coordinate with Er(III) may indicate that this ligand is not optimally constructed and, in fact, the ligand may not be as good of an extractant as the bifunctional CMP ligands. Characterization of that extraction chemistry is in progress in collaboration with co-workers at Los Alamos National Laboratories. In addition, efforts are under way to isolate and structurally characterize complexes of **1** containing early lanthanides, as well as two metal centers. The structure of **2** and the propensity for high coordination numbers for Ln(III) ions also suggest that ligands containing additional methylene groups, $(CH_2)_x$ (x = 2, 3), in the long-leg carbamide group may prove to have useful multidentate coordination properties.

Acknowledgment. R.T.P. wishes to recognize financial support for this work from the Department of Energy, Office of Basic Energy Sciences, Contract No. 82ER-10465. He also wishes to recognize NSF Grants CHE-7802921 and CHE-8201374, which facilitated the purchases of the X-ray diffractometer and the NMR spectrometer.

Registry No. **2**, 99248-86-9.

Supplementary Material Available: Listings of structure factors, hydrogen atom positional parameters, and thermal parameters and a full listing of bond angles (36 pages). Ordering information is given on any current masthead page.

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Structural Characterization of Tridentate 11-Membered Phosphino Macrocyclic Complexes of Transition Metals. Examples of Octahedral, Square-Pyramidal, and Tetrahedral Geometries[1]

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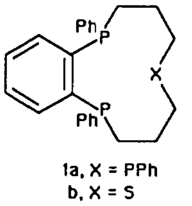
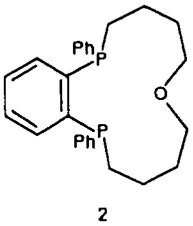
Three structures of 11-membered phosphino macrocyclic complexes of transition metals have been determined: tri(carbonyl-κC)[*meso-cis*-6-methyl-2,10-diphenyl-6-aza-κ*N*-2,10-diphospha-κ²*P*-bicyclo[9.4.0]pentadeca-11(1),12,14-triene]molydenum(0) (**3a**, $C_{28}H_{29}MoNO_3P_2 \cdot 0.5C_6H_5CH_3$), tri(carbonyl-κ*C*)[*meso-cis*-2,6,10-triphenyl-2,6,10-triphospha-κ³*P*-bicyclo[9.4.0]pentadeca-11(1),12,14-triene]tungsten(0) (**3b**, $C_{33}H_{31}O_3P_3W$), and dichloro[*meso-cis*-2,10-diphenyl-6-aza-κ*N*-2,10-diphospha-κ²*P*-bicyclo[9.4.0]pentadeca-11(1),12,14-triene]nickel(II) (**4**, $C_{24}H_{27}Cl_2NNiP_2$). Structures **3a,b** are *fac* octahedral, and **4** is square pyramidal with the NH moiety in the apical position. These structures are compared with each other and with another described previously, chloro[*meso-cis*-2,10-diphenyl-2,10-diphospha-κ²*P*-6-thia-κ*S*-bicyclo[9.4.0]penta-11(1),12,14-triene]copper(I) (**5**), which is approximately tetrahedral. Unusually long metal–nitrogen bond lengths are observed for **3a** (Mo–N = 2.428 (3) Å) and for **4** (Ni–N = 2.428 (3) Å). The conformations of the trimethylene strands joining the heteroatoms in the coordinated macrorings are analyzed, and explanations are proposed for the observation of chair–chair conformations for the two 6-membered rings $\overline{\mathrm{WPCH_2CH_2CH_2P}}$ in **3b** and the two 6-membered rings $\overline{\mathrm{CuPCH_2CH_2CH_2S}}$ in **5** but chair–boat conformations for the two 6-membered rings $\overline{\mathrm{MoPCH_2CH_2CH_2N}}$ in **3a** and the two 6-membered rings $\overline{\mathrm{NiPCH_2CH_2CH_2N}}$ in **4**. X-ray data were collected on a Syntex $P2_1$ autodiffractometer and refined by the full-matrix least-squares method. For **3a** from toluene (as $\mathbf{3a} \cdot {}^1/_2C_7H_8$), a = 10.083 (1) Å, b = 17.509 (3) Å, c = 9.082 (1) Å, α = 96.36 (1)°, β = 112.70 (1)°, γ = 77.89 (1)°, triclinic, $P\bar{1}$, Z = 2, and R_1 = 0.0314, R_2 = 0.0322 for 5647 reflections with $|F_o| > 4\sigma_{|Fo|}$. For **3b**, a = 12.366 (1) Å, b = 15.436 (2) Å, c = 16.867 (2) Å, β = 103.914 (8)°, monoclinic, $P2_1/c$, Z = 4, and R_1 = 0.0365, R_2 = 0.0364 for 4761 reflections with $|F_o| > 4\sigma_{|F_o|}$. For **4**, a = 9.240 (1) Å, b = 15.474 (3) Å, c = 9.035 (2) Å, α = 96.90 (2)°, β = 67.38 (2)°, γ = 111.69 (1)°, triclinic, $P\bar{1}$, Z = 2, and R_1 = 0.0348, R_2 = 0.0349 for 4136 reflections having $|F_o| > 4\sigma_{|Fo|}$.

