J. Am. Chem. Soc. **1980**, *102*, 5809–5815

where

$$\alpha = (h\nu_{\text{in}})^2(E_{\text{in}} + E_{\text{out}})/4E_{\text{in}}E_{\text{out}}RT$$

Evaluation of this integral yields eq 36a.

Appendix C

The relationship between eq 39a and eq 41a can be shown as follows. Equation 39a can be rewritten as

$$k_{\text{in}} = \left(\frac{4\pi^2 H_{AB}{}^2}{h}\right)W \tag{C1}$$

where

$$W = \frac{1}{h\nu_{\text{in}}Q_A}\sum_{m=0}^{+\infty} e^{-mh\nu_{\text{in}}/kT}S_{m,m}{}^2 \tag{C2}$$

and

$$Q_A = \frac{1}{1 - e^{-h\nu_{\text{in}}/kT}}$$

The Franck–Condon factors can be expressed in terms of Laguerre polynomials[43,48]

$$S_{m,m}{}^2 = e^{-E_{\text{in}}/h\nu_{\text{in}}}\left(L_{m,m}\left(\frac{E_{\text{in}}}{h\nu_{\text{in}}}\right)\right)^2 \tag{C3}$$

Substitution in eq C2 gives

$$W = \frac{1 - e^{-h\nu_{\text{in}}/kT}}{h\nu_{\text{in}}}e^{-(E_{\text{in}}/h\nu_{\text{in}})}\sum_m (e^{-(h\nu_{\text{in}}/kT)})^m\left(L_{m,m}\left(\frac{E_{in}}{h\nu_{\text{in}}}\right)\right)^2 \tag{C4}$$

With the aid of the identity[49]

$$\sum_m y^m(L_{m,m}(x))^2 = \frac{1}{1-y}e^{-(2xy/(1-y))}I_0\left(\frac{2xy^{1/2}}{1-y}\right) \tag{C5}$$

where $I_0(2xy^{1/2}/(1-y))$ is a zero-order modified Bessel function, W can be rewritten as follows:

$$W = \frac{1}{h\nu_{\text{in}}}e^{-(E_{\text{in}}/h\nu_{\text{in}})(1+\exp(-h\nu_{\text{in}}/2kT)\operatorname{csch}(h\nu_{\text{in}}/2kT))}I_0(z)$$

where z has been defined in Appendix B. For large values of z (that is, at high temperatures)

$$I_0(z) = \frac{1}{(2\pi z)^{1/2}}e^z$$

and W becomes

$$W = \frac{1}{\left(2\pi E_{\text{in}}h\nu_{\text{in}} \operatorname{csch}\left(\frac{h\nu_{\text{in}}}{2kT}\right)\right)^{1/2}}e^{-E_{\text{in}}F/h\nu_{\text{in}}} \tag{C6}$$

where

$$F = 1 + e^{-h\nu_{\text{in}}/2kT}\operatorname{csch}\left(\frac{h\nu_{\text{in}}}{2kT}\right) - \operatorname{csch}\left(\frac{h\nu_{\text{in}}}{2kT}\right) \tag{C7}$$

Since

$$(\cosh(x) - 1)/\sinh(x) = \tanh(x/2)$$

the expression for F reduces to

$$F = \tanh\left(\frac{h\nu_{\text{in}}}{4kT}\right)$$

and therefore the expression for W is

$$W = \left(\frac{\sinh(h\nu_{\text{in}}/2kT)}{2\pi E_{\text{in}}h\nu_{\text{in}}}\right)^{1/2}e^{-(E_{\text{in}}/h\nu_{\text{in}})\tanh(h\nu_{\text{in}}/4kT)} \tag{C8}$$

Substitution of this expression into eq C1 gives eq 41a.

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(48) Keil, T. H. *Phys. Rev. A* **1965**, *140*, 601.

(49) Copson, E. T. "Functions of a Complex Variable"; Oxford University Press: London, 1935; p 207.

Phosphole [2 + 2] and [4 + 2] Dimerizations around Metal Carbonyl Moieties. Structure and Chemistry of a New Type of Exo [4 + 2] Dimers

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Abstract: UV irradiation of mixtures of 3,4-dimethylphospholes (L) with $M(CO)_6$ (M=Cr, Mo, W) leads mainly to $(L{-}L)M(CO)_4$ complexes derived from Diels–Alder [4 + 2] phosphole dimers acting as chelating ligands. An X-ray structural study of one of these complexes shows that, contrary to normal endo phosphole dimers, these compounds have the exo configuration and that the phosphorus bridge is very strained: ∠CPC = 79.4°. With 1-phenylphosphole and $Mo(CO)_6$, the $(L{-}L)Mo(CO)_4$ complex has unexpectedly the structure of a [2 + 2] "head-to-head" dimer. At 50 °C the [4 + 2] dimeric complexes react with sulfur to yield the corresponding [4 + 2] exo dimeric phosphole sulfides, the spectral and chemical properties of which are compared with those of the corresponding endo dimeric sulfides. Contrary to the endo sulfides, the exo sulfides collapse at a relatively low temperature to yield a phosphinidene sulfide and a phosphindole derivative. Phenylphosphinidene sulfide thus prepared has been trapped by 2,3-dimethyl-1,3-butadiene to give a phospholene sulfide. Also based upon these observations, a two-step conversion of 1-phenylphosphole into 1-phenylphosphindole *P*-sulfide is described.

Weakly substituted λ^5 phospholes are known to dimerize instantly even at low temperature (eq 1). The structure of one such Diels–Alder dimer has been studied by X-ray.[2] The most interesting features are (1) the endo configuration at the junction

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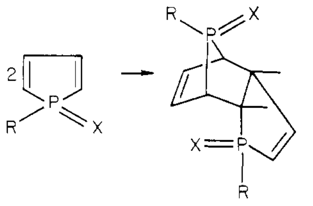


(1)

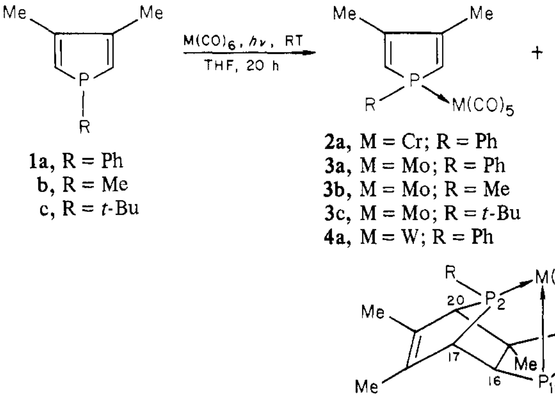
and (2) the high cyclic strain of the phosphorus at the bridge of the six-membered ring (∠CPC = 87°). This high cyclic strain has many interesting chemical consequences. Thus a P–O–C bond at the bridge hydrolyzes much faster than a P–O–C bond on the five-membered ring phosphorus atom.[3] Besides, the phosphorus bridge can be split off either thermally[4] or by reaction with *m*-chloroperbenzoic acid[5] to yield a phosphindole derivative.

Contrary to their λ^5 counterparts, λ^3 phospholes do not dimerize under normal conditions. In only one case a head-to-tail [2 + 2] dimerization of 1,2,5-triphenylphosphole was observed under UV irradiation,[6a] but this phosphole is known not to be representative of its class.[6b]

However, while studying the reaction of 1-phenyl-3,4-dimethylphosphole with molybdenum hexacarbonyl, we discovered a general and original [4 + 2] dimerization reaction leading to the unknown Diels–Alder exo phosphole dimers. Hereafter we report on this and on the structure and chemistry of these dimers.

