has occurred. Most notably, the carbene carbon in **1**-Cl is now bonded directly to one of the α-carbons of the original metallacycle ring. In addition, the metallacyclopentadiene has undergone a novel ring contraction to a metallacyclobutene structure.[9] The largest deviation from the metallacycle mean plane is 0.0231 Å at C(2). The Ir-C(1) distance of 2.045 Å is similar to that observed for the related iridium–(sp^2)carbon distances in iridiacyclopentadiene complexes such as **2**-CO (2.101–2.161 Å).[1,10] The metallacycle bond distances also agree closely with those observed by Thorn for a related iridium(III) metallacyclobutene complex.[11]

The rate of reaction of **1**-Cl in $CDCl_3$ was monitored by ^1H NMR spectroscopy. In the presence of added PPh_3, the observed pseudo-first-order kinetics for conversion to **5** indicate an inverse dependence on the phosphine concentration.[12] The trans geometry of the carbene ligand and one of the α-metallacycle carbons in **1**-Cl prohibits a direct migration of the cis α-metallacycle carbon to the carbene ligand.[13] Phosphine dissociation, however, leads to an unsaturated intermediate, which may adopt a square-pyramidal geometry (**6**, Scheme I) from which a migration is feasible.[14] Migration and phosphine addition leads to a metallacyclohexadiene intermediate, **7**. A 1,3-shift of iridium and coordination of the methoxycarbonyl oxygen would then generate **5**.[15,16] Whether or not the reaction is chelate-assisted requires further investigation.

The thermal stability of the metallacycle–carbene complex depends greatly on the nature of the non-phosphine ligand. Thus, heating a chloroform solution of **2**-CO at 75 °C for 48 h results in only a trace of decomposition, with no evidence for metallacyclohexadiene or cyclopentadiene formation. The much more labile aquo complex **2**-H_2O decomposes in dry chloroform solution, even at 23 °C over the course of 3 days, to give a complex mixture of the products.[7,17] In wet chloroform **2**-H_2O is stable for more than 3 days under similar conditions. The neutral fluoro derivative **1**-F decomposes slowly at 75 °C and also gives a complex mixture of products.[7] Efforts are underway to prepare related metallacycle–carbene complexes that will lead to isolable metallacyclohexadiene products.

Acknowledgment. Support of the National Science Foundation (CHE-9005973) is gratefully acknowledged.

Supplementary Material Available: Full spectroscopic and analytical data for compounds **2**-H_2O, **1**-F, and **5**, listings of fractional coordinates, bond distances, bond angles, hydrogen atom coordinates, and thermal parameters (8 pages); table of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(8) Crystal data for **5** (296 K): $C_{52}H_{48}ClIrO_9P_2\cdot{}^1/_2CHCl_3$, triclinic $P\bar{1}$, a = 10.209 (3) Å, b = 13.516 (7) Å, c = 19.888 (7) Å, α = 83.57 (4)°, β = 84.85 (3)°, γ = 72.63 (4)°, V = 2598 (2) Å^3, Z = 2, D_{calc} = 1.491 g cm^{-3}, μ = 28.0 cm^{-1}. A platelike yellow specimen (0.06 × 0.23 × 0.31 mm) was used for data collection (Siemens R3m/V, 4.0° ≤ 2θ ≤ 45.0°, Mo Kα, 24–25 °C). Of 6784 reflections collected, 6478 were independent (R_{int} = 0.00%) and 4926 with $F > 6.0\sigma(F)$ were considered observed and corrected for absorption by using face-indexed numerical method. (T_{min}/T_{max} = 0.9475/0.9862). The Ir atom was located by a heavy atom method. With all non-hydrogen atoms anisotropically refined and hydrogen atoms treated as riding model, fixed isotropic U = 0.08 Å^2: $R(F)$ = 5.88%, $R(wF)$ = 7.94%, all data $R(F)$ = 8.50%, GOF = 0.85, Δ/σ = 0.045, $\Delta(\rho)$ = 2.62 e A^{-3}. All computer programs and sources of scattering factors are contained in the SHELXTL program library (Siemens Corp., Madison, WI).

(9) For a treatment of metallacycle ring strain, see: Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948.

(10) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2060.

(11) Calabrese, J. C.; Roe, D. C.; Thorn, D. L.; Tulip, T. H. *Organometallics* **1984**, *3*, 1223.

