Table I. Crystallographically Observed Torsion Angles for Tetrathioethers **1–3** and for Their Ni(II) Complexes[a]

	1	+Ni	**2**	+Ni	**3**	+Ni
S(1)–C(2)–C(3)–S(4)	−176	−61	58	−58	71	−60
C(2)–C(3)–S(4)–C(5)	−60	159	162	155	75	156
C(3)–S(4)–C(5)–C(6)	−62	−175	165	−178	−161	−178
S(4)–C(5)–C(6)–C(7)	178	71	−65	67	59	69
C(5)–C(6)–C(7)–S(8)	177	−72	−60	−68	59	−69
C(6)–C(7)–S(8)–C(9)	63	178	104	176	−156	177
C(7)–S(8)–C(9)–C(10)	67	−157	72	−155	−167	−156
S(8)–C(9)–C(10)–S(11)			173	59		
C(9)–C(10)–S(11)–C(12)			64	−156		
C(10)–S(11)–C(12)–C(13)			−99	177		
S(11)–C(12)–C(13)–C(14)			−168	−70		
C(12)–C(13)–C(14)–S(1)			−54	71		
C(13)–C(14)–S(1)–C(2)			−84	−177		
C(14)–S(1)–C(2)–C(3)			76	156		

[a] The data for compound **1** (α form) are taken from ref 6, and the data for **1**-Ni(II) are taken from ref 7. Because of crystallographic symmetry, the omitted torsion angles in the lower half of the table for **1**,**1**-Ni(II), **3**, and **3**-Ni(II) occur in the same sequence as those printed in the upper half, but with change of sign. The backbone atoms in all macrocycles are numbered according to IUPAC convention; thus, in **2** carbon 6 bears the *gem*-dimethyl pair, and in **3** carbons 6 and 13 bear *gem*-dimethyl pairs.

presently conducting experiments designed to distinguish between these possibilities.

Data from a number of laboratories suggest that macrocyclization, alone, is not a powerful strategy for preorganizing polythioether chelators.[8,9] Our results demonstrate that peripheral modifications of a chelating tetrathioether skeleton can produce significant increases in metal ion binding strength, if those modifications force the sulfur atoms to adopt endodentate positions even in the absence of the metal ion.

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Cleavage of a Phosphorus–Carbon Double Bond and Formation of a Linear Terminal Phosphinidene Complex

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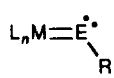
Terminal imido complexes have attracted significant attention over the past few years.[1] Both angular (**1a**) and linear (**2a**) modes of coordination have been well established for this ligand system.



1a, E = N
b, E = P

2a, E = N
b, E = P

However, information concerning the analogous terminal phosphinidene complexes is much more sparse. Although metal phosphinidenes have been recognized as transient species for several years,[2] it was not until 1987 that the first (and thus far unique) base-stabilized[3] and angular (**1b**)[4] terminal phosphinidenes were isolated. We report the first example of a linearly coordinated (**2b**) terminal phosphinidene.

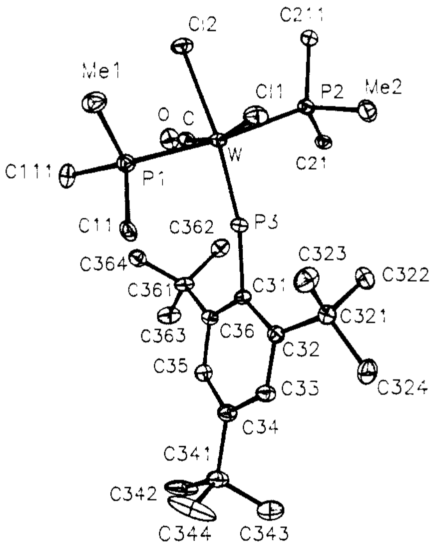


Figure 1. Structure of **4** showing the atom-numbering scheme. Important parameters: W–P(3) 2.169 (1), W–P(1) 2.525 (2), W–P(2) 2.529, (2), W–C 1.966 (6), C–O 1.151 (7), W–Cl(1) 2.478 (2), W–Cl(2) 2.433 (2), P(3)–C(3) 1.805 (5) Å; W–P(3)–C(31) 168.2 (2), Cl(1)–W–Cl(2) 87.48 (6), Cl(2)–W–P(1) 84.68 (5), Cl(2)–W–P(2) 90.30 (5), Cl(1)–W–C 167.2 (2), P(1)–W–C 95.4 (2), P(3)–W–C 90.1 (2), Cl(2)–W–P(3) 169.37 (6), P(2)–W–P(3) 93.75 (5)°.

