Table IV. Selected Best Planes through Groups of Atoms in the Molecule[a]

	A	*B*	*C*	*D*	δ
plane 1 (Pt, Cl(1), Cl(2), P(1), P(2))[Pt (0.031), Cl(1) (0.500), Cl(2) (−0.511), P(1) (0.403), P(2) (−0.424)]	−0.6732	0.4664	0.5738	1.9710	0.413
plane 2 (C(1.1)–C(6.1))[P(1) (−0.188), C(1.1) (−0.004), C(2.1) (0.003), C(3.1) (−0.010), C(4.1) (0.018), C(5.1) (−0.021), C(6.1) (0.014)]	0.9230	−0.1795	0.3405	1.8133	0.013
plane 3 (C(1.2)–C(6.2))[P(2) (0.033), C(1.2) (−0.009), C(2.2) (−0.003), C(3.2) (0.009), C(4.2) (−0.003), C(5.2) (−0.009), C(6.2) (0.015)]	0.7124	0.3256	0.62163	7.0415	0.009

[a] The equations are in the form $Ax + By + Cz = D$, where x, y, and z are orthogonal coordinates. δ is the mean square displacement (in Å). Deviations of the relevant atoms from the plane are given in square brackets.

Table V. List of the Shortest Packing Distances (in Å) Based on Atomic Radii (1.80 for Aromatic Carbons, 1.95 for Methyl Groups, 1.10 for Hydrogens, and 1.80 Å for Chlorines)[a]

C(8.1)	C(13.2)^{ii}	3.86
C(9.1)	C(9.2)^{i}	3.67*
C(4.1)	C(14.2)^{vi}	3.55*
C(3.2)	C(3.2)^{iv}	3.59
C(3.2)	C(4.2)^{iv}	3.55
H(3.1)	Cl(2)^{i}	2.80
H(5.1)	C(13.1)^{v}	2.74*
H(3.2)	C(13.2)^{ii}	2.96
H(3.1)	H(5.2)^{iii}	2.11

[a] The packing operators indicated are as follows: i = $-x, y - {}^1/_2, {}^1/_2 - z$; ii = $1 - x, y - {}^1/_2, {}^1/_2 - z$; iii = $-x, -y, 1 - z$; iv = $1 - x, -y, 1 - z$; v = $x, {}^1/_2 - y, z - {}^1/_2$; vi = $x - 1, y, z$.

from 3.20 to 3.26 Å, are present.

The cis structure of the present compound with the P–M–P angle of 107.3° seems to indicate a certain ability of the bulky $P(t\text{-}Bu)_2Ph$ ligands to coordinate on a metal atom, meshing the protrusions of a molecule with the hollows of another and achieving a P–M–P angle smaller than Tolman's cone aperture. A variable-aperture cone model (see ref 2 and 15) appears to us a more effective model for describing the phosphine behavior.

In Figure 2 the shape of the two cones of the present case is depicted by means of a polar diagram as suggested by Smith.[16] The two cones are oriented like the phosphines in the complex, and the centers are separated by 107.3°, i.e., the actual P–M–P angle. It is evident that the actual orientation of the cones allows a very moderate cone overlap and explains the stability of the *cis*-$PtCl_2L_2$ complex.

This kind of representation is also useful for understanding the stability of PtL_3 complexes. In order that a given ML_3 complex be stable, it is necessary that each of the three cones be drawn near adjacent cones with little or no mutual overlap. Figure 3 (top) shows this representation for the C_3 symmetrical $Pt(P(c\text{-}Hx)_3)_3$ complex[17] (c-Hx = cyclohexyl). It is interesting to consider the possibility that the inability to synthesize $Pt(P(t\text{-}Bu)_2Ph)_3$[3] corresponds to the difficulty of finding some cone orientation with acceptable overlap. Among the numerous trials, using both the ligand conformation observed in the present case and C_3 symmetry, one of the more acceptable solutions is shown in Figure 3 (bottom).

Conclusions

The steric behavior of tertiary phosphines in coordination complexes seems to be predictable on the basis of their variable-aperture cone models. The case of $PtCl_2(P(t\text{-}Bu)_2Ph)_2$ demonstrates the importance of considering the irregular cone as a whole with its protrusions and hollows. Tolman's cone angle θ and Immirzi and Musco's solid angles Ω are only overall measures which ought to be considered with caution. As a matter of fact, Ω values seem to be more meaningful than θ ones in most cases (see ref 2). In the current case, for instance, while θ values are much greater than ${}^1/_3(360°)$ for both the phosphines (170° in both cases), the Ω angle can achieve values $< {}^1/_3(4\pi)$ for $P(c\text{-}Hx)_3$ (4.18 rad in $Pt(P(c\text{-}Hx)_3)_3$[17]), whereas it is never less than 4.51 rad for $P(t\text{-}Bu)_2Ph$ (observed for P(2) phosphine in our case).