(12) For [**1**-Cl] = 29.7 mM, [PPh_3] = 1.14 M, k_{obs} = 1.15 × 10^{-4} s^{-1}; [**1**-Cl] = 31.2 mM, [PPh_3] = 0.58 M, k_{obs} = 2.67 × 10^{-4} s^{-1}; [**1**-Cl] = 31.8 mM, [PPh_3] = 0.30 M, k_{obs} = 4.13 × 10^{-4} s^{-1}; [**1**-Cl] = 31.2 mM, [PPh_3] = 0.15 M, k_{obs} = 7.73 × 10^{-4} s^{-1}.

(13) By analogy to alkyl migration to a carbonyl ligand, carbene–alkyl coupling reactions presumably involve an alkyl migration to the carbene ligand rather than a carbene insertion into the metal–alkyl bond. Thorn has observed alkyl–carbene ligand couplings at iridium(III), which support an alkyl migration pathway: Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. Thorn, D. L. *Organometallics* **1985**, *4*, 192.

(14) Migration of the metallacycle carbon to the carbene ligand is geometrically feasible from either a square-pyramidal intermediate as shown for **6** or an octahedral bis(phosphine) complex with a facial arrangement of the three carbon-bound ligands. The required orthogonal carbene ligand orientation with respect to the metallacycle may be facilitated by loss of phosphine; however, a metallacycle migration to the carbene ligand will still require one of the above geometries.

(15) Metallacyclohexadiene complex **7** may exist as a 1,2,3,5-η-penta-2,4-dienediyl ligand in which one of the metallacycle double bonds is coordinated to the metal. The 1,3 iridium shift would then be described as an η^3 to η^1 rearrangement of a π-allyl intermediate: Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1578. Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.: Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694. Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576.

(16) We cannot completely exclude a mechanism involving metallacycle reversion to two alkynes, with subsequent alkyne–carbene coupling. Thermolysis of **1** at 75 °C in the presence of excess dimethyl acetylenedicarboxylate-d_6 leads to catalytic formation of hexa(carboxymethyl)benzene, **8**-d_n. Compound **1** decomposes under these conditions and no identifiable iridium-containing products are observed (by ^1H NMR spectroscopy). The partially labeled **8**-d_n is 10% d_{12} and 90% d_6. This *may* be indicative of a minor amount of metallacycle reversion under these conditions.

(17) **2**-H_2O decomposes in dry chloroform-d_1 at 23 °C over the course of 3 days to give a number of decomposition products in addition to one major prouct in 39% yield (by ^1H NMR spectroscopy). This product was not isolated, but spectroscopy on the crude reaction mixture indicated nonequivalent cis PPh_3 ligands [^{31}P NMR: δ −25.38 (d, J = 11 Hz) and −2.2 (br d, J = 11 Hz)] as was observed for **5**.

Incremental Preorganization of a Chelating Macrocycle

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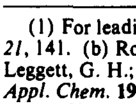
Received May 21, 1990

Complexation of the environmentally and economically important late-transition-metal ions by polythioethers has been studied in many laboratories.[1] Surprisingly, however, relatively little effort has been devoted to exploring how changes in polythioether structure affect the strength and specificity with which thiophilic metal ions are bound, particularly in comparison with the large body of work on optimization of poly*oxo*ether complexing agents for oxophilic cations.[2] We now report that simple peripheral modifications of a macrocyclic tetrathioether can have a substantial impact on chelation efficacy. A comparison of structural and solution data on Ni(II) binding by tetrathiothers **1**–**3**[3] reveals that successive additions of appropriately placed *gem*-dimethyl groups induce macrocycle conformations that are



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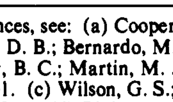

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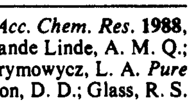

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(3) Synthetic and crystallographic details on all new compounds will be provided in a full paper. Tetrathioether **2** and the $Ni(ClO_4)_2$ complexes of **2** and **3** have not been previously reported. Yoshida et al. have described Rh(I) and Ru(II) complexes of **3**, but we can find no report on the origin of the macrocycle itself. See: (a) Yoshida, Y.; Ueda, T.; Adachi, T.; Yamamoto, K.; Higuchi, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1137. (b) Ueda, T.; Tamanaka, H.; Adachi, T.; Yoshida, T. *Chem. Lett.* **1988**, 525.