Results and Discussion

1. Reaction of Phospholes with Group 6B Metal Hexacarbonyls. When reacting 3,4-dimethylphospholes (L) with hexacarbonyls $M(CO)_6$ (M=Cr, Mo, W) at room temperature in THF under UV irradiation (eq 2) we obtained mainly two types of complexes.



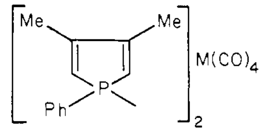
1a, R = Ph
b, R = Me
c, R = *t*-Bu

2a, M = Cr; R = Ph
3a, M = Mo; R = Ph
3b, M = Mo; R = Me
3c, M = Mo; R = *t*-Bu
4a, M = W; R = Ph

(2)

5a (35% yield)
6a (45%)
6b (50%)
6c (33%)
7a (36%)

The first ones belong to the classical $LM(CO)_5$ family. Such complexes have been already described with L = 1,2,5-triphenylphosphole[7] and they have no particular interest. The second ones correspond to the $L_2M(CO)_4$ stoichiometry. However, an inspection of the ^1H and ^{31}P NMR spectra of these species shows quite conclusively that they derive from Diels–Alder phosphole dimers acting as chelating ligands and thus having the unusual exo configuration. We have studied in depth the ^1H NMR spectrum of **6a** at 100 MHz with ^{31}P decoupling. The main problem lies in the attribution of the signals at 2.64, 2.68, and 3.01 ppm to HC16, HC17, and HC20 protons. The proton at 2.64 ppm is coupled with both phosphorus atoms and thus corresponds either to HC16 or to HC17. It is also coupled to the proton at 3.01 ppm which thus corresponds either to HC17 or HC16. According to the X-ray study of **6a** (vide infra), the dihedral H–C16–C17–P2 and H–C17–C16–P1 angles are close respectively to 178 and 73°. Thus, if we admit that the Karplus-like relationship which has been established for ^3J(H–P) coupling constants in the case of phosphoryl compounds[8a] holds true for phosphine complexes,[8b] then the signal at 2.64 ppm is necessarily attributed to HC16 (^3J(H–P2) = 41.4 Hz corresponds to the maximum of the curve) and the signal at 3.01 ppm to HC17 (^3J(H–P1) ~ 0 Hz corresponds to the minimum of the curve). Similar results have been also obtained for a dimeric phosphole sulfide with the exo configuration (vide infra). From another standpoint the low values of the ^2J(P1–P2) coupling constants and the multiplicity of the CO bands in respectively the ^{31}P NMR and IR spectra of **5a**–**7a** complexes are in line with a cis configuration around the molybdenum atom. Finally, the very low field resonance of P2 is characterisitic of the phosphorus bridges in phosphole dimers.[9] We have checked separately that phospholes **1 a–c** did not dimerize when irradiated at room temperature in THF for 20 h. Thus the dimerization leading to complexes **5a**–**7a** necessarily takes place within the coordination spheres of the metal atoms. The first step probably includes the formation of a cis $L_2M(CO)_4$ complex in which the dimerization takes place because of the vicinity of the two phosphole nuclei[10] and because the cyclic delocalization of the phosphole ring has been switched off. Such a cis $L_2M(CO)_4$ complex **8a** has been isolated together with **2a** and **5a** in the case of chromium. In that case the dimerization is more difficult, probably because the chromium atom is too small to be efficiently chelated by the phosphole dimer (atomic radii: Cr, 1.27; Mo, 1.40; W, 1.46 Å).



cis

8a, M = Cr
9a, M = Mo

The second step (intramolecular dimerization) is, as the first one, promoted by UV irradiation. Indeed, the thermal reaction of phosphole **1a** with $(C_5H_{10}NH)_2Mo(CO)_4$ according to a procedure developed by Darensbourg[11] yields complex **9a** and not complex **6a**. Moreover, complex **9a** gives complex **6a** under UV irradiation (50% yield). However, in view of the Woodward–Hoffman rules and of the results of the UV-promoted dimerization of 1,2,5-triphenylphosphole[6] it seemed very likely that [2 + 2] dimers were the initial products of the dimerization and that [4 + 2] dimers were only the final results of a thermally allowed intramolecular rearrangement of these [2 + 2] dimers. This hypothesis is strongly supported by the results observed when reacting 1-phenylphosphole with molybdenum hexacarbonyl under UV (eq 3). The original head-to-head structure of complex **12** was established by NMR and mass spectroscopy.

Since only minor changes in the ^{13}C chemical shifts are observed when complexing a chelating diphosphine with a $Mo(CO)_4$ moiety,[12] the attributions have been made for **12** by comparison

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(1) (a) Equipe SNPE-CNRS; (b) Institut Le Bel.

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(9) L. D. Quin and K. A. Mesch, *Org. Magn. Reson.*, **12**, 442 (1979).

(10) One referee has pointed out that the principle of enhancing the reactivity of two unsaturated ligands via cis coordination to a metal has already been described: A. J. Carty, N. J. Taylor, and D. K. Johnson, *J. Am. Chem. Soc.*, **101**, 5422 (1979).

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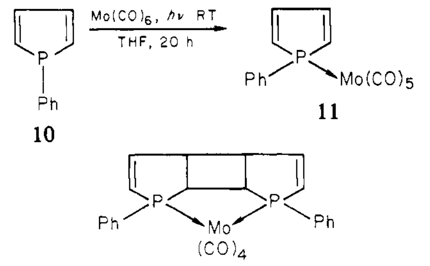


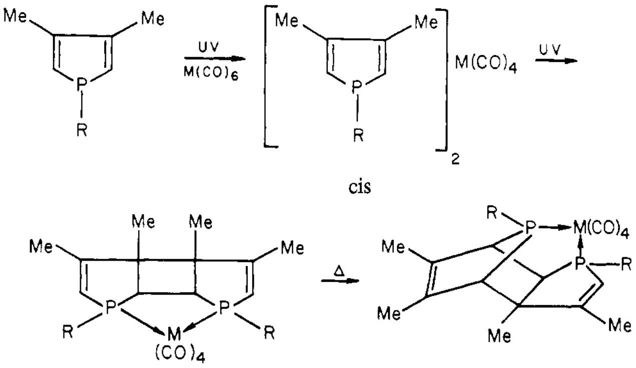
10 **11** **12** (3)

with the ^{13}C spectrum of 1-phenylphosphol-2-ene.[13] The perfectly symmetrical structure of complex **12** is well in evidence on the ^1H and ^{31}P NMR spectra (only two types of saturated protons and only one ^{31}P signal are observed). The postulated [2 + 2] → [4 + 2] thermal rearrangement of **12** has been indirectly demonstrated by chemical experiments described in the third part of the Discussion. Scheme I summarizes the postulated mechanism for the [4 + 2] dimerization of phospholes around metal carbonyl moieties.