Registry No. *cis*-$PtCl_2(P(t\text{-}Bu)_2Ph)_2$, 73889-59-5.

Supplementary Material Available: A list of the observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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Chloro[*cis*-2,10-diphenyl-2,10-diphospha-κ²*P*-6-thia-κ*S*-bicyclo[9.4.0]pentadeca-11(1),12,14-triene]copper. Synthesis and Structure[1]

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Received January 16, 1980

The title complex was synthesized by reaction of the tridentate 11-membered macrocycle *cis*-2,10-diphenyl-2,10-diphospha-6-thiabicyclo[9.4.0]pentadeca-11(1),12,14-triene and either $CuCl_2$ under reducing conditions or CuCl. Spectroscopic (IR, ^1H, ^{31}P, ^{13}C NMR) properties are reported. Crystal structure data: $a = 15.746$ (2) Å, $b = 9.288$ (1) Å, $c = 18.476$ (2) Å, $\beta = 123.43$ (1)°, $R = 0.038$, $R_w = 0.054$, 3874 reflections with $I > 3.0\sigma_I$. X-ray data were collected at −35 °C on a Syntex $P2_1$ autodiffractometer with monochromated Mo Kα radiation. Triligation of the macrocycle to CuCl results in a tetrahedral complex in which the Cu–P (2.236 (1), 2.248 (1) Å) and Cu–Cl (2.249 (1) Å) are shorter and the Cu–S bond (2.378 (1) Å) is longer than usually observed in comparable Cu(I) complexes.

Tertiary phosphine complexes of Cu(I) have received considerable attention recently and are rich in stoichiometrical variety of the type $(R_3P)_nCu_mX_m$ (n = 1–4; m = 1, 2; X = halogen).[2] Of particular interest to us have been the mo-

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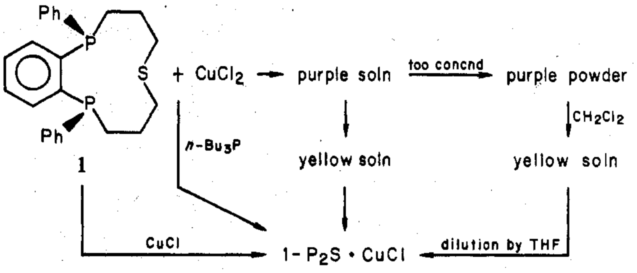
nomeric, tetracoordinate poly(tertiary phosphine)copper(I) species, of which there have been several structural determinations. Structures of the type $(Ph_3P)_2Cu(\overset{\frown}{L\,L}^-)$ where $\overset{\frown}{L\,L}^-$ is BH_4^-,[3] $B_3H_8^-$,[4] $(B_{10}H_{10}^{-2})_{1/2}$,[5] NO_3^-,[6] and $CF_3COCHCOCH_3^-$[7] exhibit P–Cu–P angles in the range 120–131°, rather large for a pseudotetrahedral bonding arrangement. Such large angles are also present in several dimeric structures where the $\overset{\frown}{Cu\,Cu}$ ring size should have little effect on such angles. Thus $[(Ph_3P)CuN_3]_2$ and $[(Ph_3P)_2Cu(BH_3CN)]_2$ feature average P–Cu–P angles of ca. 122°[8a] and 124°,[8b] respectively. Indeed, of the five cases studied in which three tertiary phosphines and a monodentate anion are bonded to Cu(I),[9] all but one structure, $(Ph_3P)_3CuCl$,[9b] had average P–Cu–P bond angles significantly greater than tetrahedral. Although an attempt has been made to rationalize observed P–Cu–P bond angles and P–Cu bond lengths in terms of s character in the Cu hybrid orbitals,[7b] more recent considerations indicate that the steric bulk and basicity of the phosphine ligand as well as the basicity of the negatively charged ligand may be crucial in determining these bond angles and lengths.[2c]