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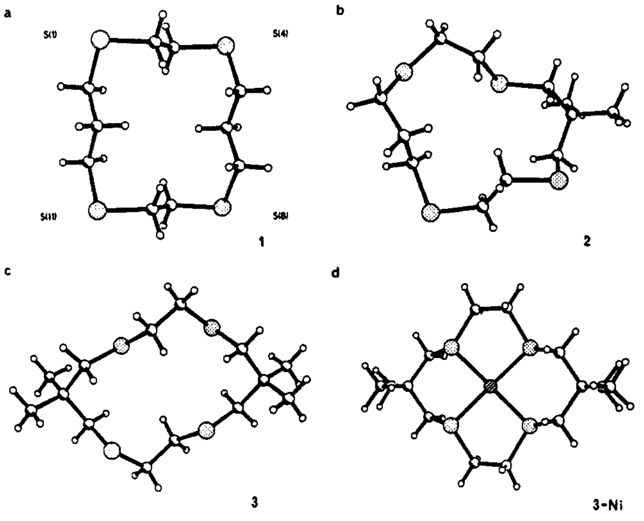

Figure 1. Ball-and-stick representation of the crystallographically observed thioether conformations. (a) Macrocycle **1** (α form, ref. 6); (b) macrocycle **2**; (c) macrocycle **3**; (d) **3**-Ni(II) (ClO_4 counterions not shown). The macrocycle backbone conformations observed in the crystalline complexes **1**-$Ni(BF_4)_2$[7] and **2**-$Ni(ClO_4)_2$ are nearly identical with that observed in **3**-$Ni(ClO_4)_2$.

increasingly preorganized to receive the Ni(II) ion.

Structural data on a variety of thioethers indicate that the $CH_2S-CH_2CH_2$ torsional unit has a slight inherent preference for gauche dispositions, while SCH_2-CH_2S and $SCH_2-CH_2CH_2$ units are significantly more stable in anti conformations.[4] Because of these preferences, the sulfur atoms in macrocyclic polythioethers with polymethylene spacers usually adopt exodentate positions (the lone pairs point away from the center of the ring),[5] as has previously been observed in the α crystalline form of **1** (Figure 1a).[6] Ni(II) chelation completely reorganizes the backbone of **1**: the crystal structure of **1**-$Ni(BF_4)_2$ shows that every bond that was gauche in the free macrocycle is anti in the complex, and vice versa.[7]

Smith and Margerum have reported the Ni(II) affinity of **1** to be approximately 180-fold larger than that of an analogous acyclic tetrathioether in nitromethane solution.[8,9] This "macrocyclic effect" is modest compared to the 10^4–10^6-fold macrocyclic effects observed with polyethers and polyamines for appropriately sized cations,[10] although patterns of behavior among these different classes of chelators are not necessarily comparable. Cooper has suggested that the relatively small macrocyclic effect observed for **1** is related to the substantial backbone rearrangement implied by the crystal structures of the metal-free and metal-bound ligand.[1a]

A comparison of Ni(II) binding across the series **1**–**3** provides insight on the relationship between macrocyclic conformational preferences and chelation efficacy. We find that the two pairs of *gem*-dimethyl groups dramatically alter the backbone conformation of metal-free **3** in the solid state (Figure 1c), relative to **1**. All four sulfur atoms of **3** adopt endodentate configurations (i.e., they point one lone pair toward the center of the ring). The solid-state conformation of **2** (Figure 1b) displays torsional features reminiscent of **1** in one portion of the molecule and torsional features reminiscent of **3** in another (Table I). This dual nature of the 14-membered ring of **2** suggests that the characteristic conformation-directing effects of the *gem*-dimethyl-substituted propylene segment and of the unsubstituted propylene segment each dominate a local set of torsional potentials within the ring, and that crystal packing forces are not exerting an overriding effect on macrocycle conformation.

Some of the conformational changes induced by the *gem*-dimethyl groups were anticipated. The $CS-CC(H_2)$ bonds of the propylene segments adopt exclusively gauche torsion angles in **1**, for example, but the analogous $CS-CC(Me_2)$ units of **2** and **3** prefer anti torsion angles (one of two in **2** and all four in **3**). Other changes were unexpected, particularly the occurrence of gauche SC–CS angles in the methylated macrocycles (one of two in **2** and both in **3**). These unexpected variations probably reflect an interplay between nonbonded repulsions involving the added methyl groups and the inherent constraints associated with the 14-membered-ring backbone.

