (3.71 mmol) in tetrahydrofuran (300 mL) was placed in a photolysis apparatus and irradiated for 60 min with a 150-W medium-pressure mercury lamp. The yellow solution of the formed complex [W(CO)$_5$(thf)] was transferred through a cannula into a flask containing the solid phosphirane **7** (3.27 mmol) and the mixture was stirred for 1 day. The solvent was removed in vacuo. The resulting oil was purified by chromatography over silica gel with toluene/cyclohexane (1:3) as eluent.

Pentacarbonyl(3′,5′-diphenylspiro[fluorene-9,6′-[2]thia[1]phosphabicyclo[3.1.0]hex[3]ene]-κP)tungsten (10a): Synthesis by the general procedure from [W(CO)$_6$] (1.31 g, 3.71 mmol) and **7a** (1.37 g, 3.27 mmol). Yellow solid (2.35 g, 97%), m.p. 185 °C (dec.). IR (KBr): ṽ = 2076 (s), 1995 (m), 1935 (vs, br), 1445 (m), 1261 (w), 773 (m), 754 (m), 736 (m) cm^{-1}. ^{1}H NMR: δ = 5.98 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 1-H$_{Fluo}$), 6.48 (d, $^3J_{P,H}$ = 16.9 Hz, 1 H, 4′-H), 6.73 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 7′-H$_{Ph}$), 6.89 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, 2-H$_{Fluo}$), 7.15 (t, $^3J_{H,H}$ = 7.1 Hz, 1 H, 8′-H$_{Ph}$), 7.25–7.45 (m, 8 H, H$_{Ph}$, H$_{Fluo}$), 7.58 (m, 3 H, 10′-H$_{Ph}$, *o*-3′-Ph*H*), 7.84 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 4-H$_{Fluo}$), 7.88 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, 11′-H$_{Ph}$), 7.95 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 5-H$_{Fluo}$) ppm. ^{13}C NMR: δ = 35.2 (d, $^1J_{P,C}$ =

30.0 Hz, C-5′), 67.0 (d, $^1J_{P,C}$ = 28.5 Hz, C-6′), 120.0, 120.3, 124.7, 125.5, 126.5, 126.6, 126.8, 127.1, 128.4, 128.6 (d, $^2J_{P,C}$ = 28.5 Hz, C-4′), 129.1, 129.6, 130.1, 130.9, 133.1, 135.7, 139.9, 140.1, 141.4, 141.7, 146.7, 194.1 (d, $^2J_{P,C}$ = 7.3 Hz, CO_{eq}), 197.0 (d, $^2J_{P,C}$ = 41.7 Hz, CO_{ax}) ppm. ^{31}P NMR: δ = –35.2 ($^1J_{P,W}$ = 277.8 Hz) ppm. MS (CI, 100 eV): *m*/*z* (%) = 742 (3) $[M]^+$, 714 (22) $[M – CO]^+$, 711 (90), 709 (100) $[M – S]^+$, 388 (100) $[MH – S – W(CO)_5]^+$ 357 (77). $C_{33}H_{19}O_5PSW$ (742.4): calcd. C 53.39, H 2.58; found C 53.36, H 2.65.