Results and Discussion

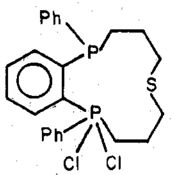
Addition at room temperature of cupric chloride dihydrate (1 equiv) in 95% ethanol to macrocycle 11-P_2S (**1**, 1 equiv)[10] in tetrahydrofuran (THF) gave rise to a deep purple solution which decolorized to a yellow solution over about 20 min (eq 1). Within an hour, deposition of crystals of complex **2** began, to give ultimately about a 45% yield of analytically pure material. This complex could be obtained in 68% yield by pretreatment of the $CuCl_2$ solution with 0.5 equiv of tributylphosphine, followed by addition of a solution of **1**. Good yields of **2** could be realized also by the addition of solid CuCl[11] to a dichloromethane solution of **1**, whereupon it dissolved in ca. 2–3 min to give a light yellow solution. Treatment of this solution with 3 volumes of THF and slow evaporation gave crystalline **2** in 55% yield.



The coordinated phosphines in **2** exhibit a ^{31}P NMR chemical shift only slightly deshielded relative to the free ligand [δ_P(coord) − δ_P(free) = −23.9 − (−29.4) = 5.5], typical of such Cu(I) species.[12] Although the ^1H NMR spectrum was not particularly informative, the ^{13}C NMR spectrum featured, in addition to absorptions in the range of 144–128 ppm due to aromatic carbon atoms, absorptions at δ 37.3 (broadened singlet), 27.3 (triplet, J = 8.1 Hz), and 24.1 (broadened singlet), due to the methylene carbon atoms. The corresponding chemical shifts in the free ligand[10b] were 32.4 (triplet, J = 5 Hz), 27.4 (triplet, J = 5 Hz), and 27.1 (triplet, J = 9 Hz). Thus it is apparent that coordination of this macrocyclic ligand to Cu(I) results in both deshielding and shielding effects on the carbon atoms, as well as strongly affecting the coupling constants between the phosphorus and carbon atoms.[13]

If the solutions of **1** and Cu(II) (eq 1) are too concentrated, or if the addition of the salt to **1** is too rapid, a deep purple powder is precipitated. This material has not been investigated beyond establishing that it is diamagnetic (Faraday balance)[14] and that treatment with dichloromethane results in a yellow solution which deposits **2** upon addition of 3 volumes of THF and slow evaporation of the solution. The purple color observed by us may be analogous to that reported in the reaction of triethylphosphine and $CuCl_2$ at low temperature, where it was suggested that the color was due to transient copper(II)–phosphine complex.[15] Since our material is diamagnetic, it may be this species is a dimer exhibiting antiferromagnetic properties at ambient temperature, such as that recently observed by Weiss and co-workers.[16]

The chemistry associated with the reaction of **1** and $CuCl_2$ is well-known.[15,17] Thus **1** apparently functions as a reducing agent to produce Cu(I) and is oxidized, presumably to a species such as **3**,[15,17c] which might be expected to react further with water ultimately to give **4**. No attempt was made to isolate any oxidation products of the macrocycle.



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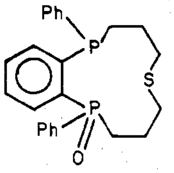

4

The molecular geometry is depicted in the two stereoscopic drawings of Figure 1 and described by the bond lengths and angles in Figure 2. Triligation of the macrocycle results in a tricyclic system consisting of two six-membered rings and one five-membered ring fused with the Cu atom in common.

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(9) (a) $(Ph_3P)_3CuBF_4$: ref 1b. (b) $(Ph_3P)_3CuCl$ and $(Ph_2PMe)_3CuCl$: ref 2c. (c) $(Ph_3P)_2Cu(NO_3)$: Mathew, M.; Palenik, G. J.; Carty, A. J. *Can J. Chem.* **1971**, *49*, 4119. (d) $(Ph_2PMe)_3Cu(SPh)(SO_2)$: Eller, P. G.; Kubas, G. J. *J. Am. Chem. Soc.* **1977**, *99*, 4346.

(10) The trivial name 11-P_2S is more convenient than 2,10-diphenyl-2,10-diphospha-6-thiabicyclo[9.4.0]pentadeca-11(1),12,14-triene. See: (a) Kyba, E. P.; Hudson, C. W.; McPhaul, M. J.; John, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 8053; (b) Kyba, E. P.; John, A. M.; Brown, S. B.; Hudson, C. W.; McPhaul, M. J.; Harding, A.; Larsen, K.; Niedzwiecki, S.; Davis, R. E. *Ibid.* **1980**, *102*, 139.