2. Crystal Structure of Complex 6a. The crystal structure of **6a** consists of dicrete molecules linked by van der Waals interactions and hydrogen bonds. Figure 1 represents a molecule without hydrogen atoms together with the labeling scheme used.[14]

Molybdenum is octahedrally surrounded by four carbonyl groups and by the phosphorus atoms of the ligand which are in cis positions. The MoC_4P_2 octahedron is distorted as shown by bond lengths and angles around Mo, listed in Table I. The P1–Mo–P2 angle of 74.11 (4)° is smaller than 79.39°, the mean value found in four other Mo–P–C–C–P five-membered rings.[15,16]

The two phosphorus atoms of the ligand lie on the same side of the bridge between the phospholene rings as shown in Figure 1 and by the distances of atoms P1 and P2 to the mean plane through C15, C16, C17, C20 (Table II, plane PL1); as expected, the conformation of this dimeric structure is different from that found by Chiu and Lipscomb in $P_2O_4C_{12}H_{18}$,[2] where the two phosphorus atoms are trans to the same mean plane. The C–C double bonds are well localized: C13–C14 and C18–C19 with a mean bond length of 1.327 (5) Å corresponding to a sp^2 hybridization. The two phospholene rings are not planar as shown by the dihedral angles of the mean planes PL2/PL3 and PL4/PL5 (Table II) in contrast with the structure of $P_2O_4C_{12}H_{18}$ in which the five-membered ring containing P1 is planar within rather large experimental errors. The values of the dihedral angles between PL2/PL3 and PL4/PL5 are related to the strain at the P1 and P2 bridges as also indicated by bond angles C13–P1–C16 (92.6 (2)°) and C17–P2C20 (79.4 (2)°). This last data clearly indicates that the strain at the P2 bridge is much higher in phosphole Diels–Alder exo dimers than in the corresponding endo dimers (ca. 7.5° higher; see ref 2). This is probably why the dimerization of λ^5 phosphole leads exclusively to the endo dimers. From another standpoint it is obvious that the peculiar properties of the phosphorus P2 bridge which were observed on endo dimers will be enhanced in exo dimers. This point is illustrated hereafter. It must be also stressed that only the instable three-membered phosphirane rings are more strained at phosphorus than our exo dimers (∠CPC ca. 47°); on the contrary, even the four-membered phosphetane rings are less strained (∠CPC ca. 82°; see ref 17). Other bond angles are considerably different from normal tetrahedral angles, such as P2–C20–C19 (99.4°) and P2–C17–C16 (96.2°). The remaining bond angles around P1, P2, C16, C17, and C20 are close to the tetrahedral values.



Scheme I. Postulated Mechanism of the Diels–Alder Dimerization of 3,4-Dimethylphospholes around Group 6B Metal Tetracarbonyl Moieties

Table I. Selected Bond Distances (Å) and Angles (deg) in Complex **6a**

Mo-P1	2.480 (1)		P1-Mo-P2	74.11 (4)
Mo-P2	2.470 (1)		P1-Mo-C27	170.2 (2)
Mo-C25	1.998 (5)		P2-Mo-C25	166.9 (1)
Mo-C26	2.020 (6)		C26-Mo-C28	172.8 (2)
Mo-C27	1.974 (6)			
Mo-C28	2.045 (6)			
P1-C1	1.812 (5)			
P1-C13	1.803 (5)			
P1-C16	1.881 (4)			
P2-C7	1.815 (5)		C13-P1-C16	92.6 (2)
P2-C17	1.853 (4)		C13-P1-C1	107.9 (2)
P2-C20	1.889 (4)		C1-P1-C16	107.1 (2)
			C14-C13-P1	110.9 (4)
C13-C14	1.328 (7)	1.327 (5)	C15-C14-C13	116.9 (4)
C18-C19	1.327 (7)		P1-C16-C15	103.6 (3)
			P1-C16-C17	112.2 (3)
C14-C15	1.509 (7)	1.528 (2)	C14-C15-C20	115.0 (4)
C14-C21	1.495 (7)		C15-C16-C17	106.9 (3)
C15-C16	1.573 (6)		C16-C15-C20	101.8 (3)
C15-C20	1.590 (6)			
C16-C17	1.556 (6)			
C17-C18	1.520 (6)			
C18-C23	1.493 (7)			
C19-C24	1.501 (7)			
C19-C20	1.518 (7)		C17-P2-C20	79.4 (2)
			C7-P2-C20	104.9 (2)
C1-C2	1.387 (8)	1.373 (2)	C7-P2-C17	110.9 (2)
C2-C3	1.360 (8)		P2-C20-C19	99.4 (3)
C3-C4	1.355 (11)		C20-C19-C18	110.4 (4)
C4-C5	1.349 (11)		C19-C18-C17	110.3 (4)
C5-C6	1.395 (9)		P2-C17-C18	102.1 (3)
C6-C1	1.369 (8)		P2-C17-C16	96.2 (3)
C7-C8	1.372 (7)		P2-C20-C15	103.9 (3)
C8-C9	1.352 (9)			
C9-C10	1.431 (11)			
C10-C11	1.334 (11)			
C11-C12	1.390 (8)			
C12-C7	1.381 (7)			
C25-O1	1.139 (6)	1.138 (3)		
C26-O2	1.135 (6)			
C27-O3	1.149 (7)			
C28-O4	1.132 (6)			

The strain around P1 and P2 is probably also reflected by the dissymmetry of the P–C bond distances in both rings, as observed in $P_2O_4C_{12}H_{18}$, and by the C–C bridging bond lengths between the two rings, C15–C20 (1.590 (6) Å) and C16–C17 (1.556 (6) Å). The lengthening of the C16–C17 bridge by comparison to the corresponding C–C bridge in $P_2O_4C_{12}H_{18}$ (1.46 (4) Å, ref 2) is certainly the result of the chelation of molybdenum in **6a**.

Each molecule of **6a** is connected by van der Waals contacts and hydrogen bonds to nine other molecules as indicated in Table III.

3. Chemistry of Exo [4 + 2] Phosphole Dimers. When reacting complex **6a** with sulfur in benzene near 50 °C a smooth decom-

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(14) Drawings are done using program ORTEP II: C. K. Johnson, Report ORNL 3794, Oak Ridge, Tenn., 1965.

(15) M. R. Churchill and F. J. Rotella, *Inorg. Chem.*, **17**, 668 (1978).

(16) M. Sato, T. Tatsumi, T. Kodama, M. Hidai, T. Uchida, and Y. Uchida, *J. Am. Chem. Soc.*, **100**, 4447 (1978).

(17) D. E. C. Corbridge, "The Structural Chemistry of Phosphorus", Elsevier, Amsterdam, 1974, p 396.

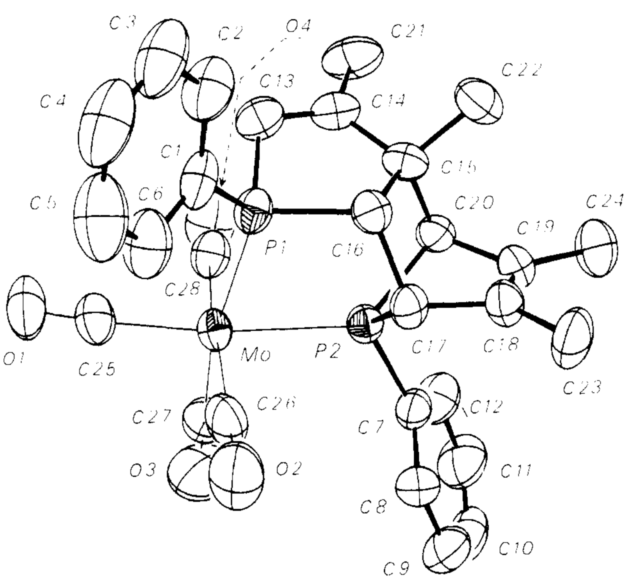


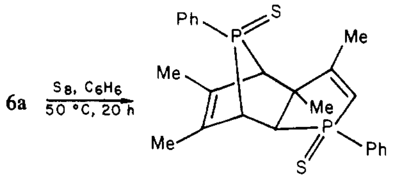
Figure 1. Stereoview of complex **6a**; atoms are represented by their thermal motion ellipsoids scaled to enclose 50% of the electron density.