Pentacarbonyl(3′-(4-methoxyphenyl)-5′-phenylspiro[fluorene-9,6′-[2]thia[1]phosphabicyclo[3.1.0]hex[3]ene]-κP)tungsten (10b): Synthesis by the general procedure from $[W(CO)_6]$ (1.31 g, 3.71 mmol) and **7b** (1.46 g, 3.27 mmol). Yellow solid (2.20 g, 87%), m.p. 145 °C (dec.). IR (KBr): ṽ = 2078 (s), 2003 (m), 1937 (vs, br), 1598 (m), 1444 (m), 1259 (m), 1177 (m) cm^{-1}. ^{1}H NMR: δ = 3.86 (s, 3 H, C*H*$_3$), 6.00 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, 1-H_{Fluo}), 6.35 (d, $^3J_{P,H}$ = 17.2 Hz, 1 H, 4′-H), 6.72 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, 7′-H_{Ph}), 6.89 (t, $^3J_{H,H}$ = 8.1 Hz, 1 H, 2-H_{Fluo}), 6.95 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *m*-3′-Ph*H*), 7.14 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, 8′-H_{Ph}), 7.15–7.29 (m, 2 H, 3-H_{Fluo}, 7-H_{Fluo}), 7.35 (m, 2 H, 8-H_{Fluo}, 9-H_{Fluo}), 7.46 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, 6-H_{Fluo}), 7.52 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *o*-3′-Ph*H*), 7.56 (t, $^3J_{H,H}$ = 6.7 Hz, 1 H, 10′-H_{Ph}), 7.83 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 4-H_{Fluo}), 7.88 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, 11′-H_{Ph}), 7.95 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 5-H_{Fluo}) ppm. ^{13}C NMR: δ = 35.4 (d, $^1J_{P,C}$ = 30.7 Hz, C-5′), 55.4 (s, CH_3), 67.0 (d, $^1J_{P,C}$ = 28.5 Hz, C-6′), 114.4, 120.1, 124.8, 125.5, 125.7, 126.5, 126.7, 126.9, 127.1, 128.0, 128.4, 128.5, 129.0, 130.1, 130.9, 135.9, 140.1, 141.6, 160.7, 194.2 (d, $^2J_{P,C}$ = 6.6 Hz, CO_{eq}), 197.3 (d, $^2J_{P,C}$ = 41.0 Hz, CO_{ax}) ppm. ^{31}P NMR: δ = –37.0 ($^1J_{P,W}$ = 275.6 Hz) ppm. MS (CI, 100 eV): *m*/*z* (%) = 773 (1) $[MH]^+$, 744 (9) $[M – CO]^+$, 740 (33) $[M – S]^+$, 417 (34) $[MH – S – W(CO)_5]^+$, 285 (100) $[C_{16}H_{13}OPS$ (= **5b**) + 1$]^+$. $C_{34}H_{21}O_6PSW$ (772.4): calcd. C 52.87, H 2.74; found C 52.39, H 2.93.

Pentacarbonyl(2,7-dibromo-3′,5′-diphenylspiro[fluorene-9,6′-[2]thia-[1]phosphabicyclo[3.1.0]hex[3]ene]-κP)tungsten (10c): Synthesis by the general procedure from $[W(CO)_6]$ (1.31 g, 3.71 mmol) and **7c** (1.88 g, 3.27 mmol). Yellow solid (2.44 g, 83%), m.p. 211 °C (dec.). IR (KBr): ṽ = 2078 (s), 1997 (m), 1937 (vs, br), 1594 (m), 1567 (m), 1446 (s), 1396 (m), 1063 (m), 1005 (m), 923 (m), 812 (s) 757 (m), 700 (m) cm^{-1}. ^{1}H NMR: δ = 6.07 (d, $^4J_{H,H}$ = 1.0 Hz, 1 H, 1-H_{Fluo}), 6.47 (d, $^3J_{P,H}$ = 17.4 Hz, 1 H, 4′-H), 6.71 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 7′-H_{Ph}), 7.19 (m, 1 H, 8′-H_{Ph}), 7.41–7.50 (m, 5 H, 3-H_{Fluo}, 6-H_{Fluo}, H_{Ph}), 7.51 (s, 1 H, 8-H_{Fluo}), 7.59 (m, 4 H, H_{Ph}), 7.65 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 4-H_{Fluo}), 7.76 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, 5-H_{Fluo}), 7.87 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, 11′-H_{Ph}) ppm. ^{13}C NMR: δ = 36.6 (d, $^1J_{P,C}$ = 25.9 Hz, C-5′), 67.4 (d, $^1J_{P,C}$ = 27.8 Hz, C-6′), 119.8, 121.2, 121.4, 125.3, 126.9, 128.3, 128.6, 129.0, 129.2, 129.3 (d, $^2J_{P,C}$ = 6.5 Hz, C-4′), 130.2, 132.7, 134.7, 138.0, 139.4, 141.4, 143.6, 144.8, 147.4, 193.0 (d, $^2J_{P,C}$ = 7.3 Hz, CO_{eq}), 196.1 (d, $^2J_{P,C}$ = 39.5 Hz, CO_{ax}) ppm. ^{31}P NMR: δ = –30.3 ($^1J_{P,W}$ = 280.2 Hz) ppm. $C_{33}H_{17}Br_2O_5PSW$ (900.2) +0.4 toluene: calcd. C 45.61, H 2.18; found C 45.58, H 2.41.

Thermally Induced Reaction of Complex 10a

Procedure A: A solution of **10a** (1.25 g, 1.68 mmol) in toluene (25 mL) was heated at 80 °C for 48 h. The solvent was removed in vacuo and the brown residue was subjected to column chromatography over silica gel with toluene/cyclohexane (1:2) as eluent to give thiaphosphirane **11a** (0.99 g, 80%) and 1,3,2-dithiaphospholane **12a** (0.13 g, 7%) as a 7:1 mixture of isomers (10:1 ratio after repeated chromatography).