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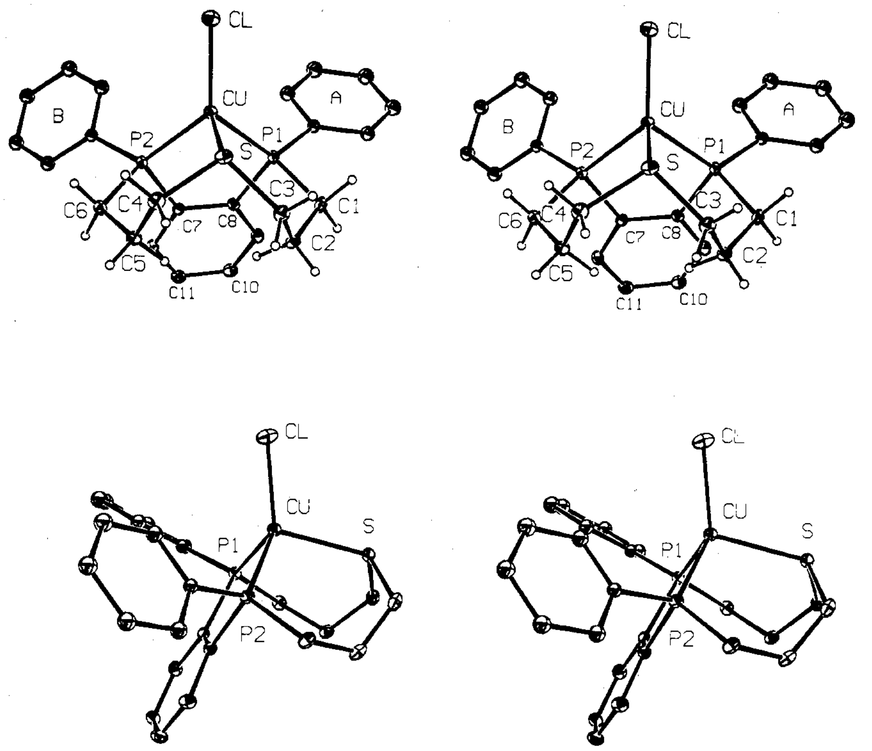

Figure 1. Stereoscopic drawings of molecular geometry of **2**, with atom numbering system used in the crystallographic study. Nonhydrogen atoms are shown as 30% equiprobability ellipsoids.

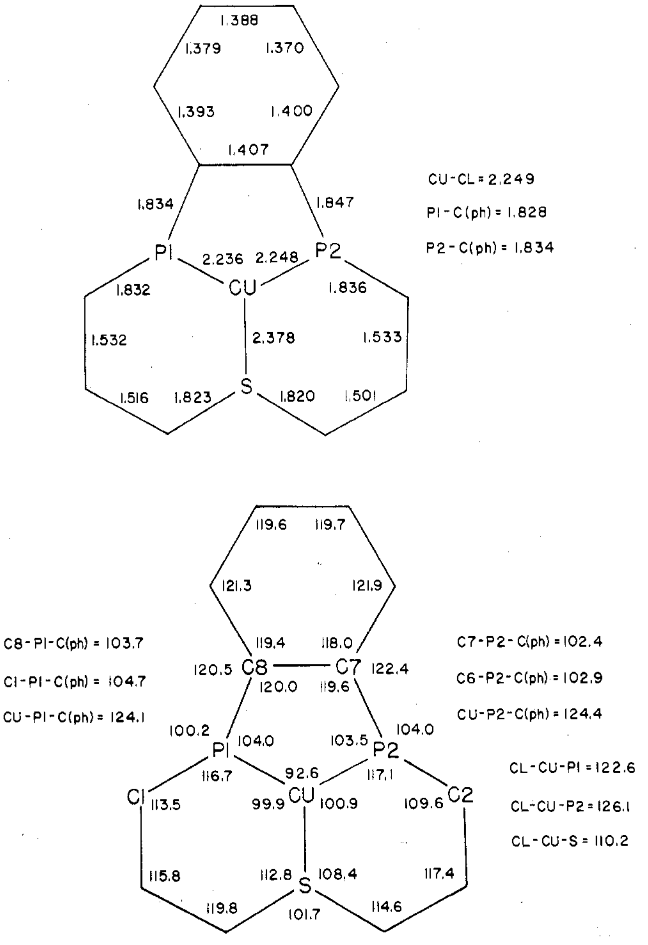

Figure 2. (Top) Bond lengths in **2**. Estimated standard deviation ranges (Å): Cu–P, 0.001; Cu–S, 0.001; P–C, 0.003–0.004; S–C, 0.004; C–C, 0.005–0.006. (Bottom) Bond angles in **2**. Estimated standard deviation ranges (deg) (where X = P or S): X–Cu–X, 0.1; Cu–X–C, 0.1; C–X–C, 0.1–0.2; C–C–X, 0.2–0.3; C–C–C, 0.2–0.4.