In developing a new synthetic approach to terminal phosphinidene complexes, we noted that heterocumulenes such as carbon dioxide and isocyanates undergo cleavage reactions with WCl_2(phosphine)$_4$ complexes.[5,6] Accordingly, the phosphaketene Ar′P=C=O (Ar′ = 2,4,6-*t*-$Bu_3C_6H_2$)[7] was treated with $WCl_2(PMePh_2)_4$[8] (**3**) in THF solution at room temperature. Immediate reaction took place as evidenced by the development of a green-colored reaction mixture. Dark green crystals of diamagnetic **4** (mp 178 °C dec) formed in ether/pentane solution at −20 °C. The yield of **4** after recrystallization was 55%. Solid **4** is relatively air stable; however, solutions of **4** decompose in a few hours when exposed to the atmosphere.

In principle, Ar′P=C=O could react with **3** in several ways, including P=C cleavage to afford angular (**1b**) or linear (**2b**) terminal phosphinidene complexes of composition $WCl_2(CO)(PMePH_2)_2(=PAr')$, C=O cleavage to produce an isophosphaalkyne complex, $W(O)Cl_2(PMePh_2)_2(=CPAr')$ (**5**), or 1,2-addition of a $WCl_2(PMePh_2)_3$ moiety to an uncleaved phosphaketene. The absence of a W≡O stretch and the presence of a CO stretch (1903 cm^{-1}, KBr disk) in the IR spectrum of **4** eliminated the isophosphaalkyne complex **5**. Moreover, the ^{31}P NMR chemical shift and ^{31}P–^{183}W coupling constant for **4** (δ +193.0; $^1J_{PW}$ = 649 Hz) were sufficiently different from those for $W(\eta\text{-}C_5H_5)_2(=PAr')$(δ +661.1; $^1J_{PW}$ = 153.5 Hz)[4] to eliminate an angular phosphinidene structure (**1b**). However, we were not confident about distinguishing between a linear phosphinidene

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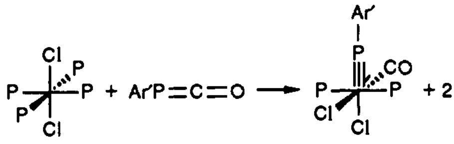
structure (**2b**) and a 1,2 P=C addition product on solely spectroscopic evidence.[9,10] An X-ray crystal structure of **4** was therefore undertaken.[11] The solid state of **4** (Figure 1) comprises isolated molecules with no short intermolecular contacts. The geometry at tungsten is octahedral, and the chloride and phosphine ligands adopt mutually cis and trans geometries, respectively.



P = PMePh$_2$; Ar′ = 2,4,6-*t*-Bu$_3$C$_6$H$_2$

Ignoring the phosphine substituents, there is close to a mirror plane through the atoms W, Cl(1), Cl(2), C, O, and P(3). Although there is appreciable variation in the bond angles at tungsten, there is no evidence for distortion toward a bound η^2-OCPAr′ form as evidenced by the following facts: (i) the P(3)-W-C angle is 90.1 (2)°, (ii) the W-C-O angle is essentially linear (177.9 (6))°, and (iii) the P(3)···C distance (2.93 Å) greatly exceeds the sum of covalent radii (1.83 Å). The phosphorus-tungsten distance (2.169 (1) Å) and C-P-W angle (168.2 (2)°) in **4** are particularly noteworthy. These data contrast with the analogous parameters for Mo(η-C$_5$H$_5$)$_2$(=PAr′) (Mo-P 2.370 (2) Å and Mo-P-C 115.8 (2)°)[4] and clearly establish that **4** is a linear terminal phosphinidene complex. In fact, the phosphorus-tungsten distance is the shortest such distance we are aware of and is consistent with a triple-bond description, viz., W$\equiv$P. The triple bond designation also explains the relatively upfield ^{31}P chemical shift for **4** since it is well-known that the phosphorus atoms of phosphaalkynes (RC$\equiv$P) are more shielded than those of phosphaalkenes (R$_2$C=PR′).[12]

The strong π-donor character of the phosphinidene moiety can be inferred from the observation that the CO stretching frequency for **4** is significantly less than those for sulfido or terminal imido complexes (W(X)Cl$_2$(CO)(PMePh$_2$)$_2$: X = S, ν_{CO} = 1986 cm^{-1}; X = NAr, ν_{CO} = 1964 cm^{-1}).[5b] Such a view is consistent with the observation that the W-Cl bond trans to the phosphinidene ligand is ~0.04 Å shorter than that trans to CO.