Table II. Least-Squares Planes[a]

atoms in plane	coefficients	distance of other atoms to plane, A		x^2	N^o
C15,C16,C17,C20	$a = -0.2397$	P1	−1.833 (1)	1774	1
	$b = 0.7389$	P2	−1.269 (1)		
	$c = -0.6297$				
	$d = 3.3417$				
P1,C13,C16	$a = 0.4576$	C14	−0.475 (4)	0	2
	$b = -0.1202$	C15	−0.595 (4)		
	$c = -0.8810$				
	$d = 5.0343$				
C13,C14,C15,C16	$a = 0.5059$	P1	−0.518 (1)	69	3
	$b = 0.2878$	C21	0.100 (5)		
	$c = -0.8132$	C22	1.199 (5)		
	$d = 8.8573$				
P2,C17,C20	$a = 0.8843$	C18	−1.145 (4)	0	4
	$b = -0.4504$	C19	−1.189 (4)		
	$c = -0.1230$				
	$d = 5.9281$				
C17,C18,C19,C20	$a = 0.6908$	P2	−1.183 (1)	132	5
	$b = 0.2718$	C23	0.178 (5)		
	$c = -0.6701$	C24	0.039 (6)		
	$d = 9.6989$				
C1,C2,C3,C4, C5,C6	$a = -0.6699$			3	6
	$b = 0.4684$				
	$c = -0.5761$				
	$d = -5.8967$				
C7,C8,C9,C10, C11,C12	$a = -0.2370$			3	7
	$b = 0.7856$				
	$c = -0.5715$				
	$d = 2.7537$				

[a] The reference system used is described by D. A. Blow, *Acta. Crystallogr.*, **13**, 168 (1960).

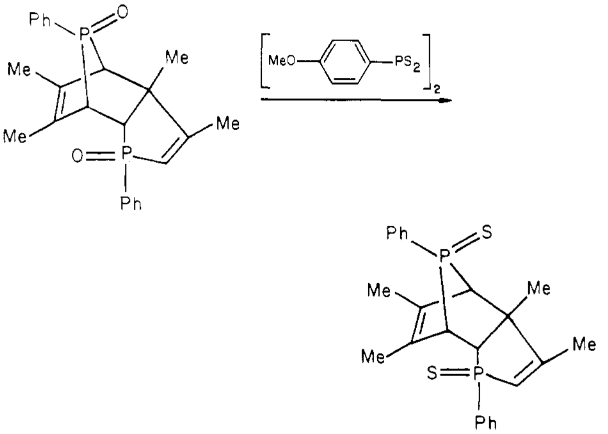
plexation takes place leading to the exo dimeric sulfide **13** (eq 4). In order to compare this exo dimer with the corresponding



(4)

exo dimer **13** (yield 66%)

endo dimer we reacted the dimeric oxide of **1a**[18] (which was assumed to have the normal endo structure) with a smooth reagent introduced by Pedersen et al.[19] for the C=O → C=S conversion. The O → S exchange took place and we obtained the original[20] endo dimeric sulfide **14**, which was indeed sharply different from **13** (eq 5). The first striking difference between **13** and **14** was



(5)

endo dimer
14 (yield 78%)

observed on their ^{31}P NMR spectra (for the notations, see Figure 1): **13**, δP1 52.4 ppm, δP2 87.6 ppm, ^3J(P1–P2) ~ 0 Hz (CDCl$_3$); **14**, δP1 57.6 ppm, δP2 103.8 ppm, ^3J(P1–P2) = 45 Hz (CDCl$_3$). The very large ^3J(P1–P2) coupling constant in **14** (which has been already stressed as a characteristic feature of endo phosphole dimers[9]) probably has a conformational origin. Indeed, if we assume that our own structural data on complex **6a** and those of Chiu and Lipscomb[2] on their dimeric phosphole ester are representative of the structures of **13** and **14**, we calculate dihedral P1–C16–C17–P2 angles of 56° for **13** and 163° for **14**. It is very tempting to assume that there is a Karplus-like relationship between ^3J(P–C–C–P) coupling constants and the corresponding dihedral angles with a minimum around 90° and a maximum around 180° and thus to explain the data obtained for **13** and **14**. Notable features are also observed on the ^{1}H NMR spectra (see Experimental Section).

Even though the spectrum of **13** is less well resolved than that of **14**, some characteristic differences appear. The huge ^3J(H–C16–C17–P2) coupling observed in **6a** and **13** disappears in **14**. Indeed the calculation of the corresponding dihedral angle in **14** on the basis of the data of Chiu and Lipscomb[2,21] yields a value of 101°, close to the minimum of the Karplus-like curve of Benezra.[8a] From another standpoint the high shielding of HC16 in **13** probably indicates that this proton is cis to the P1–Ph bond and thus shielded by the phenyl ring. This means that the Mo → S exchange when converting **6a** into **13** takes place with retention of configuration at phosphorus. Conversely HC16 is probably trans to the P1–Ph bond in **14**. Finally the five-bond coupling of the olefinic proton with P2 in **14** is noteworthy but we have no explanation for it.

As indicated in the second part of the Discussion the strain at the P2 bridge in **13** has some interesting chemical consequences. Whereas **14** does not decompose even when heated at 200 °C in the presence of sulfur, **13** decomposes at much lower temperature to yield phenylphosphinidene sulfide and a dihydrophosphindole derivative. Two experiments demonstrate this assumption. First, by treating complex **6a** with sulfur in boiling toluene, dihydrophosphindole **15** is directly obtained in good yield (eq 6). Second, when heating **13** with an excess of 2,3-dimethylbuta-1,3-diene in

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(18) F. Mathey and R. Mankowski-Favelier, *Bull. Soc. Chim. Fr.*, 4433 (1970).

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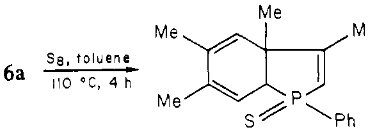
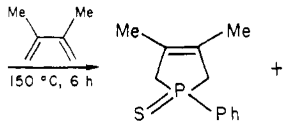
(20) Whereas the oxidation of **1a** yields directly the dimeric *P*-oxide, the sulfuration of **1a** (by S$_8$ in boiling benzene) yields only the monomeric *P*-sulfide (see ref 18), which does not dimerize to any great extent even in boiling xylene. Thus up to now even the normal endo dimeric *P*-sulfide of **1a** was unknown.

(21) We assume that HC16 is perpendicular to the P1–C15–C17 plane (HC9 perpendicular to P2–C10–C12 with the notations of Chiu and Lipscomb).