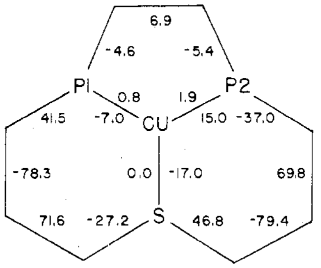

Figure 3. Bond torsion angles (deg) within the rings of the macrocycle–Cu complex system in **2**.

The conformation of this fused ring system is described by the bond torsion angles within each ring, presented in Figure 3. Construction of molecular models of this ring system suggests that a relatively strain-free symmetric conformation could exist in which the two six-membered rings each adopt a chair conformation. In such a model, however, the principal nonbonded contact between rings would be a close H–H contact between hydrogens on C2 and C5. The observed molecular conformation may be described as one in which this short H–H contact is alleviated by a skewing of the skeleton in such a fashion that one six-membered ring (the ring involving P2) can remain in a somewhat flattened chair while the other one (involving P1) flattens to a much greater degree. The differences in the geometries of these two rings can be seen in the torsion angles (Figure 3) and can also be discerned on careful inspection of Figure 1. The ring containing P1 is flattened to such an extent that the five atoms Cu, S, P1, C1, and C3 are coplanar to within ±0.08 Å, with C2 lying 0.70 Å out of this plane. The five-membered ring adopts a twist, rather than an envelope conformation (see Figure 3) but, somewhat surprisingly, with the largest torsion angle involving the two carbons which are part of the benzo bridge.

Comparison of bond lengths involving Cu with related structures reveals that all Cu bonds observed in this structure are near or beyond the previously observed ranges for comparable structures. Thus, Cu–P bonds are unusually short as is the Cu–Cl length, while the Cu–S bond is long.

In a comparison of Cu(I)–P(phosphine) bond lengths, Lippard et al.[2c] have observed that the Cu–P lengths are correlated primarily with the number and steric bulk of the phosphine ligands. Thus, in $[(C_6H_5)_3P]_3Cu$ complexes, Cu–P ranged from 2.280 to 2.355 Å, while the corresponding length in (diphenylmethylphosphine)copper complexes was somewhat shorter, viz., 2.282–2.294 Å in $[(C_6H_5)_2(CH_3)P]_3CuCl$, attributable by Lippard to the latter phosphine being both a smaller ligand and a stronger base. The corresponding distances in **2** are 2.236 (1) and 2.248 (1) Å. Along the lines of the rationale presented by Lippard et al., it could be concluded that this shortness of Cu–P bonds in **2** suggests that (1) since the two phosphine sites in **2** are linked by the benzo bridge, they are effectively smaller ligands, and (2) the phosphines in **2** may be acting as somewhat stronger bases than does diphenylmethylphosphine in its Cu(I) complexes. That the second factor may be somewhat more important is suggested by the observation of Cu–P lengths of 2.295 and 2.319 Å in the chelated diphos–Cu complex $(diphos)_3Cu_2(N_3)_2$[18a] and similar distances in the analogous $(diphos)_3Cu_2(NCS)_2$ complex.[18b] Since the ring P–Cu–P angles in the above two complexes and **2** are all within 2° of one another (~91°), the steric differences due to chelation must be small.

In a tabulation of representative Cu–Cl bond lengths, Lippard et al.[2c] have concluded that the primary factor which determines this length is the coordination number of Cu. From this summary, it is clear that when Cu coordination number is 4, Cu–Cl lengths lie generally in the range 2.3–2.53 Å. Thus, the value 2.249 Å observed in **2** is unusually short; indeed, it lies near the middle of the range determined by Lippard for the case when Cu coordination number is 3 (2.21–2.31 Å). In **2**, the stereochemical feature most clearly associated with this Cu–Cl length is the distribution of angles around Cu. Thus, the result of the P and S ligating sites being part of the macrocycle system is a pinning back of those ligands, with P–Cu–P bond angle of 92.6° and P–Cu–S angles 99.9 and 100.9°, so that these three average 97.8°, while the three angles involving chlorine (110.2, 126.1, 122.6°) average 119.6°. Thus, the short Cu–Cl bond lengths could be attributed either to (1) the decreased steric crowding of Cl by the other ligands or to (2) the increased s character in the Cu–Cl bond which would accompany closing of the P–Cu–P and P–Cu–S angles to significantly less than tetrahedral. The relative importance of these two effects cannot be ascertained in this structure.