For some time now we have been involved in the synthesis of tertiary-phosphino-containing macrocycles and the study of their coordination behavior toward transition metals.[2] We have shown that the 11-membered cycles **1** can function in a tridentate or a bidentate fashion depending on several factors. The thermal reaction of **1** with group 6 metal hexacarbonyls produced tridentate facial complexes in good yields when X was relatively soft, i.e., **1a–c**[3] and **1d**,[4] but only bidentate complexes were formed when X was hard (**1f,g**).[3] Additionally, the configuration of PPh[3] and AsPh[4] was important; only the meso-cis ligands gave tridentate complexes unless temperatures were reached that allowed pyramidal inversion of phosphorus. With Co(II), we found that **1e** could behave in a tridentate fashion, but the 13-membered analogue (**2**) would not.[1]



1a, X = PPh
b, X = S
c, X = NMe
d, X = AsPh
e, X = O
f, X = NPh
g, X = NH



2

We have been interested in how ligands **1** "wrap" themselves around the metal center, a question that can only be approached conveniently by X-ray crystallography. Although ligands such as **1** readily form complexes with many transition metals, our problem has been that crystals of X-ray quality from these complexations have been relatively rare. Nonetheless, we have been able to obtain examples of complexes of **1** that include tetrahedral, square-pyramidal, and octahedral types, and we describe their structural details herein.

Results and Discussion

Octahedral Complexes. The thermal reaction of **1c** with $Mo(CO)_6$ in boiling toluene to give **3a** in 60% yield (eq 1) has been described.[3] Similarly, a mixture of *meso-cis-* and *meso-trans-***1a**[2b] upon being heated with $W(CO)_6$ in boiling mesitylene for 16 h gave **3b** in 41% yield. The reaction was monitored as a function of time by IR spectroscopy, which showed that about 10 h was required for all of the $W(CO)_6$ to react. At this time all of the

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[1] Phosphino Macrocycles. 15. Part 14: Kyba, E. P.; Liu, S.-T. *Inorg. Chem.* **1985**, *24*, 1613.

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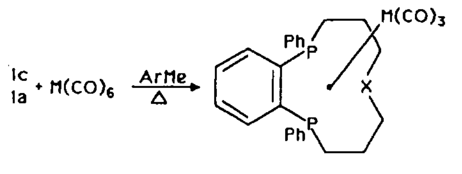
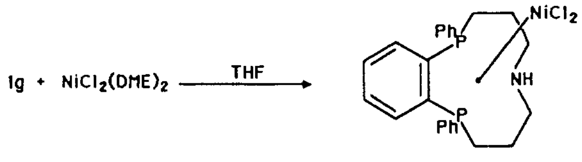


(1)

3a, X = NMe, M = Mo
b, X = PPh, M = W

absorptions in the carbonyl stretching region in the IR spectrum could be accounted for as due to either the *cis*-$W(CO)_4$ or the *fac*-tricarbonyl (**3b**) species.[5] The tetracarbonyl species presumably originated from the meso-trans ligand; continued heating caused the IR absorptions due to **3b** to increase and those of the tetracarbonyl species to decrease. We have discussed these types of observations previously.[4] Crystals of X-ray quality of **3a** containing 0.5 mol of solvent were obtained from toluene, and those of **3b** from mesitylene.