6a  (6)

15 (yield 70%)

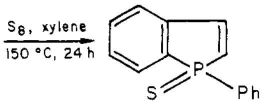
a sealed tube at 150 °C, 1-phenyl-3,4-dimethylphosphol-3-ene sulfide (**16**) is obtained in fair yield besides **15** (eq 7). This last

13  + 15 (yield 90%) (7)

16 (yield 50%)

observation must be compared with the results obtained by Nakayama et al.[22] when reacting dimethylbutadiene with $PhP(S)Cl_2$ and magnesium. Instead of obtaining **16** they obtained a six-membered ring with a P–S–C bond. Thus our data cast a great doubt upon the postulated intermediacy of phenylphosphinidene sulfide in the experiments of the Japanese chemists. Some objections against this intermediacy have been already raised by Schmidt[23] in his review on phosphinidenes.

The results obtained when starting from complex **6a** are paralleled by those obtained when starting from complex **12**. Indeed, whereas dimeric 1-phenylphosphole sulfide[24] when heated at 250 °C yields only minor amounts (less than 10%) of 1-phenylphosphindole sulfide (**17**), on the contrary complex 12 reacts with sulfur in boiling xylene to give **17** in fair yield (eq 8). This route

12  (8)

17 (yield 55%)

to C-unsubstituted phosphindoles is probably simpler than the ones previously known[25] and, even though based on the same principle (extrusion of the phosphorus bridge of a phosphole dimer), gives a better overall yield of **17** than the method of Hughes et al.[4] Finally, it must be stressed that obtaining phosphindole **17** requires a rearrangement of the [2 + 2] dimer **12** into the corresponding [4 + 2] dimer. This rearrangement necessarily takes place within the coordination sphere of molybdenum since only exo and not endo dimers are able to generate **17** at 150 °C. Thus the thermal [2 + 2] → [4 + 2] dimer rearrangement postulated in the first part of the Discussion becomes very likely.

Experimental Section

General. NMR spectra [chemical shifts in parts per million from internal Me_4Si for ^1H and ^{13}C and from H_3PO_4 (external reference) for ^{31}P; δ is positive for downfield shifts in all cases] were recorded for the proton on a Perkin-Elmer R12 at 60 MHz and a JEOL PS 100Ft at 100 MHz, and for the phosphorus and the carbon on a Brucker WH-90 at 36.447 and 22.63 MHz, respectively; mass spectra were recorded on a MS30AEI spectrometer at 70 eV. Elemental analyses were performed by Service de Microanalyse de l'Ircha (Vert le Petit). All reactions and manipulations were carried out under argon atmosphere. Tetrahydrofuran (THF) was freshly distilled from sodium-benzophenone. Chromatographic separations were performed on silica gel columns (70–230 mesh, Merck). Irradation was performed with a medium-pressure mercury burner (Hanovia). 1-Phenyl-3,4-dimethylphosphole (DMP), 1-phenylphosphole (PP), 1-*tert*-butyl-3,4-dimethylphosphole (TBP), and 1,3,4-trimethylphosphole (TMP) were synthesized according to the literature.[16,26]

General Procedure. $M(CO)_6$ (10^{-2} mol) and phosphole (10^{-2} mol) were stirred together for 20 h in THF (250 mL) under irradiation and a stream of argon, at room temperature. The solvent was removed under vacuum and the residue was chromatographed with benzene–hexane (30:70). Monosubstituted phosphole complexes were eluted first (R_f 0.8) and then dimeric phosphole complexes (R_f 0.3–0.4). The latter complexes were further purified by recrystallization from benzene–methanol (4:1).

Reaction of $Cr(CO)_6$ with 1-Phenyl-3,4-dimethylphosphole. [1-Phenyl-3,4-dimethylphosphole]pentacarbonylchromium (2a) was a yellow solid, yield 53%, mp 79–80 °C. Anal. Calcd for $C_{17}H_{13}CrO_5P$: C, 53.69; H, 3.44. Found: C, 53.68; H, 3.47, IR: ν(CO) 2060 m, 1980 vw, 1946 s, 1938 s. Mass spectrum (100 °C): *m/e* 380 (10%, M), 240 (100%, $C_{12}H_{12}CrP$). ^1H NMR: 2.05 (s, CH_3), 6.5 ppm (d, J(HP) = 36 Hz, =CH). ^{31}P NMR: 48.8 ppm.

***cis*-Bis[1-phenyl-3,4-dimethylphosphole]tetracarbonylchromium (8a)** was a pale yellow solid (R_f 0.5), yield ~20%, mp 110 °C. IR: ν(CO) 2005 m, 1920 s, 1901 s cm^{-1}. ^1H NMR: 1.93 (s, CH_3), 6.15 ppm (d, J(HP) = 34 Hz, =CH). ^{31}P NMR: 51.5 ppm.

[Dimeric (1-phenyl-3,4-dimethylphosphole]tetracarbonylchromium (5a) was a pale yellow solid (R_f 0.4), yield 35%, mp 253 °C. Anal. Calcd for $C_{28}H_{26}CrO_4P_2$: C, 62.22; H, 4.85. Found: C, 61.98; H, 4.92. IR: ν(CO) 1999 s, 1908 s, 1873 vs, shoulder at 1915 cm^{-1}. Mass spectrum (200 °C): *m/e* 540 (13%, M), 426 (100%, $C_{24}H_{26}CrP_2$). ^1H NMR: 1:13 (s, 3 H, CH_3), 1.72 (s, 3 H, CH_3), 1.77 (s, 3 H, CH_3), 2.52 (s, 3 H, CH_3), 5.84 ppm (d, J(HP) = 32.8 Hz, 1 H, =CH). ^{31}P NMR: 192.6 (P_2), 76.8 (P_1) ppm, ^2J(PP) = 30 Hz.

Reaction of $Mo(CO)_6$ with 1-Phenyl-3,4-dimethylphosphole. [1-Phenyl-3,4-dimethylphosphole]pentacarbonylmolybdenum (3a) was a pale yellow solid, yield 15%, mp 91.5–92 °C. Anal. Calcd for $C_{17}H_{13}MoO_5P$: C, 48.13; H, 3.08. Found: C, 48.33; H, 2.93. IR: ν(CO) 2060 m, 1980–1970 sh m, 1945 s cm^{-1}. Mass spectrum (^{98}Mo, 110 °C): *m/e* 426 (21%, M), 286 (100%, $C_{12}H_{13}MoP$). ^1H NMR: 2.0 (s, CH_3), 6.2 ppm (d, J(HP) = 35.5 Hz, =CH). ^{31}P NMR: 27.2 ppm.

[Dimeric (1-phenyl-3,4-dimethylphosphole)]tetracarbonylmolybdenum (6a) was obtained as yellow crystals, yield 45%, mp 170 °C. Anal. Calcd for $C_{28}H_{26}MoO_4P_2$: C, 57.54; H, 4.48. Found: C, 57.18; H, 4.41. $^1H\{^{31}P\}$ NMR (100 MHz) (notations as in Figure 1): δ 1.20 (s, 3 H, Me), 1.51 (s, 3 H, Me), 1.55 (s, 3 H, Me), 2.0 (s, 3 H, Me), 2.64 (ddd, ^2J(H–P1) = 6.35, ^3J(H–P2) = 41.4, ^3J[H(C16)–H(C17)] = 3.19 Hz, 1 H, HC16), 2.68 (dd, ^2J(H–P2) = 5.83, ^4J[H(C20)–H(C17)] = 1.9 Hz, 1 H, HC20), 3.01 (ddd, ^2J(H–P2) = 2.2 Hz, 1 H, HC17), 6.23 (d, ^2J(H–P1) = 34.3 Hz, 1 H, =CH), 7.35, 7.5, 7.66, 7.77 (m, 10 H, Ph) ppm. ^{31}P NMR: 159.8 (P2), 52.6 ppm (P1), ^2J(PP) ≃ 10 Hz. Mass spectrum (^{98}Mo, 120 °C): *m/e* 586 (20%, M), 474 (100%, $C_{25}H_{26}MoP_2$). IR: ν(CO) 2007 m, 1915 s, 1875 vs, shoulders at 1921 and 1887 cm^{-1}.