The Cu–S length, 2.378 (1) Å, in **2** is longer than has been observed in any of the few thioether–Cu(I) complexes which have been studied. The range of Cu–S bond lengths in six diverse tetrahedral complexes which involve thioether–copper(I) species is 2.247–2.345 Å.[19] A possible rationale for the lengthening in **2** is that the skewing of the molecular framework described earlier causes the sulfur bonding orbital to point less directly toward the Cu atom, decreasing the effectiveness of the overlap, while the stronger basicity of the phosphine ligands demands that these not lose in bonding effectiveness.

Experimental Section

General Procedure. Melting points were obtained by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analysis was performed by Chemalytics, Inc., Tempe, Ariz.

Table I. Crystallographic Summary

A. Crystal Data at −35 °C[a]

$a = 15.746$ (2) Å	fw = 507.5
$b = 9.288$ (1) Å	$d_{calcd} = 1.494$ g/cm^3
$c = 18.476$ (2) Å	$d_{measd}{}^{b} = 1.480$ g/cm^3
$\beta = 123.43$ (1)°	$Z = 4$
$V = 2255$ Å^3	$F(000) = 1048$ e
cryst syst: monoclinic	
space group: $P2_1/c$ (No. 14)	

B. Collection at −35 °C and Processing of Intensity Data

Syntex $P2_1$ autodiffractometer equipped with graphite monochromator and Syntex LT-1 low-temperature gas (N_2) delivery system
radiation: Mo $K\bar{\alpha}$, $\lambda = 0.710\,69$ Å
mode: ω scan
scan range: 4–55°
bkgd: offset 1.0° and −1.0° in ω from $K\alpha_{1,2}$ maximum
scan rate: variable, 2–5 °/min
2θ range: 4–55°
reflctns measd: 5173
check reflctns: 4 reflections—$(\overline{25}\bar{2})$, (208), $(60\bar{2})$, and (040)—remeasured after every 96 reflections; analysis[c] of these data revealed a decay according to $1 - sx - tx^2$ with $s = 0.000\,49$ (6) and $t = 0.000\,001$ (1) over the 94 h of exposure time; the data were corrected accordingly with maximum relative correction factor 1.039
data cryst dimens: 0.42 × 0.30 × 0.34 mm
data cryst vol: 0.0570 mm^3
abs coeff, μ(Mo Kα): 13.6 cm^{-1}
transmission factor range: 0.60–0.68

[a] Unit cell parameters were obtained by least-squares refinement against the observed setting angles of 45 locally intense reflections with $26.5 < 2\theta < 28°$. [b] Flotation, *p*-xylene/1,1,2,2-tetrabromoethane. [c] Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B* 1975, *31*, 1511.

Infrared spectra (IR) were recorded on a Perkin-Elmer 237B grating spectrophotometer.

Proton magnetic resonance spectra (^1H NMR) were obtained on Perkin-Elmer R-12, Varian A-60, or Varian HA-100 instruments. Chemical shifts are given as parts per million (ppm) downfield from tetramethysilane in δ units, and coupling constants are reported in hertz. Multiplicities are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Carbon-13 and phosphorus-31 NMR were determined on a Bruker instrument at 22.6 and 36.4 MHz, respectively. Chemical shifts are given as parts per million (ppm) relative to Me_4Si for ^{13}C NMR and relative to 85% H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield from 85% H_3PO_4 are defined as negative for the ^{31}P spectra. The ^{13}C and ^{31}P NMR spectra are proton decoupled.

X-ray structure determination was performed on a Syntex $P2_1$ autodiffractometer.