Procedure B: A solution of **10a** in [D$_1$]chloroform was allowed to stand at ambient temperature for 4 weeks. The solvent was removed in vacuo and the residue was purified by preparative thin-layer chromatography on silica gel with toluene/cyclohexane (1:2) to give **12a** as a 2.3:1 mixture of isomers (26 mg, 68% yield).

Pentacarbonyl(3′,5′-diphenylspiro[fluorene-9,2′-[6]thia[1]phosphabicyclo[3.1.0]hex[3]ene]-κP)tungsten (11a): Yellow solid (0.99 g, 80%), m.p. 140 °C (dec.). IR (KBr): ṽ = 2078 (m), 1996 (m), 1948 (vs), 1444 (w), 742 (w) cm^{-1}. ^{1}H NMR: δ = 6.66 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, *o*-3′-Ph*H*), 6.94 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, *m*-3′-Ph*H*), 7.04 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, *p*-3′-Ph*H*), 7.17 (m, 1 H, 1-H_{Fluo}), 7.27 (m, 5 H, 2-H_{Fluo}, 8-H_{Fluo}, *p*/*m*-5′-Ph*H*), 7.46 (m, 4 H, 4′-H, 3-H_{Fluo}, 6-H_{Fluo}, 7-H_{Fluo}), 7.70 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, *o*-5′-Ph*H*), 7.84 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 4-H_{Fluo}), 7.92 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, 5-H_{Fluo}) ppm. ^{13}C NMR: δ = 59.9 (d, $^1J_{P,C}$ = 5.5 Hz, C-5′), 69.8 (d, $^1J_{P,C}$ = 9.2 Hz, C-2′), 120.6, 121.7, 124.4, 124.6, 125.3, 126.6, 127.2, 128.2, 128.3, 128.6, 128.9, 129.8, 134.5, 135.6, 140.0, 141.3, 142.7, 143.2, 144.0 (d, $^2J_{P,C}$ = 7.3 Hz, C-4′), 193.0 (d, $^2J_{P,C}$ = 7.3 Hz, CO_{eq}), 196.1 (d, $^2J_{P,C}$ = 41.0 Hz, CO_{ax}) ppm. ^{31}P NMR: δ = –6.4 ($^1J_{P,W}$ = 291.6 Hz) ppm. MS (CI, 100 eV): *m*/*z* (%) = 742 (39) $[M]^+$, 713 (80) $[M – CO – 1]^+$, 711/709 (80/100) $[M – S + 1/–1]^+$, 686 (10) $[M – 2CO]^+$, 658 (17) $[M – 3CO]^+$, 630 (7) $[M – 4CO + 1]^+$, 602 (13) $[M – 5CO]^+$, 570 (10) $[M – S – 5CO]^+$, 419 (12) $[M – W(CO)_5]^+$, 387 (54) $[M – S – W(CO)_5]^+$. $C_{33}H_{19}O_5PSW$ (742.4): calcd. C 53.39, H 2.58; found C 53.56, H 2.70.