Reaction of $Mo(CO)_6$ with 1,3,4-Trimethylphosphole. [1,3,4-Trimethylphosphole]pentacarbonylmolybdenum (3b) was contaminated by traces of free TMP. IR: ν(CO) 2070 m, 2020 vw, 1987 m, 1945 s, 1900 m cm^{-1}. Mass spectrum (^{98}Mo, 100 °C): *m/e* 364 (M). ^1H NMR: 1.47 (d, J(HP) = 10 Hz, Me–P), 2.03 (s, Me–C), 6.25 ppm (d, J(HP) = 37 Hz, =CH). ^{31}P NMR: 10.5 ppm.

[Dimeric (1,3,4-trimethylphosphole)]tetracarbonylmolybdenum (6b) was obtained as translucid, pale yellow crystals, yield 50%, mp 168 °C dec. Anal. Calcd for $C_{18}H_{22}MoO_4P_2$: C, 46.97; H, 4.82; P, 13.46. Found: C, 46.78; H, 4.61; P, 13.31. IR= ν(CO) 2015 m, 1946 s, 1903 vs, 1853 s, shoulder at 1926 cm^{-1}. Mass spectrum (^{98}MO, 170 °C): *m/e* 462 (1%, M), 191 (100%, $C_{12}H_{16}P$). ^1H NMR: 1.07 (s, 3 H, Me), 1.60 (d, J(HP) = 7.9 Hz, 3 H, CH_3P), 1.62 (d, J(PH) = 5.28 Hz, 3 H, CH_3P), 1.78 (s, 6 H, Me), 1.80 (s, 3 H, Me), 6.10 (d, J(HP) = 35.1 Hz, H, =CH). ^{31}P NMR: 139.2 (P2), 35.6 ppm (P1), ^2J(PP) ≃ 12 Hz.

Reaction of $Mo(CO)_6$ with 1-*tert*-Butyl-3,4-dimethylphosphole. [1-*tert*-Butyl-3,4-dimethylphosphole]pentacarbonylmolybdenum (3c) was not isolated in pure form (traces of free TBP), yield (NMR) ~12%. IR: ν(CO) 2067 w, 1985 vw, 1947 sh, 1945 s cm^{-1}. Mass spectrum (^{98}Mo, 180 °C): 406 (M). ^1H NMR: 0.9 (d, J(HP) = 15 Hz, *t*BuP), 1.55 (s, Me), 5.7 ppm (d, J(HP) = 34.5 Hz, = CH). ^{31}P NMR: 51.8 ppm.

[Dimeric (1-*tert*-butyl-3,4-dimethylphosphole)]tetracarbonylmolybdenum (6c) was obtained as yellow crystals, yield 33%, dec 178 °C (without melting). Anal. Calcd for $C_{24}H_{34}MoO_4P_2$: C, 52.95; H, 6.29; P, 11.38. Found: C, 52.66; H, 6.15; P, 11.21. IR: ν(CO) 2005 m, 1885 s, 1853s, shoulder at 1895 cm^{-1}. Mass spectrum (^{98}Mo, 190 °C): *m/e* 518 (36%, M − CO), 279 (100%, $C_{16}H_{25}MoP_2$). ^1H NMR: 1.0 (s, 3 H, Me), 1.15 (d, J(HP) = 16 Hz, 9 H, *t*-Bu), 1.21 (d, J(HP) = 16 Hz, 9 H, *t*-Bu), 1.71 (s, 6 H, Me), 1.78 (m, 3 H, Me), 1.92–2.8 (m, 3 H, CH),

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5.92 ppm (d, *J*(HP) = 34 Hz, =CH). ^{31}P NMR: 164.6 (P2), 68 ppm (P1), ^2J(PP) ≃ 12 Hz.

Reaction of W(CO)$_6$ with 1-Phenyl-3,4-dimethylphosphole. [1-Phenyl-3,4-dimethylphosphole]pentacarbonyltungsten (4a) was a pale yellow solid, yield 39%, mp 101 °C. Anal. Calcd for $C_{17}H_{13}O_5PW$: C, 39.87; H, 2.55. Found: C, 40.01; H, 2.45. IR: ν(CO) 2067 m, 1970 w, 1942 vs, 1912 cm^{-1}. Mass spectrum (^{184}W, 100 °C): *m/e* 512 (40%, M), 372 (100%, $C_{12}H_{13}PW$). ^{1}H NMR: 2.06 (s, Me), 6.39 ppm (d, *J*(HP) = 36 Hz, =CH). ^{31}P NMR: 7.5 ppm.

[Dimeric (1-phenyl-3,4-dimethylphosphole)]tetracarbonyltungsten (7a) was obtained as yellow crystals, yield 36%, mp 200 °C. Anal. Calcd for $C_{28}H_{26}O_4P_2W$: C, 50.02; H, 3.89. Found: C, 48.94; H, 3.77. IR: ν(CO) 2005 m, 1905 s, 1865 s, shoulders at 1940 and 1925 cm^{-1}. Mass spectrum (^{184}W, 125 °C): *m/e* 672 (62%, M), 644 (100%, M − CO). ^{1}H NMR: 1.18 (s, 3 H, Me), 1.51 (s, 6 H, Me), 2.03 (s, 3 H, Me), 2.26 (m, 1 H, CH), 2.68 (m, 1 H, CH), 3.0 (m, 1 H, CH), 6.17 ppm (d, *J*(HP) = 32 Hz, =CH). ^{31}P NMR: 135 (P2), 31.2 ppm (P2), ^2J(PP) ≃ O Hz.

Reaction of Mo(CO)$_6$ with 1-Phenylphosphole. [1-Phenylphosphole]-pentacarbonylmolybdenum (11) was a yellow oil. IR: ν(CO) 2072 m, 1991 m, 1950 s cm^{-1}. Mass spectrum (^{98}Mo, 120 °C): *m/e* 398 (M). ^{31}P NMR: 37.81 ppm.

[Dimeric (1-phenylphosphole)]tetracarbonylmolybdenum (12) was obtained as pale yellow crystals, yield 46%, mp 212–213 °C. Anal. Calcd for $C_{24}H_{18}MoO_4P_2$: C, 54.56; H, 3.43. Found: C, 56.74; H, 3.47. IR: ν(CO) 2012 m, 1938 w, 1925 m, 1912 s, 1880 w sh, 1873 s cm^{-1}. ^{1}H{^{31}P} NMR (100 MHz): δ 3.12 (dm, *J*(HP) = 17.7 Hz, 2 H, saturated cyclic CH), 4.35 (m, ^3J(HH) = 8.5 Hz, coupling with signal at 3.12, 2 H, saturated cyclic CH), 6.15 (ABX system, ^3J(HP) = 25, ^3J(HH) = 7.64 Hz, 2 H, olefinic cyclic CβH), 6.37 (ABX system, ^2J(HP) = 34 Hz, 2 H, olefinic cyclic CαH), 7.36 (m, 6 H, Ph meta, para), 7.61 (m, 4 H, Ph ortho) ppm. ^{31}P NMR: δP 89 ppm. ^{13}C{^{1}H} NMR: δ 46.25 (d, ^1J(CP) = 19 Hz, saturated cyclic Cα), 53.37 (s, saturated cyclic Cβ), 128.2–132.2 (m, Ph and olefinic cyclic Cα), 140.2 (s, olefinic cyclic Cβ). Mass spectrum (^{98}Mo, 200 °C): *m/e* 530 (44%, M), 456 (100%, M − 3CO).