Square-Pyramidal Complex. When **1g** in THF was combined with $NiCl_2 \cdot 2DME$ (DME = dimethoxyethane) in the same solvent at room temperature, complex **4** was formed immediately (eq 2),

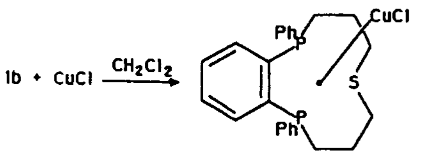


(2)

4

as evidenced by a color change from yellow to deep brown upon mixing the two solutions. Species **4** precipitated rapidly from solution in quantitative yield and was further purified by recrystallization from dichloromethane.

Tetrahedral Complex. The formation of **5** by reaction of **1b** with cuprous chloride in dichloromethane (eq 3), as well as by



(3)

5

other routes starting with cupric chloride, has been described.[6]

Structural Descriptions. The ORTEP plots in Figure 1 show the structures determined in this work (**3a,b** and **4**), as well as that determined previously (**5**),[6] for comparison. Even a cursory examination of these structures indicates that, from the point of view of the ligand conformation, **3a** and **4** are related but different from **3b** and **5**, which are also related. Table I presents torsion angles around the macrocyclic ligands, which quantify these comparisons. Species **3b** and **5** have very similar torsion angles for all the bonds in the ring. In contrast, **3a** and **4** are very similar to **3b** and **5** in the string of bonds X–C4 to C8–P1 but differ substantially in the P1–C1 to C3–X string. Focusing on the two fused 6-membered rings, $\overline{\mathrm{M,P1,C1,C2,C3,X}}$ and $\overline{\mathrm{M,P2,C6,C5,C4,X}}$, one can see that torsional angles around the rings in the latter strings have the typical alternating +g,–g alternation characteristic of a chair conformation (Table I, entries 12–23). In addition, the former strings for **3b** and **5** have a similar alternation, but the two for **3a** and **4** are quite different (four positive and two negative torsional angles), similar to a twist-boat conformation.

Table I. Selected Torsional Angles (deg) for Complexes **3a,b**, **4**, and **5**[a]