Pentacarbonyl{6-[(*E*)-2-(9*H*-fluoren-9-yl)-2-phenylethenyl]-3,5,6-triphenylspiro[7,8-dithia-1-phosphabicyclo[3.2.1]oct-3-ene-2,9′-fluorene]-κP}tungsten (12a): Yellow solid (0.13 g, 7%), m.p. 230 °C (dec.). IR (KBr): ṽ = 2075 (s), 1991 (w), 1950 (vs), 1445 (m), 1030 (w), 741 (s), 699 (s) cm^{-1}. ^{1}H NMR: δ = 5.07 (s, 1 H, 9-H_{Fluo}), 6.58 (dd, $^3J_{H,H}$ = 8.2, 1.1 Hz, 1 H, *o*-1-Ph*H*), 6.76 (dd, $^3J_{H,H}$ = 8.5, 1.4 Hz, 1 H, *o*-2-Ph*H*), 6.84 (m, 3 H, *m*/*p*-1-Ph*H*), 6.96 (m, 4 H, *m*-2-Ph*H*, H_{Ph}), 7.04 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, *p*-2-Ph*H*), 7.17 (m, 3 H, 4-H, H_{Ph}, H_{Fluo}), 7.27 (m, 2 H, H_{Ph}, H_{Fluo}), 7.39–7.58 (m, 17 H, H_{Ph}, H_{Fluo}), 7.62 (d, $^3J_{H,H}$ = 7.3 Hz, 1 H, H_{Fluo}), 7.70 (dd, $^3J_{H,H}$ = 6.7, 1.9 Hz, 1 H, H_{Fluo}), 7.77 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, H_{Fluo}), 8.28 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, H_{Fluo}), 8.32 (dd, $^3J_{H,H}$ = 7.1, 2.5 Hz, 1 H, H_{Fluo}), 8.50 (m, 1 H, H_{Fluo}) ppm. ^{13}C NMR: δ = 51.6 (s, C_{Fluo}-9), 60.6 (d, $^1J_{P,C}$ = 3.7 Hz, C-2), 74.7 (d, $^4J_{P,C}$ = 2.2 Hz, C-5), 84.7 (d, $^5J_{P,C}$ = 2.9 Hz, C-6), 119.6, 120.8, 125.5, 125.6, 126.4, 126.8, 126.8, 127.0, 127.5, 127.5, 127.6, 127.6, 127.7, 127.8, 127.9, 128.9, 129.0, 129.3, 129.8, 131.6, 133.9, 136.6, 140.8, 141.2, 141.6, 141.7, 142.0, 142.5, 143.1, 143.5, 144.5, 145.3, 147.5, 194.0 (d, $^2J_{P,C}$ = 6.6 Hz, CO_{eq}), 197.0 (d, $^2J_{P,C}$ = 32.9 Hz, CO_{ax}) ppm. ^{31}P NMR: δ = 54.3 ($^1J_{P,W}$ = 273.2 Hz) ppm. MS (ESI): *m*/*z* = 1169 $[M + K]^+$, 1153 $[M + Na]^+$, 1113 $[M + K – 2CO]^+$, 1097 $[M + Na – 2CO]^+$, 1029 $[M + K – 5CO]^+$, 1013 $[M + Na – 5CO]^+$, 845 $[M + K – W(CO)_5]^+$, 829 $[M + Na – W(CO)_5]^+$. $C_{61}H_{39}O_5PS_2W$ (1130.9): calcd. C 64.79, H 3.48; found C 64.42, H 3.99.

Thermally Induced Reaction of Complex 10b: A solution of **10b** (1.32 g, 1.68 mmol) in toluene (25 mL) was heated at 80 °C for 3 h. The solvent was removed in vacuo and the yellow residue was subjected to column chromatography over silica gel with toluene/cyclohexane (3:1) as eluent to give thiaphosphirane **11b** (0.91 g, 70%). When **10b** was heated at 50 °C for 24 h, a mixture of **10b**, **11b** and **12b** (two isomers, δ_P(**12b**) = 53.6 and 52.2 ppm) was formed (1:3.5:1 by ^{31}P NMR integration), which was not worked up.

Pentacarbonyl(5′-(4-methoxyphenyl)-3′-phenylspiro[fluorene-9,2′-[6]thia[1]phosphabicyclo[3.1.0]hex[3]ene]-κP)tungsten (11b): Yellow solid (0.91 g, 70%), m.p. 158 °C (dec.). IR (KBr): ṽ = 2077 (m), 1945 (vs, br), 1260 (m), 1097 (m), 1027 (m), 804 (m) cm^{-1}. ^{1}H NMR: δ = 3.85 (s, 3 H, C*H*$_3$), 6.65 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, *o*-3′-Ph*H*), 7.00 (m, 4 H, 1-H_{Fluo}, *m*/*p*-3′-Ph*H*), 7.03 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, 2-H_{Fluo}), 7.42 (m, 2 H, 3-H_{Fluo}, 6-H_{Fluo}), 7.55 (m, 4 H, 7-H_{Fluo}, 8-H_{Fluo}, *m*-5′-Ph*H*), 7.59 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, *o*-5′-Ph*H*),