***cis*-[Bis(1-phenyl-3,4-dimethylphosphole)]tetracarbonylmolybdenum (9a).** *cis*-$[C_5H_{10}NH]_2Mo(CO)_4$ (1.9 g, 5 × 10^{-3} mol) and DMP (1.88 g, 10^{-2} mol) were stirred together for 1 h in refluxing dichloromethane. The product was separatted from starting material by chromatography with benzene–hexane (40:60) (R_f 0.6); 2.8 g (ρ = 95%) of bright yellow crystals were obtained, mp 98–99 °C. Anal. Calcd for $C_{28}H_{26}MoO_4P_2$: C, 57.54; H, 4.48. Found: C, 56.90; H, 4.29. IR: ν(CO) 2013 s, 1920 br s, 1877 br s cm^{-1}. Mass spectrum (^{98}Mo, 120 °C): *m/e* 586 (10%, M), 286 (100%, $C_{12}H_{13}MoP$). ^{1}H NMR: 1.97 (s, Me), 6.2 ppm (d, *J*(HP) = 35.5 Hz, =CH). ^{31}P NMR: 29.3 ppm.

[Dimeric (1-phenyl-3,4-dimethylphosphole)]tetetracarbonylmolybdenum (6a) from *cis*-Bis(1-phenyl-3,4-dimethylphosphole)tetracarbonylmolybdenum (9a). 9a (1 g, 1.7 × 10^{-3} mol) was stirred under irradation for 20 h in THF (250 mL). The solvent was removed under vacuum and the residue was dissolved in benzene filtered on silica gel. After evaporation the resulting yellow solid was recrystallized from benzene–methanol (1:4) at room temperature, yielding 0.5 g (~50%) of dimeric complex **6a**.

Exo-Dimeric (1-phenyl-3,4-dimethylphosphole sulfide) (13). A mixture of **6a** (2.2 g, 3.76 × 10^{-3} mol) and S_8 (1 g, 3.1 × 10^{-2} mol) in benzene (100 mL) was heated at 50 °C and stirred in argon atmosphere for 20 h. After cooling to room temperature, the black precipitate that formed was filtered and the solvent evaporated. The residue when chromatographed (eluant benzene–ethyl acetate, 95:5) gave **13** (1.1 g, 66.7%), mp 178 °C (MeOH). Anal. Calcd for $C_{24}H_{26}P_2S_2$: C, 65.43; H, 5.94. Found: C, 65.31; H, 5.95. Mass spectrum (200 °C): *m/e* 440 (7%, M), 300 (50%, $C_{18}H_{21}PS$), 285 (100%, $C_{17}H_{18}PS$), 140 (35%, C_6H_5PS). ^{1}H NMR: δ 1.26 (s, 3 H, Me), 1.47 (s, 3 H, Me), 1.53 (s, 3 H, Me), 2.19 (dm, ^3J(H–P2) ~ 30 Hz, 1 H, HC16), 2.30 (s, 3 H, Me), 3.04 (dd, ^2J(H–P2) = 2.8, ^4J|H(C20)–H(C17)| = 1.94 Hz, 1 H, HC20), 3.70 (m, 1 H, HC17), 5.90 (d, ^2J(H–P1) = 25.3 Hz, 1 H, =CH), 7.33, 7.48, 7.95 (m, 10 Ph).

Endo-Dimeric (1-Phenyl-3,4-dimethylphosphole sulfide) (14). A mixture of 1-phenyl-3,4-dimethylphosphole oxide (4.5 g, 1.10 × 10^{-2} mol) and (p-$MeOC_6H_4PS_2)_2$ (4.5 g, 1.02 × 10^{-2} mol) in toluene (200 mL) was heated at reflux with stirring and under argon atmosphere for 2 h. After cooling to room temperature, the solvent was evaporated. The chromatography (eluant benzene–ethyl acetate, 95:5) gave first a white solid (1.7 g) characterized as (p-$MeOC_6H_4POS)_3$ (R_f 0.7), then the sulfide (3.8 g, 78.3%) (R_f 0.2), mp 211 °C. Anal. Calcd for $C_{24}H_{26}P_2S_2$: C, 65.43; H, 5.94. Found: C, 64.89; H, 5.80. Mass spectrum (180 °C): *m/e* 440 (28%, M), 408 (52%, $C_{24}H_{26}P_2S$), 300 (71%, $C_{18}H_{21}PS$), 285 (100%, $C_{17}H_{18}PS$), 140 (10% C_6H_5PS). ^{1}H NMR: δ 1.45 (s, 3 H, Me), 1.79 (s, 3 H, Me), 1.93 (s, 3 H, Me), 2.0 (s, 3 H, Me), 3.01 (dd, ^2J(H–P2) = 4.5, ^4J|H(C20)–H(C17)| = 2.08 Hz, 1 H, HC20), 3.53 (m, *J*(H–P) = 2.43 and 5.28, ^3J|H(C17)–H(C16)| = 2.57 Hz, 1 H, HC17), 3.71 (m, *J*(H–P) = 2.37 and 4.65 Hz, 1 H, HC16), 5.76 (dd, ^2J(H–P1) = 26.8, ^5J(H–P2) = 5.5 Hz, 1 H, =CH), 7.37, 7.46, 7.85 (m, 10 H, Ph).

1-Phenyl-3,5,6,9-tetramethyl-8,9-dihydrophosphindole sulfide (15). A mixture of **6a** (0.8 g, 1.35 × 10^{-3} mol) and S_8 (0.3 g, 9 × 10^{-3} mol) in toluene (60 mL) was heated at reflux for 4 h. After cooling to room temperature the solvent was evaporated. The chromatography (eluant toluene–ethyl acetate 95:5) gave 0.25 g (70%) of **15**, mp 190 °C (ether). Mass spectrum (100 °C): *m/e* 300 (88%, M), 285 (100%, $C_{17}H_{18}PS$). ^{1}H NMR: 1.1 (s, 3 H, Me), 2.0 (m, 9 H, Me), 2.7 (dm, 1 H), 4.9, 5.06, 5.3 (3 m, 2 H), 5.8 ppm (dm, *J*(HP) = 25 Hz). ^{31}P NMR: 58.7 ppm. See ref 5 for the corresponding *P*-oxide.

1-Phenylphosphindole sulfide (17). A mixture of **12** (1.2 g, 2.2 × 10^{-3} mol) and S_8 (0.4 g, 1.25 × 10^{-2} mol) was stirred for 24 h in refluxing xylene. After evaporation the residue was chromatographed, yielding 0.3 g (55%) of **17** as colorless crystals, mp 81.7 °C (hexane). Anal. Calcd for $C_{14}H_{11}PS$: C, 69.54; H, 4.57. Found: C, 68.97; H, 4.52. Mass spectrum (100 °C): *m/e* 242 (100%, M). ^{1}H NMR: 6.35 ppm (dd, *J*(HP) = 29, *J*(HH) = 7 Hz). ^{31}P NMR: 45.6 ppm.