		3a	4	3b	5
1	C8–P1–C1–C2	–119.8 (2)	–93.9 (2)	–65.0 (5)	–70.0 (3)
2	P1–C1–C2–C3	61.0 (3)	39.7 (3)	–80.8 (7)	–78.4 (4)
3	C1–C2–C3–X	–94.6 (3)	–83.2 (3)	68.8 (8)	71.7 (5)
4	C2–C3–X–C4	172.9 (2)	–171.6 (2)	94.7 (7)	88.6 (3)
5	C3–X–C4–C5	–63.5 (3)	–79.4 (3)	–72.4 (6)	–72.3 (4)
6	X–C4–C5–C6	–86.6 (3)	–74.4 (4)	–80.0 (7)	–79.3 (5)
7	C4–C5–C6–P2	66.6 (2)	70.1 (3)	70.5 (8)	69.6 (4)
8	C5–C6–P2–C7	77.0 (2)	61.8 (2)	77.2 (5)	76.3 (3)
9	C6–P2–C7–C8	–125.1 (2)	–132.5 (2)	–127.2 (5)	–128.2 (3)
10	P2–C7–C8–P1	0.5 (3)	0.8 (3)	2.5 (7)	6.9 (3)
11	C7–C8–P1–C1	124.3 (2)	131.8 (2)	120.7 (5)	116.4 (3)
12	C2–C1–P1–M	1.5 (2)	26.6 (2)	55.7 (5)	41.5 (3)
13	C3–C2–C1–P1	61.0 (3)	39.7 (3)	–80.8 (7)	–78.4 (4)
14	X–C3–C2–C1	–94.6 (3)	–83.2 (3)	68.8 (8)	71.7 (5)
15	M–X–C3–C2	44.1 (3)	48.7 (2)	–32.5 (7)	–27.3 (3)
16	P1–M–X–C3	8.4 (2)	7.4 (2)	11.1 (3)	0.0 (1)
17	C1–P1–M–X	–28.1 (1)	–40.1 (1)	–21.4 (3)	–7.0 (1)
18	C5–C6–P2–M	–44.8 (2)	–57.7 (2)	–46.0 (6)	–37.0 (3)
19	C4–C5–C6–P2	66.6 (3)	70.1 (3)	70.5 (8)	69.6 (4)
20	X–C4–C5–C6	–86.6 (3)	–74.4 (4)	–80.0 (7)	–79.3 (5)
21	M–X–C4–C5	68.3 (3)	60.4 (3)	59.0 (5)	46.7 (4)
22	P2–M–X–C4	–37.2 (1)	–42.1 (2)	–30.4 (3)	–17.1 (1)
23	C6–P2–M–X	28.3 (1)	37.0 (1)	26.1 (3)	14.9 (2)
24	C7–P2–M–P1	–0.7 (1)	11.4 (1)	–3.8 (2)	1.9 (1)
25	C8–P1–M–P2	0.9 (1)	–11.0 (1)	4.9 (2)	0.8 (1)
26	C13–X–M–C32[b]	34.7 (2)	33 (3)	40.7 (3)	
27	C13–X–M–C31[b]	–60.5 (2)	–63 (3)	–55.2 (3)	

[a] X = N(**3a**), P3(**3b**), N(**4**), and S(**5**). [b] Replace C32 with Cl1 and C31 with Cl2 in **4**. Replace C13 with H in **4** and C13 with C25 in **3b**.

The reason for the twist-boat-like conformation with **3a** and **4** arises from the "flagpole" interactions between H2B and H5B. The distances between these two atoms in **3b** and **5** are 2.54 and 2.23 Å, respectively. Since C–P and C–S distances are about 0.35 Å longer than C–N distances (Table II), the effect of shortening the C–X bond length is to bring the two chains closer together, as seen in the nonbonded distances C3–C4, which are ca. 0.4 Å shorter for **3a** and **4** than for **3b** and **5**. Comparison of distances, both bonded and nonbonded, measured on Dreiding models of all the complexes, with those in Table II indicates a close correspondence. If **3a** and **4** were forced into a chair–chair conformation, analogous to those of **3b** and **5**, then the H2B–H5B distance would become prohibitively close (<1.7 Å),[7] so one of the strands adopts a twist-boat conformation, which relieves the interaction.

The coordination geometry about the metal atoms may be described by the following distances (Å) from an "equatorial" plane in **3a,b** and from the basal plane in **4**: In **3a**, distances from the least-squares plane [P1,P2,C31,C32] are P1 0.015 (1), P2 –0.016 (1), C31 0.017 (3), C32 –0.016 (3), Mo 0.063 (0), C33 –1.879 (3), and N 2.485 (2). In **3b** distances from plane [P1,P2,C31,C32] are P1 0.070 (2), P2 –0.071 (2), C31 0.076 (6), C32 –0.076 (6), W –0.004 (0), C33 –1.989 (7), and P3 2.489 (2). In **4**, distances from plane [P1,P2,Cl1, Cl2] are P1 0.062 (1), P2 –0.059 (1), Cl1 –0.056 (1), Cl2 0.053 (1), Ni 0.124 (0), and N 2.538 (2). The bond angles in **3a,b** and **4** are within 5° of the expected 90° for either octahedral or square-pyramidal complexes, with a few exceptions. The P1–M–P2 bond angles are "pinched" by about 10° in **3a,b** but not in **4**. These bond angles of ca. 80° are expected from the "natural" angles related to the benzo group (C8–C7–P2 and C7–C8–P1 = 119°) and the near-tetrahedral angles at P1 and P2 (111°): since a planar pentagon has a total of 540° of internal angles and four of these account for (2 × 119°) + (2 × 111°) = 460°, then the remaining angle P1–M–P2 would be 540° – 460° = 80°. Angles of a similar or even lower magnitude have been observed for other 5-membered diphosphine

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(6) Davis, R. E.; Kyba, E. P.; John, A. M.; Yep, J. M. *Inorg. Chem.* **1980**, *19*, 2540.