7.84 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 4-H$_{Fluo}$), 7.92 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, 5-H$_{Fluo}$) ppm. ^{13}C NMR: δ = 55.5 (s, CH$_3$), 59.7 (d, $^1J_{P,C}$ = 4.4 Hz, C-5′), 69.9 (d, $^1J_{P,C}$ = 14.6 Hz, C-2′), 113.6, 114.3, 119.2, 120.6, 121.8, 123.2, 124.4, 124.4, 124.6, 126.6, 127.2, 127.4, 128.2, 128.3, 128.6, 128.9, 129.0, 129.2, 129.8, 130.2, 140.0, 140.8, 142.8, 144.0, 145.2, 146.3, 159.9 (s, *p*-5′-Ph), 193.1 (d, $^2J_{P,C}$ = 8.0 Hz, CO$_{eq}$), 196.3 (d, $^2J_{P,C}$ = 42.4 Hz, CO$_{ax}$) ppm. ^{31}P NMR: δ = –6.21 ($^1J_{P,W}$ = 289.2 Hz) ppm. MS (CI, 100 eV): *m*/*z* (%) = 773 (1) [MH]$^+$, 744 (8) [M – CO]$^+$, 740 (34) [M – S]$^+$, 417 (30) [M – S – W(CO)$_5$]$^+$, 285 (87) [C$_{16}$H$_{13}$OPS (= **5b**) + 1]$^+$.

Thermally Induced Reaction of Complex 10c: A solution of **10c** (1.54 g, 1.68 mmol) in toluene (25 mL) was heated at 80 °C for 8 h. The ^{31}P NMR spectra indicated the presence of a mixture of **10c**, **11c** and **12c** in a 12:70:15 ratio. Efforts to separate thiaphosphirane complex **11c** from this mixture by column chromatography were unsuccessful because the compound underwent partial decomposition. NMR spectroscopic data of **11c**: ^{1}H NMR: δ = 6.66 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, *o*-3′-Ph*H*), 7.00 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, *m*-3′-Ph*H*), 7.10 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, *p*-3′-Ph*H*), 7.17 (m, 1 H, H$_{Ph/Fluo}$), 7.40–7.70 (m, 11 H, H$_{Ph/Fluo}$) ppm. ^{31}P NMR: δ = –6.92 ($^1J_{P,W}$ = 296.0 Hz) ppm.

Pentacarbonyl(3′,5′-diphenylspiro[fluorene-9,2′-[2*H*]phosphole])tungsten (13): Tri-*n*-butylphosphane (0.140 mL, 0.570 mmol) was added under argon to a solution of thiaphosphirane complex **11a** (0.280 g, 0.38 mmol) in dry dichloromethane (10 mL). The color of the solution changed immediately from yellow to orange. Complete conversion of **11a** into **13** within 1 min was indicated by ^{31}P NMR spectroscopy. Owing to the extreme sensitivity of **13** to oxygen, purification was not possible. ^{1}H NMR: δ = 6.82 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, *o*-3′-Ph*H*), 7.04 (m, 3 H, *m*/*p*-3′-Ph*H*), 7.16 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, 1-H$_{Fluo}$, 8-H$_{Fluo}$), 7.19 (m, 1 H, 2-H$_{Fluo}$ or 7-H$_{Fluo}$), 7.23 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, 2-H$_{Fluo}$ or 7-H$_{Fluo}$), 7.45 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, *m*/*p*-5′-Ph*H*), 7.51 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, 3-H$_{Fluo}$, 6-H$_{Fluo}$), 7.77 (dd, $^3J_{H,H}$ = 7.4, 1.4 Hz, 2 H, *o*-5′-Ph*H*), 7.91 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, 4-H$_{Fluo}$, 5-H$_{Fluo}$), 7.96 (d, $^3J_{P,H}$ = 19.8 Hz, 1 H, 4′-H) ppm. ^{31}P NMR: δ = 233.6 ($^1J_{P,W}$ = 275.6 Hz) ppm. MS (CI, 100 eV): *m*/*z* (%) = 711 (13) [MH]$^+$.

Sulfuration of 2*H*-Phosphole 13: An excess of elemental sulfur (60.8 mg, 1.90 mmol) was added to a solution of freshly prepared 2*H*-phosphole **13** (see above) in dichloromethane (10 mL). Thiaphosphirane **11a** was formed quantitatively. ^{31}P NMR: δ = –6.4 ($^1J_{P,W}$ = 291.6 Hz) ppm.