Compound **3** also reacts with Ar′P=C=NPh.[13] Initially a ^{31}P{^{1}H} NMR spectrum is observed that is very similar to that of **4** and thus indicative of the composition WCl$_2$(CNPh)(PMePh$_2$)$_2$(=PAr′) (**6**). However, **6** is not thermally stable and decomposes in a few hours at 25 °C.

The reactivity of **4** and the reactions of **3** with other group 15 multiply bonded compounds are under active investigation.

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Supplementary Material Available: Tables of bond lengths, angles, positional parameters, and thermal parameters for **4** (6 pages); table of observed and calculated structure factors for **4** (30 pages). Ordering information is given on any current masthead page.

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(9) ^{31}P{^{1}H} NMR (121.5 MHz, 295 K, 85% H$_3$PO$_4$ external standard): **4** (C$_6$D$_6$) $\delta_{phosphinidene}$ = 193.0, t, with ^{183}W satellites, $^2J_{PP}$ = 50.0 Hz, $^1J_{PW}$ = 649 Hz; $\delta_{phosphine}$ = −0.1, d, with ^{183}W satellites, $^2J_{PP}$ = 50.0 Hz, $^1J_{PW}$ = 253 Hz. ^{13}C{^{1}H} NMR (75.5 MHz, 295 K, TMS): **4** (THF) δ 16.2 (d of t, $^1J_{PC}$ = 15.0 Hz, $^3J_{PC}$ = 1.5 Hz, P-*Me*), 31.1 (q, J_{PC} = 9.5 Hz, para-C-*Me*$_3$), 33.1 (pseudo q, J_{PC} = 8.7 Hz, ortho-C-*Me*$_3$), 36.4 (s, para-*C*-Me$_3$), 38.3 (s, ortho-*C*-Me$_3$), 122.9–123.1 (m, para Ph), 128.4 (s, meta Ar′), 129.8–130.3 (m, meta Ph), 133.4–133.7 (m, ortho Ph), 138.8–140.3 (t, $^1J_{PC}$ = 20.5 Hz, ipso *C* (Ph)), 148.4 (d, $^1J_{PC}$ = 37.7 Hz, ipso *C*(Ar′)), 154.9 (d, $^2J_{PC}$ = 4.2 Hz, ortho Ar′), 156.9 (s, para Ar′), 244.6 (d of t, J_{PC} = 25.5 Hz, J_{PC} = 6.4 Hz, CO).

(10) The highest *m/e* peak in the FAB-MS of **4** occurred at 932 and is attributable to M$^+$ − CO.

(11) Crystal data for **4**: C$_{45}$H$_{55}$Cl$_2$OP$_3$W, monoclinic, $P2_1/n$, a = 11.238 (3) Å, b = 18.527 (3) Å, c = 21.487 (2) Å, β = 103.27 (1)°, V = 4354 Å^3, Z = 4, D_{calcd} = 1.469 g cm^{-3}, μ(Mo Kα) = 29.83 cm^{-1}. A suitable single crystal of **4** was sealed in a Lindemann capillary under a nitrogen atmosphere and mounted on an Enraf-Nonius CAD 4 diffractometer. A total of 7568 unique reflections were collected (23 °C) in the range $2° < 2\theta < 50°$. Of these, 5068 reflections were considered observed ($I > 6.0\sigma(I)$) and were used to solve (Patterson) and refine (full-matrix, least squares) the structure of **4**. The final R and R_w values were 0.0324 and 0.0407, respectively.

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Corner Attack on Cyclopropane by Thallium(III) Ions. A Highly Stereospecific Cleavage and Skeletal Rearrangement of 3α,5-Cyclo-5α-cholestan-6α-ol

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Two different mechanisms can be discerned for the electrophilic cleavage of cyclopropanes, namely, the "corner" or the "edge" attack by the electrophile,[1] resulting in the inversion or retention, respectively, at the center to which the electrophile becomes linked. Transition metals capable of back-donation (Pd, Pt, and Ir) favor the latter mechanism,[1,2] while mercury(II) ions and protons have recently been found to prefer the former reaction course.[3,4] Thallium(III) is another ion capable of the cleavage of cyclopropanes,[5] although only a few examples are known from the literature.[6] However, the stereochemistry and mechanism of these reactions have not been established and their synthetic potential is largely unexplored.

We report herein, for the first time, evidence for stereospecific corner attack at the cyclopropane ring by thallium(III), which is in line with the behavior of mercury(II) and contrasts with the oxidative edge addition of transition metals.

Treatment of model compound[7] **1** with Tl(NO$_3$)$_3$·3H$_2$O and a trace of HClO$_4$ in dioxane at room temperature for 5 h led to

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