(7) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1940; Chapter 5. The van der Waals radius of H was estimated to be 1.2 Å, and that for the CH_2 moiety, 2.0 Å. Another measure of closeness of the contacts between C2 and C5 in **3b** and **5** is the C–C nonbonded distances, 3.721 and 3.783 Å (Table II), respectively; i.e., these atoms are in van der Waals contact.

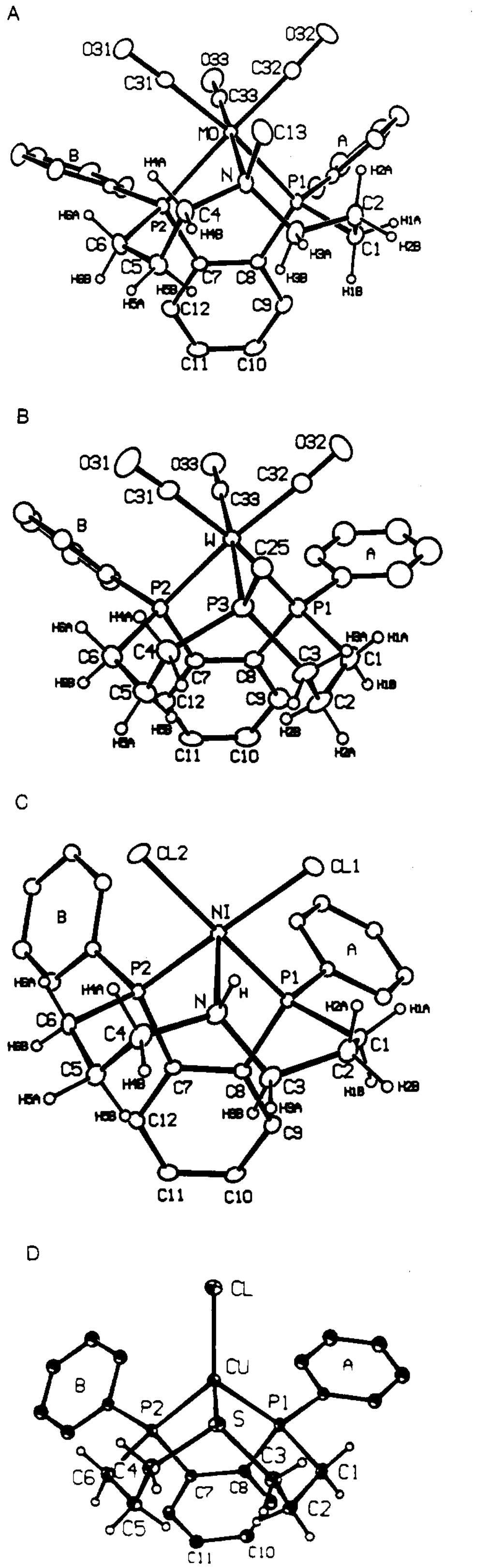
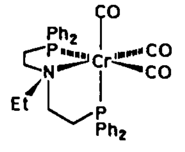


Figure 1. (A) ORTEP plot of structure **3a**. The hydrogen atoms on C13 are not shown. (B) ORTEP plot of structure **3b**. Only the ipso carbon atom (C25) of the phenyl group attached to P3 is shown. (C) ORTEP plot of structure **4**. (D) ORTEP plot of structure **5** as previously described.[6]

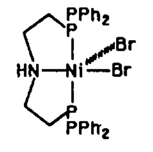
chelates of Mo and W.[8] The P1–Ni–P2 bond angle of 88.3° in **4** is also in the range typical of 5-membered diphosphine chelates.[9]

The geometry of the C_2P_2Ni ring is a compromise of maintaining rather short Ni–P bond lengths[9] and narrowing the P2–C7–C8 and P1–C8–C7 angles by about 5° each from the 119–121° observed in the other complexes in this study and in the free ligands.[2b] Similar considerations for **5** account for the P1–Cu–P2 angle of 91.6° and the P2–C7–C8 and P1–C8–C7 angles of 120°, since the P–Cu bond lengths are ca. 0.11 Å longer than the P–Ni bond lengths in **4**.