3-(9*H*-Fluoren-9-ylidene)-1,3-diphenylpropan-1-one (14): Exposure to air of a freshly prepared solution (see above) of 2*H*-phosphole **13** in dichloromethane (10 mL) led to the fast disappearance (<1 min) of the orange color of the reaction mixture. The solvent was removed in vacuo and the residue was purified by chromatography over silica gel with toluene/cyclohexane (1:1) to yield **14** as a colorless solid (0.170 g, 80%), m.p. 199 °C (lit.:[35] 204–205 °C). IR (KBr): $\tilde{\nu}$ = 1687 (vs, C=O), 1594 (m), 1446 (s), 1420 (m), 1322 (m), 1300 (m), 1262 (m), 1209 (s), 804 (m), 780 (s), 729 (vs), 696 (s) cm^{-1}. ^{1}H NMR: δ = 4.84 (s, 2 H, CH$_2$), 6.23 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, 8-H$_{Fluo}$), 6.86 (t, $^3J_{H,H}$ = 7.7 Hz, 1 H, 7-H$_{Fluo}$), 7.17 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, 2-H$_{Fluo}$), 7.20 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, 6-H$_{Fluo}$), 7.33 (dt, $^3J_{H,H}$ = 7.6, 0.6 Hz, 1 H, *p*-3-Ph*H*), 7.38 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, 6-H$_{Fluo}$), 7.40–7.52 (m, 5 H, *m*-1-Ph*H*, *m*-3-Ph*H*, 1-H$_{Fluo}$), 7.53 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, *o*-3-Ph*H*), 7.60 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, *p*-1-Ph*H*), 7.67 (m, 2 H, 5-H$_{Fluo}$, *o*-3-Ph*H*), 7.75 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, 4-H$_{Fluo}$), 8.04 (m, 2 H, *o*-1-Ph*H*) ppm. ^{13}C NMR: δ = 48.5 (CH$_2$), 119.1 (C$_{Fluo}$-5), 119.7 (C$_{Fluo}$-4), 120.3 (*m*-3-Ph), 124.1 (C$_{Fluo}$-1), 124.2 (*o*-3-Ph), 125.0 (C$_{Fluo}$-8), 126.6 (C$_{Fluo}$-7), 127.1 (C$_{Fluo}$-2), 127.4 (C$_{Fluo}$-6), 127.8 (C$_{Fluo}$-3), 127.9 (*o*-3-Ph), 128.1 (*o*-1-Ph), 128.8 (*m*-1-Ph), 129.1 (*p*-3-Ph), 133.4 (*p*-1-Ph), 136.4 (C=*C*-CH$_2$), 136.8 (*m*-3-Ph), 138.0 (C$_{Fluo}$-9a), 138.4 (*C*=C-CH$_2$), 138.5 (*ipso*-1-Ph), 140.0 (C$_{Fluo}$-8a), 141.0 (C$_{Fluo}$-4a or C$_{Fluo}$-4b), 144.1 (C$_{Fluo}$-4a or C$_{Fluo}$-4b), 144.5 (*ipso*-3-Ph), 195.5 (CO) ppm. MS (CI, 100 eV): *m*/*z* (%) = 373 (100) [MH]$^+$, 105 (69) [C$_6$H$_7$CO]$^+$.

Dithiaphospholane Pentacarbonyltungsten Complex 18

Procedure A: A solution of **10a** (40.0 mg, 54.0 μmol) and thiobenzophenone (21.3 mg, 0.110 mmol) in toluene (10 mL) was stirred at ambient temperature. A color change from deep-blue to deep-violet occurred. After 3 h, the solvent was removed at 0.05 mbar/20 °C. The crude product was purified by thin-layer chromatography on silica gel with toluene/cyclohexane (1:1) to give **18** as a yellow solid (47.0 mg, 93%).