Crystal structures of $Ni(ClO_4)_2$ complexes of **2** and **3** (Figure 1d) show the macrocycle conformations in both cases to be virtually identical with that previously observed in the $Ni(BF_4)_2$ complex of **1**[7] (Table I). Thus, the *gem*-dimethyl substitutions apparently do not affect the favorability of this conformation for Ni(II) chelation, relative to other conformations of the 14-membered ring that would allow tetradentate interaction. Among tetrathioethers **1**–**3**, the macrocycle conformation observed for metal-free **3** is closest to that seen in the Ni(II) complexes.

We determined the relative affinities of **1**–**3** for Ni(II) in nitromethane-d_3 by ^1H NMR. The spectra of the individual preformed Ni(II) complexes suggested that at least two slowly exchanging metal-bound macrocycle conformations exist in solution in each case.[11] Uncomplexed macrocycle could not be detected in the presence of 1 equiv of Ni(II) for any of the tetrathioethers (12.5 mM in each component). The ratio of the Ni(II) association constants between pairs of macrocyclic tetrathioethers was measured by direct competition. Solutions containing 1 equiv of either **2** or **3**, 1 equiv of **1**, and 1 equiv of Ni(II) were examined after equilibrium had been reached (several days at room temperature). Signals for metal-bound and metal-free forms of both macrocycles were observed in each case. Integration of isolated signals (methyl groups) indicated that K_a for Ni(II) binding by **2** is 7 times larger than K_a for **1**, and that K_a for **3** is 50 times larger than K_a for **1**. Thus, each additional *gem*-dimethyl pair leads to an incremental enhancement in Ni(II) affinity.

In originally formulating his "principle of preorganization", Cram pointed out that a variety of factors can contribute to stronger "host-guest" interactions.[12] Most work on noncovalent complexation has tended to focus on one particular mode of preorganization, minimization of host conformational flexibility. Structural rigidification may play a role in the incremental improvement in Ni(II) binding observed for **2** and **3** relative to **1**, but the enhanced chelation could also result from the strain built into **2** and **3** by incorporating the *gem*-dimethyl groups. We are

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(11) (a) The existence of two slowly exchanging Ni(II)-chelated conformations of **1** in nitromethane solution has been previously detected by ^{13}C NMR; see: Herron, N.; Howarth, O. W.; Moore, P. *Inorg. Chim. Acta* **1976**, *20*, L43. (b) Two Rh(I)-complexed conformations of **3** have been detected by ^1H NMR in dimethyl sulfoxide; see ref 3a.

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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.

Acknowledgment. We are grateful to Professor Hans J. Reich for helpful suggestions. We thank the Graduate School of the University of Wisconsin—Madison for support in the form of a fellowship to J.M.D. We also gratefully acknowledge partial support from the Searle Scholars Program (S.H.G.) and an American Cancer Society Junior Faculty Research Award (S. H.G.).

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

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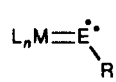
Received May 31, 1990

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.

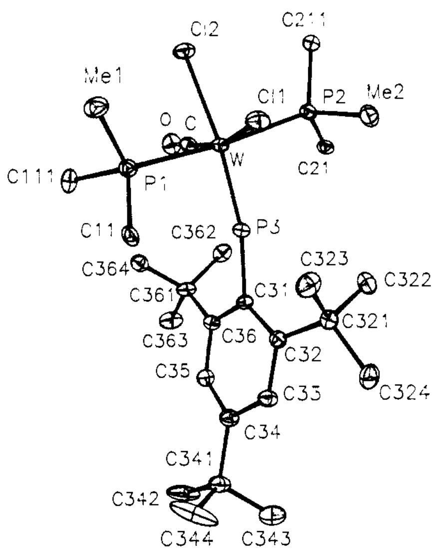


Figure 1. Structure of **4** showing the atom-numbering scheme. Important parameters: W–P(3) 2.169 (1), W–P(1) 2.525 (2), W–P(2) 2.529, (2), W–C 1.966 (6), C–O 1.151 (7), W–Cl(1) 2.478 (2), W–Cl(2) 2.433 (2), P(3)–C(3) 1.805 (5) Å; W–P(3)–C(31) 168.2 (2), Cl(1)–W–Cl(2) 87.48 (6), Cl(2)–W–P(1) 84.68 (5), 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; $^{1}J_{PW}$ = 649 Hz) were sufficiently different from those for $W(\eta-C_5H_5)_2(=PAr')$(δ +661.1; $^{1}J_{PW}$ = 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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0002-7863/90/1512-6734$02.50/0 © 1990 American Chemical Society