The N–M bond lengths in **3a** and **4** deserve comment. Cotton and LaPrade[10] have described the Cr–N bond length of 2.31 Å in **6** as "astonishingly long". Since atomic radii increase by 0.08–0.12 Å from the first to the second transition series[11] and since the Mo–N bond length in **3a** is ca. 0.12 Å longer than the corresponding one in **6**, then one can conclude that the Mo–N bond length in **3a** is also unusually long. A similar conclusion would be reached simply by noting that the P–Mo and N–Mo bond lengths differ by only 0.01 and 0.04 Å in **3a**, whereas the difference in covalent radii of P and N is 1.10 Å–0.70 Å = 0.40 Å.[7] Similar considerations indicate that the N–Ni bond in **4** is very long, about 0.3 Å longer than the P–Ni bond lengths. Much of this is due to its position as an axial group. Structure **7** affords the opportunity to compare an axial and an equatorial Ni–Br bond; the former is 0.4 Å longer than the latter.[12] In the same structure the equatorial N–Ni bond length is 2.01 Å, i.e., about 0.4 Å shorter than that in **4**. It has been suggested[10] that the cause of the long N–Cr bond in **6** is ring strain in the chelate, and this could be one of the causes of our observed long N–M bonds. It should be noted, however, that these N–M bonds are part of 6-membered rather than 5-membered chelates in **6** and **7** and thus would presumably be less strained. In addition, the P3–W bond length in **3b** and the S–Cu bond length in **5** show little, if any, evidence of the extraordinary bond lengthening discussed above.[13] Thus, there may be a yet unknown effect operating in concert with ring strain (and the axial positioning in **4**) that is causing the long N–M bonds.



6



7

Experimental Section

General Information. Proton resonance spectra were obtained on a Varian EM-390, a Varian FT-80, or a Nicolet NT360 spectrometer. Carbon-13 NMR spectra were determined on an FT-80 spectrometer at 20.1 MHz. Proton-decoupled ^{31}P NMR spectra were determined on a Varian PT-80 or Bruker WH90 spectrometer at 32.2 and 36.4 MHz, respectively. Chemical shifts are given in parts per million relative to Me_4Si for ^{13}C and relative to 85% H_3PO_4 for ^{31}P NMR spectra. Chemical shifts upfield of the standard are defined as negative. Syntheses of ligands **1** have been published,[2] as well as those for complexes **3a**[3] and **5**.[6]

Tri(carbonyl-κ*C*)[*meso-cis*-2,6,10-triphenyl-2,6,10-triphospha-κ^3*P*-bicyclo[9.4.0]pentadeca-11(1),12,14-triene]tungsten(0) (3b).[14] A solution of **1a** (60.0 mg, 0.124 mmol; 1:1 mixture of meso-cis and meso-trans

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(8) See, inter alia: (a) Darensbourg, M. Y.; Hankel, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 6979. (b) Sato, M.; Tatsumi, T.; Kodama, T.; Hidai, M.; Uchida, T.; Uchida, Y. *Ibid.* **1978**, *100*, 4447. (c) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *Ibid.* **1979**, *101*, 865.

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(14) For a discussion of the nomenclature used, see: Sloan, T. E.; Busch, D. H. *Inorg. Chem.* **1978**, *17*, 2043.