Procedure B: A solution of hexacarbonyltungsten (0.40 g, 1.13 mmol) in THF (250 mL) was placed in a photolysis apparatus and irradiated for 60 min using a 150 W medium-pressure mercury lamp. The yellow solution of the [W(CO)$_5$(thf)] complex formed was transferred to a flask containing solid dithiaphospholane **19** (0.62 g, 1.01 mmol) and the mixture was stirred for 1 day. The solvent was removed under reduced pressure. The resulting oil was purified by chromatography on silica gel with toluene/cyclohexane (1:1) to give **18** as a yellow solid (0.90 g, 95%); m.p. 233 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2073 (s), 1936 (vs), 1489 (m), 1444 (m), 1262 (m), 1103 (m), 1032 (m), 743 (m), 696 (m) cm^{-1}. ^{1}H NMR: δ = 5.99 (dd, $^3J_{H,H}$ = 8.2, 1.1 Hz, 2 H, *o*-3-Ph*H*), 6.72 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, *m*-3-Ph*H*), 6.86 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, *p*-3-Ph*H*), 7.12 (m, 3 H, 4-H, *o*-5-Ph*H*), 7.20 (m, 2 H, 6-H$_{Fluo}$, *p*-5-Ph*H*), 7.23–7.30 (m, 6 H, 7-H$_{Fluo}$, *m*/*p*-6-Ph′*H*, *m*-5-Ph*H*), 7.41 (m, 4 H, 2-H$_{Fluo}$, *m*/*p*-6-Ph*H*), 7.54 (dt, $^3J_{H,H}$ = 7.5, 1.4 Hz, 1 H, 3-H$_{Fluo}$), 7.59 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, *o*-6-Ph′*H*), 7.64 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 5-H$_{Fluo}$), 7.79 (m, 3 H, 4-H$_{Fluo}$, *o*-6-Ph*H*), 7.88 (dd, $^3J_{H,H}$ = 7.7, 2.7 Hz, 1 H, 8-H$_{Fluo}$), 8.28 (dd, $^3J_{H,H}$ = 7.6, 2.8 Hz, 1 H, 1-H$_{Fluo}$) ppm. ^{13}C NMR: δ = 59.2 (d, $^1J_{P,C}$ = 2.9 Hz, C-2), 71.3 (d, $^2J_{P,C}$ = 2.2 Hz, C-5), 89.9 (d, $^2J_{P,C}$ = 2.9 Hz, C-6), 120.8, 125.3, 126.6, 126.9, 127.0, 127.1, 127.3, 127.4, 127.6, 127.8, 128.1, 128.2, 128.3, 128.4, 128.4, 128.7, 128.9, 129.0, 129.0, 129.4, 129.6, 129.7, 130.1, 131.0, 132.0, 132.4, 136.1 (d, $^3J_{P,C}$ = 5.1 Hz, C-4), 137.6, 138.1, 139.4, 141.7, 141.9, 142.6, 142.9, 143.0, 143.2, 143.5, 194.0 (d, $^2J_{P,C}$ = 6.6 Hz, CO$_{eq}$), 197.9 (d, $^2J_{P,C}$ = 33.7 Hz, CO$_{ax}$) ppm. ^{31}P NMR: δ = 52.3 ($^1J_{P,W}$ = 271.0 Hz) ppm. MS (ESI): *m*/*z* = 979 [M +K]$^+$, 963 [M + Na]$^+$. C$_{46}$H$_{29}$O$_5$PS$_2$W (940.7): calcd. C 58.73, H 3.11; found C 58.50, H 3.13.

3,5,6,6-Tetraphenylspiro[7,8-dithia-1-phosphabicyclo[3.2.1]oct-3-ene-2,9′-fluorene] (19): A solution of **7a** (45.1 mg, 0.110 mmol) and thiobenzophenone (42.6 mg, 0.210 mmol) in toluene (10 mL) was stirred at ambient temperature. After 3 h, the solvent was removed at 0.05 mbar/20 °C. The crude product was purified by chromatography over silica gel with toluene/cyclohexane (1:1). Subsequent recrystallization from dichloromethane/*n*-pentane at 0 °C gave **19** as a pale-yellow solid (63.0 mg, 93%), m.p. 151 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1596 (m), 1491 (s), 1442 (s), 1035 (m), 761 (m), 738 (vs), 697 (vs) cm^{-1}. ^{1}H NMR: δ = 6.11 (dd, $^3J_{H,H}$ = 8.3, 1.0 Hz, 2 H, *o*-3-Ph*H*), 6.76 (t, $^3J_{H,H}$ = 7.7 Hz, 2 H, *m*-3-Ph*H*), 6.88 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, *p*-3-Ph*H*), 7.12 (d, $^4J_{P,H}$ = 3.3 Hz, 1 H, 4-H), 7.14–7.29 (m, 10 H, 6-H$_{Fluo}$, 7-H$_{Fluo}$, H$_{Ph}$), 7.30 (t, $^3J_{H,H}$ = 8.2 Hz, 1 H, 3-H$_{Fluo}$), 7.40 (m, 4 H, 2-H$_{Fluo}$, *m*/*p*-6-Ph*H*), 7.51 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, H$_{Ph}$), 7.54 (m, 2 H, *o*-6-Ph′*H*), 7.59 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 5-H$_{Fluo}$), 7.76 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 8-H$_{Fluo}$), 7.85 (m, 3 H, 4-H$_{Fluo}$, *o*-6-Ph*H*), 8.14 (dd, $^3J_{H,H}$ = 7.3, 2.0 Hz, 1 H, 1-H$_{Fluo}$) ppm. ^{13}C NMR: δ = 55.7 (d, $^1J_{P,C}$ = 41.7 Hz, C-2), 68.9 (d, $^1J_{P,C}$ = 3.7 Hz, C-5), 85.7 (d, $^2J_{P,C}$ = 5.1 Hz, C-6), 120.3, 120.5, 125.3, 126.3, 126.7, 126.8, 126.9, 127.1, 127.2, 127.3, 127.5, 127.6,