Reaction of 1 with $CuCl_2 \cdot 2H_2O$ To Give Chloro[*cis*-2,10-diphenyl-2,10-diphospha-κ^2P-thia-κS-bicyclo[9.4.0]pentadeca-11(1),12,14-triene]copper (2).[20] Cupric chloride dihydrate (170.5 mg, 1.0 mmol) in 95% aqueous ethanol (10 mL) was added portionwise to 11-P_2S (**1**, 408 mg, 1.0 mmol) in THF (32 mL) at room temperature over a period of 10 min. Each addition resulted in the formation of a purple color which took longer to disappear upon successive additions. About 30 min after the last addition, the solution was clear and slightly yellow. After 1 h, crystallization began, giving **2** in 3 h as light yellow crystals, suitable for X-ray analysis (201 mg, 40%): mp 316–318 °C; IR (KBr pellet), medium to strong absorptions at 1485, 1440, 1418, 1207, 1000, 813, 763, 750, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8–7.3 (complex m, 14 H), 2.85 (m, 4 H), 2.31 (m, 6 H), 1.7 (structureless m, 2 H); ^{13}C NMR ($CDCl_3$) δ 144.1 (t, $^1J_{C-P} = 32.4$ Hz),[15] 134.7 (t, $^1J_{C-P} = 13.3$ Hz),[15] 132–128 (unassigned lines due to aromatic carbon atoms), 37.3 (slightly broadened s), 27.3 (t, $^1J_{C-P} = 8.1$ Hz),[15] 24.1 ppm (slightly broadened s), ^{31}P NMR ($CDCl_3$) δ (28 °C) −23.9 (broad s, peak width at half-height = 3.5 ppm), δ (−50°C) −24.9 (s,

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Table II. Fractional Coordinates (×10^4) and Anisotropic Thermal Parameters (×10^4) for Nongroup Nonhydrogen Atoms[a]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu[b]	15430 (3)	4468 (4)	19724 (2)	348 (2)	611 (5)	227 (2)	−3 (3)	156 (2)	7 (2)
P1[b]	19243 (6)	−2262 (8)	32811 (5)	318 (4)	585 (9)	211 (3)	37 (5)	159 (3)	−20 (4)
P2[b]	20937 (6)	−16460 (8)	17628 (5)	338 (5)	582 (9)	215 (3)	−53 (5)	167 (3)	−58 (4)
Cl[b]	18923 (8)	26575 (9)	17077 (6)	824 (7)	915 (10)	482 (4)	−279 (7)	409 (5)	−123 (5)
S[b]	−2450 (6)	538 (9)	11425 (5)	306 (4)	796 (10)	276 (3)	−32 (5)	121 (3)	63 (4)
C1	851 (3)	−630 (4)	3376 (2)	38 (2)	87 (4)	29 (1)	6 (2)	24 (1)	2 (2)
C2	1 (3)	−1485 (4)	2607 (2)	37 (2)	77 (4)	35 (2)	−9 (2)	25 (2)	−1 (2)
C3	−704 (2)	−624 (4)	1793 (2)	29 (2)	90 (4)	35 (2)	−1 (2)	19 (1)	0 (2)
C4	−528 (3)	−1447 (4)	410 (2)	35 (2)	118 (5)	27 (2)	−20 (3)	13 (2)	−9 (2)
C5	97 (3)	−2801 (4)	751 (2)	46 (2)	90 (4)	31 (2)	−31 (2)	23 (2)	−18 (2)
C6	1142 (3)	−2796 (4)	875 (2)	46 (2)	80 (4)	28 (1)	−15 (2)	22 (2)	−16 (2)
C7	2485 (2)	−2688 (3)	2750 (2)	27 (2)	58 (3)	24 (1)	−1 (2)	16 (1)	−2 (2)
C8	2468 (2)	−2032 (3)	3429 (2)	24 (2)	57 (3)	23 (1)	−3 (2)	12 (1)	−5 (2)
C9	2812 (2)	−2798 (4)	4190 (4)	37 (2)	83 (4)	20 (1)	−1 (2)	13 (1)	−4 (2)
C10	3168 (2)	−4188 (4)	4292 (2)	38 (2)	74 (4)	28 (1)	5 (2)	15 (1)	11 (2)
C11	3157 (3)	−4855 (4)	3615 (2)	48 (2)	61 (4)	42 (2)	10 (2)	29 (2)	7 (2)
C12	2823 (3)	−4114 (4)	2864 (2)	49 (2)	66 (4)	35 (2)	1 (2)	29 (2)	−7 (2)

[a] See Figure 1 for identity of the atoms. Numbers in parentheses are estimated standard deviations in the units of the last significant digit for the parameter. The temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] For Cu, P, Cl, and S atoms, values are presented ×10^5.