Table II. Selected Bond Lengths (Å) and Angles (deg) of the Coordination Spheres

3a					**3b**					**4**				
1	2	3	1–2	1–2–3	1	2	3	1–2	1–2–3	1	2	3	1–2	1–2–3
P1	Mo	P2	2.470 (2)	80.88 (6)	P1	W	P2	2.4577 (14)	80.42 (5)	P1	Ni	P2	2.1248 (9)	88.27 (4)
P1	Mo	N		88.27 (7)	P1	W	P3		89.01 (6)	P1	Ni	N		90.47 (7)
P1	Mo	C31		170.88 (9)	P1	W	C31		170.7 (2)	P1	Ni	Cl1		85.34 (4)
P1	Mo	C32		93.77 (9))	P1	W	C32		92.4 (2)	P2	Ni	N	2.1361 (9)	88.90 (7)
P2	Mo	N	2.436 (2)	88.78 (8)	P2	W	P3	2.452 (2)	88.98 (6)	P2	Ni	Cl1		168.68 (3)
P2	Mo	C31		90.26 (10)	P2	W	C31		91.4 (2)	P2	Ni	Cl2		90.41 (4)
P2	Mo	C32		173.31 (7)	P2	W	C32		171.8 (2)	N	Ni	Cl1	2.428 (3)	100.46 (7)
P2	Mo	C33		88.78 (10)	P2	W	C33		89.0 (2)	N	Ni	Cl2		92.88 (7)
N	Mo	C31	2.428 (3)	93.73 (11)	P3	W	C31	2.496 (2)	86.6 (2)	Cl1	Ni	Cl2	2.2341 (9)	95.40 (4)
N	Mo	C32		95.11 (11)	P3	W	C32		94.8 (2)	Cl2	Ni	P1	2.2473 (10)	176.37 (3)
N	Mo	C33		177.19 (9)	P3	W	C33		177.3 (2)					
C31	Mo	C32	1.969 (3)	94.90 (12)	C31	W	C32	1.985 (6)	96.1 (3)					
C31	Mo	C33		87.69 (12)	C31	W	C33		91.7 (2)					
C32	Mo	C33	1.993 (3)	87.18 (13)	C32	W	C33	1.984 (7)	87.4 (3)					
C33	Mo	P1	1.942 (3)	89.96 (9)	C33	W	P1	1.985 (7)	92.4 (2)					
O31	C31	Mo	1.169 (3)	174.8 (3)	O31	C31	W	1.155 (7)	177.7 (6)					
O32	C32	Mo	1.158 (4)	175.2 (3)	O32	C32	W	1.159 (9)	176.9 (6)					
O33	C33	Mo	1.169 (4)	179.1 (3)	O33	C33	W	1.162 (8)	179.1 (6)					

Table III. Crystallographic Summary for **3a,b** and **4**

	3a	**3b**	**4**
	A. Crystal Data (−110 °C)[a]		
crystallizn solvent	toluene	mesitylene	CH_2Cl_2/pentane
a, Å	10.083 (1)	12.366 (1)	9.240 (1)
b, Å	17.509 (3)	15.436 (2)	15.474 (3)
c, Å	9.082 (1)	16.867 (2)	9.035 (2)
α, deg	96.36 (1)	90.0	96.90 (2)
β, deg	112.70 (1)	103.914 (8)	67.38 (2)
γ, deg	77.89 (1)	90.0	111.69 (1)
V, Å^3	1445.5 (3)	3125.0 (6)	1115.4 (4)
d_{measd}, g cm^{-3} (21 °C)	1.425	1.595	1.515
d_{calcd}, g cm^{-3} (−110 °C)	1.451	1.598	1.551
empirical formula	$MoP_2NC_{28}H_{29}O_3 \cdot {}^1/_2C_7H_8$	$WC_{33}H_{31}O_3P_3$	$C_{24}H_{27}NP_2NiCl_2$
fw	631.46	751.97	521.01
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Z	2	4	2
F(000), electrons	650	1488	536
	B. Data Collection (−110 °C)[b]		
scan rate, deg min^{-1}	3.0–6.0	2.0–5.0	3.0–6.0
exposure time, h	83.4	66.2	63.7
stability analysis			
computed *s*	−0.001 42 (9)	0.000 04 (4)	0.000 2 (2)
computed *t*	0.000 003 (1)	−0.000 000 (0)	0.000 000 (2)
cor range (on *I*)	1.000–1.109	*none applied*	0.986–1.000
2θ range, deg	4.0–55.0	4.0–55.0	4.0–55.0
total reflcns measd	6639	6924	5126
data cryst vol, mm^3	0.0120	0.0196	0.0093
data cryst faces	010, 110, $10\bar{1}$	100, 110, ($\bar{1}02$), ($00\bar{1}$)	100, 010, ($0\bar{1}\bar{1}$), ($0\bar{1}1$)
abs coeff (Mo Kα), cm^{-1}	5.8	41.03	12.6
transmissn factor range	0.867–0.912	0.332–0.587	0.733–0.897
	C. Structure Refinement[c]		
ignorance factor *p*	0.02	0.02	0.02
no. of reflcns used ($F > 4\sigma_F$)	5647	4761	4136
no. of variables	327	299	265
R_1, R_2	0.0314, 0.0322	0.0365, 0.0364	0.0348, 0.0349
R_1 for all data	0.0425	0.0632	0.0492
max shift/esd (non-H)	0.387	0.05	0.009
max peak in diff map, e Å^{-3}	0.71	1.64	0.74
goodness of fit, S	1.48	1.95	1.64