Table 2. Crystallographic data and details of data collection and structure refinement for **6a**, **7a**, **11a** and **12a**.[a]

	7a	**8a**	**11a**	**12a**
Empirical formula	$C_{28}H_{19}PS$	$C_{28}H_{21}OPS$	$C_{33}H_{19}O_5PSW$	$C_{61}H_{39}O_5PS_2W$
Formula weight	418.46	436.48	742.36	1130.86
Temperature [K]	193(2)	190(2)	193(2)	190(2)
Crystal size [mm]	0.46 × 0.19 × 0.08	0.38 × 0.38 × 0.31	0.58 × 0.31 × 0.19	0.38 × 0.27 × 0.15
Crystal system	monoclinic	monoclinic	tetragonal	monoclinic
Space group	$P2_1/n$	$C2/c$	$I4_1/a$	$P2_1/c$
a [Å]	11.1464(11)	17.638(2)	33.046(2)	12.8398(12)
b [Å]	9.7308(7)	21.645(3)	33.046(2)	18.3062(18)
c [Å]	19.417(2)	11.8739(14)	10.3660(6)	20.531(2)
α [°]	90	90	90	90
β [°]	101.290(12)	105.857(13)	90	99.202(12)
γ [°]	90	90	90	90
Volume [Å^3]	2065.3(3)	4360.5(9)	11320.1(12)	4763.7(8)
Z	4	8	16	4
Density [g cm^{-3}]	1.346	1.330	1.742	1.577
μ(Mo-K_α) [mm^{-1}]	0.247	0.240	4.254	2.600
F(000)	872	1824	5792	2264
θ range [°]	2.14–26.00	2.08–24.71	2.06–25.96	2.01–25.88
Reflections collected	15858	15178	54812	37383
Independent reflections (R_{int})	3865 (0.0574)	3546 (0.1585)	5316 (0.0674)	8694 (0.0746)
Completeness to θ_{max} [%]	95.4	95.2	95.9	94.0
Absorption correction	–	–	empirical	numerical
Max./min. transmission	–	–	0.446/0.200	0.7115/0.5134
Data/restraints/parameters[b]	3865/0/347	3546/0/280	5316/0/370	8694/0/631
Goodness-of-fit on F^2	0.855	0.851	1.069	0.893
Final R indices [$I > 2\sigma(I)$]:[b] R_1, wR_2	0.0315, 0.0639	0.0569, 0.1395	0.0245, 0.0558	0.0376, 0.0998
R indices (all data):[c] R_1, wR_2	0.0590, 0.0698	0.0971, 0.1542	0.0336, 0.0621	0.0588, 0.1032
Largest diff. peak and hole [e Å^{-3}]	0.20, –0.21	0.30, –0.29	0.48, –0.57	0.84, –0.94

[a] CCDC-713424 (for **7a**), -713425 (for **11a**), -713426 (for **12a**), and -713427 (for **8a**) contain the supplementary crystallographic data for this paper, These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. [b] Refinement based on F^2 values. [c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

127.7, 127.8, 127.9, 128.1, 128.2, 128.4, 128.9, 129.0, 129.6, 130.0, 131.3, 131.8, 132.0, 137.4, 139.6, 140.4, 141.0, 142.4, 142.5, 144.3, 144.5, 145.7, 147.3 ppm. ^{31}P NMR: δ = 26.9 ppm. MS (CI, 100 eV): m/z (%) = 617 (<1) $[MH]^+$, 419 (6) $[M - Ph_2CS + 1]^+$, 199 (100) $[Ph_2CS + 1]^+$. $C_{41}H_{29}PS_2$ (616.8): calcd. C 79.84, H 4.74; found C 79.64, H 4.65.

Crystal Structure Determinations: Data collection was performed on an image-plate diffractometer (Stoe IPDS) using monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by using a full-matrix least-squares method. Hydrogen atoms in **7a** were located on a ΔF map and were included in the refinement. In all other cases, they were calculated geometrically and treated as riding atoms on their bond neighbors. Software for structure solution and refinement: SHELX-97;[36] molecule plots: ORTEP-3.[37] Further details are provided in Table 2.

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