Table III. Rigid Group Parameters for Phenyl Rings[a]

ring	P atom	x_0	y_0	z_0	ϕ	θ	ρ
A	P1	0.2844 (1)	0.0704 (2)	0.4289 (1)	2.213 (2)	2.594 (1)	1.179 (2)
B	P2	0.3203 (1)	−0.1824 (2)	0.1686 (1)	1.495 (1)	−2.571 (1)	0.325 (2)

[a] A description of these group parameters is provided: Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* 1965, *4*, 77. Angular coordinates are in radians. The internal coordinate system of a phenyl ring has been defined: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* 1975, *31*, 2928.

peak width at half-height = 1.5 ppm).

Anal. Calcd for $C_{24}H_{26}ClCuP_2S$: C, 56.80; H, 5.16. Found: C, 56.70; H, 5.33.

Reaction of 1 with $CuCl_2{\cdot}2H_2O$/*n*-Bu_3P. Cupric chloride dihydrate (20.9 mg, 0.123 mmol) in 95% ethanol (1.5 mL) was added portionwise to tri-*n*-butylphosphine (12.3 mg, 0.061 mmol) in THF (2 mL). To this solution was added **1** (50.0 mg, 0.123 mmol) in THF (2 mL). The complex **2** precipitated within 0.5 h (42 mg, 68%).

Reaction of 1 with CuCl. Cuprous chloride[11] (7.3 mg, 0.074 mmol) was added in one portion to a solution of **1** (30.0 mg, 0.0735 mmol) in dichloromethane (2.5 mL). The solid dissolved in 1–2 min to give a yellow solution which was diluted with THF (7.5 mL). The resulting solution was allowed to evaporate to about 5 mL at which point the crystals which had formed were collected by filtration to give **2** (21 mg, 57%).

Crystallographic Study of 2. A large single crystal obtained from the reaction solution was cut, and an irregular fragment was selected and used for all X-ray experiments. This fragment could be described approximately in terms of seven bounding planes, of which only three—$(00\bar{1})$, $(11\bar{1})$, and $(\bar{1}\bar{1}1)$—could be clearly identified as rational crystal faces. Details of characterization of crystal data and of collection of intensity data are summarized in Table I. The measured intensities were reduced, corrected for absorption and for decay, and assigned standard deviations (with $p = 0.04$) as described elsewhere.[21]

The structure was solved by direct methods[22] and then refined by full-matrix least-squares methods, using the 3874 reflections with $I > 3.0\sigma_I$. The function minimized in refinement is $[\sum w(|F_o| - |F_c|)^2/(m - s)]^{1/2}$, where the weight w is $1/\sigma^2(|F_o|)$, the reciprocal square of the standard deviation of each observation, $|F_o|$. The conventional (R) and weighted (R_w) crystallographic agreement factors used to assess the structures are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, respectively. Neutral atom scattering factors for Cu, Cl, S, P, C,[23] and H[24] were used in these calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections[23] for anomalous dispersion were applied to the Cu, Cl, S, and P scattering curves.

Throughout the refinement, the phenyl rings were treated as rigid groups constrained with C–C = 1.392 Å, C–H = 1.00 Å, and all bond angles 120°, and with isotropic temperature factors for C varied individually while those for H were held fixed at 3.0 Å^2. Isotropic refinement omitting all H atoms reached convergence at $R = 0.069$ and $R_w = 0.097$; anisotropic convergence for the same atoms gave $R = 0.049$ and $R_w = 0.074$. At this stage, a difference density map contained peaks at all computed H positions,[25] so these were included in the refinement. Final convergence was attained with $R = 0.038$ and $R_w = 0.054$. In the final cycle of refinement, no parameter shifted by more than 22% of its esd. A final difference density map contained only very small peaks (<0.2 e/Å^3) near two carbons of rigid phenyl groups and near the quite anisotropic chlorine atom.

Final fractional crystallographic coordinates and anisotropic temperature factors for the nonhydrogen, nongroup atoms appear in Table II. . Rigid group parameters used to describe the phenyl rings are presented in Table III.

Observed and calculated structure factor amplitudes, final parameters for nongroup hydrogen atoms, and fractional crystallographic coordinates and temperature factors for the rigid group atoms appear in supplementary tables.[26]

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Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, coordinates and thermal parameters for H atoms, and derived fractional coordinates and thermal parameters for rigid group atoms (26 pages). Ordering information is given on any current masthead page.

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(25) Idealized hydrogen positions were generated by the use of the local program HIDEAL, written by R. C. Collins.

(26) Supplementary material.