Reaction of 2,3-Dimethylbutadiene with Exo-Dimeric (1-Phenyl-3,4-dimethylphosphole sulfide). 13 (0.65 g, 1.47 × 10^{-3} mol) and 5 mL of 2,3-dimethyl-1,3-butadiene were heated at 150 °C for 6 h in a sealed tube. After evaporation of volatile materials, chromatography of the residue (eluant benzene) gave first 0.16 g (50%) of 1-phenyl-3,4-dimethylphospholene sulfide (**16**), identified by its ^{1}H NMR spectrum and its R_f, and then 0.44 g (90%) of **15**.

X-ray Data Collecting and Processing

Crystals of compound **6a**, $(C_{24}H_{26}P_2)Mo(CO)_4$ = L-L Mo(CO)$_4$, suitable for X-ray study were selected from the vessel containing the crude product. Preliminary crystal data of **6a** were obtained on a Philips PW1100/16[27] diffractometer by using Mo Kα filtered radiations and confirmed with precession photographs; crystals of **6a** are monoclinic. Precise lattice parameters were determined at 18 ± 2 °C on a Picker diffractometer by using 12 high-angle reflections with the method outlined by Busing and Levy.[28] Final results: a = 15.923 (3) Å, b = 10.398 (2) Å, c = 17.058 (3) Å, β = 104.43 (2)°, V = 2735 (2) Å^3. With four molecules of $MoP_2O_4C_{28}H_{26}$ per unit cell, ρ_{calcd} = 1.42 g cm^{-3} and ρ_{obsd}, measured by flotation in a aqueous KI solution, equals 1.42 ± 0.02 g cm^{-3}. The space group is $P2_1/c(C^5_{2h})$, F_{000} = 1192, μ = 6.21 cm^{-1}.

X-ray diffraction data were collected at room temperature by using a PDP8/A computer-controlled Picker FACS/1 diffractometer with graphite-monochromated Mo Kα radiation. The pulse height analyzer was set to admit about 95% of the Mo Kα peak. Whenever the counting rate exceeded 7000 counts s^{-1}, copper foils were inserted in the diffracted beam. The crystal used in data collection was cut to have a parallelepiped shape with dimensions × 0.30 × 0.30 × 0.15 ± 0.01 mm; then it was sealed in a thin-walled glass capillary and mounted on a rotation-free goniometer head.[29]

Data of all hkl, $hk\bar{l}$, and their equivalent $\bar{h}kl$ and $\bar{h}k\bar{l}$ were measured by using the $\theta/2\theta$ flying step scan method with a step time of 2 s and a scan angle of 1.9 + (Mo Kα_1 α_2 splitting)°. Each reflection was prescanned and measured only if $\sigma^2(I)/I$ was less than 5; 4752 reflections within 3° < θ < 30° were finally scanned.

Three reflections measured every 2 h during the entire data collection period showed no significant trend in intensity.

The step-scan data were converted to intensities and standard deviations by using the Lehman–Larsen algorithm, on a Univac 1110 computer,[30] then corrected for Lorentz and polarization factors; absorption factors were computed by using the numerical integration method of Busing and Levy.[31] The data were then

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(27) "Computer-Controlled Single-Crystal X-ray Diffractometer PW1100/16 Users Manual", N. V. Philips Gloeilampenfabrieken, Eindhoven, Holland, 1974, Section 4.

(28) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).

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stored and averaged by using program DSORTH;[32] 847 reflections were measured once and 1948 had more than one contributor to average ($R_1 = \sum \mathrm{Av}|I - \mathrm{Av}(I)|/\sum \mathrm{Av}|I| = 0.016$; $R_2 = \sum|wI\ w\mathrm{Av}(I)|/\sum wI| = 0.021$); 2677 independent reflections with $I > 3\sigma(I)$ were used to refine the structure.

The independent data set was then transferred to a PDP11/60 computer and the indices of unobserved reflections were generated. The structure was solved by using the Enraf-Nonius SDP/V16 package[33] and all nonhydrogen atoms were located in an E map.[34] Hydrogen atoms were introduced but not refined by their computed coordinates with a C–H distance of 0.95 Å and an isotropic thermal parameter of 7 Å^2.

Refinement converged to $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = ((\sum w|F_o| - |F_c|))^2/\sum wF_o^2)^{1/2} = 0.027$ and 0.041, respectively, refining all nonhydrogen atoms with anisotropic thermal parameters. The estimated standard deviation of a unit weight observation was 0.96 with a fudge factor of 0.08.

The final difference Fourier map showed no significant electron density above background.

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Supplementary Material Available: Contacts less than 3.2 Å (Table III), positional and thermal parameters of all nonhydrogen atoms (Tables IV and V), and *hkl*, F_o, and F_c times 10 for all observed structure factors (Table VI) (16 pages). Ordering information is given on any current masthead page.

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Resonance Raman Spectra of Nitrosyl Heme Proteins and of Porphyrin Analogues[1]

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Abstract: Addition of inositol hexaphosphate (IHP) to nitrosylhemoglobin (NOHb) produces a new resonance Raman (RR) band at 592 cm^{-1}, identifiable with Fe–NO stretching via its ^{15}NO shift, in addition to the 553-cm^{-1} Fe–NO band observed without IHP. This observation supports previous evidence that the R → T switch induces the Fe–imidazole bonds of half the NOHb heme groups to break. The high-frequency RR spectra are similar to those reported by Szabo and Barron,[2] although slight additional shifts on IHP binding are observed. A series of analogue heme complexes have been studied and the RR spectra effects of NO, CO, imidazole, and imidazolate are analyzed in terms of π back-bonding and trans labilization. The IHP-induced shifts in NOHb are consistent with Fe–imidazole bond breaking, but additional protein influences are apparent. An alternate hypothesis, that the R → T shift in NOHb involves protonation of bound imidazolate, is not supported by the RR spectra.

Introduction

In recent studies of hemoglobin (Hb) allostery, nitrosyl (NO) Hb has played a central role because of the large changes in heme electronic properties induced by the binding of organic phosphates which alter the protein quaternary structure.[3,4] While other forms of Hb, such as high-spin derivatives of metHbA[5] or ligated forms of Hb Kansas[6] or carp Hb,[7] are also switched from the R to the T quatenary structure on addition of phosphate effectors, NOHb is the only one to show marked alterations in the spectral signatures of the heme group.[2-5,8-10] These have been interpreted as resulting from a weakening or breaking of the bond between the iron atom and the proximal imidazole ligand of two of the four Hb chains, presumably the α chains, in the T quaternary structure.[4,10] Because its odd electron is partially transferred to the iron d_{z^2} orbital, the NO ligand is strongly trans labilizing; the trans axial bond is quite long in six-coordinate nitrosyl adducts of iron tetraphenylporphine,[11a] and the five-coordinate adduct, without a trans axial ligand, is readily formed and crystallized.[11b] This weakness of the trans axial bond apparently renders it susceptible to further weakening, or breaking, under the constraints of the T quaternary structure of NOHb, although only in half the chains. The most direct evidence in support of this view is the observation of two NO stretching frequencies in the infrared spectrum of T-state NOHb,[10] attributable to five- and six-coordinate NO heme, and also the superposition of three- and nine-line electron spin resonance spectra, characteristic of five-coordinate NO heme and of six-coordinate NO heme with nitrogenous sixth ligands.[12] Hille et al.[13] have recently analyzed NOHb ESR spectra as a function

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