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 60 reflections with 25.1° $< 2\theta <$ 27.1° for **3a**, 45 reflections with 26.0° $< 2\theta <$ 28.0° for **3b**, and 60 reflections with 20.1° $< 2\theta <$ 24.0° for **4**. All diffractometer measurements were done at −35 °C for **3b**. All densities were measured by flotation in aqueous $ZnCl_2$. [b] Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system; Mo Kα radiation, λ 0.710 69 Å; ω-scan mode; scan range symmetrical over 1.0° about K$\alpha_{1,2}$ maximum; background offset 1.0 and −1.0° in ω from K$\alpha_{1,2}$ maximum. Data reduction was carried out as described in: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 381. Crystal and instrument stabilities were monitored by remeasurement of four check reflections after every 96 reflections. These data were analyzed as detailed in: Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect, B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1511. [c] Relevant expressions are as follows, where F_o and F_c represent respectively the observed and calculated structure factor amplitudes (the function minimized was $\sum w(F_o - F_c)^2$, where $w = (\sigma_F)^{-2}$): $R_1 = \sum \text{abs}(F_o - F_c)/\sum F_o$; $R_2 = [\sum w(F_o - F_c)^2/\sum w F_o^2]^{1/2}$; $S = [\sum w(F_o - F_c)^2/(m - n)]^{1/2}$.

Table IV. Fractional Coordinates and Isotropic or Equivalent Isotropic[a] Thermal Parameters (Å^2) for Non-Hydrogen Atoms of **3a**

atom	*x*	*y*	*z*	*U*
Mo	0.36151 (2)	0.219703 (12)	0.38290 (2)	0.01491 (7)
P1	0.18132 (6)	0.30165 (3)	0.16247 (7)	0.0165 (2)
P2	0.15839 (6)	0.15002 (3)	0.30838 (7)	0.0166 (2)
N	0.4422 (2)	0.13882 (11)	0.1874 (2)	0.0203 (7)
C1	0.2306 (3)	0.30507 (15)	−0.0133 (3)	0.0244 (9)
C2	0.3782 (3)	0.25338 (15)	0.0037 (3)	0.0265 (10)
C3	0.3829 (3)	0.16674 (15)	0.0201 (3)	0.0278 (10)
C4	0.4200 (3)	0.05596 (13)	0.1787 (3)	0.0236 (9)
C5	0.2628 (3)	0.04081 (15)	0.1115 (3)	0.0253 (10)
C6	0.1887 (3)	0.04853 (14)	0.2326 (3)	0.0238 (9)
C7	−0.0009 (2)	0.19739 (13)	0.1435 (3)	0.0182 (8)
C8	0.0090 (2)	0.26429 (14)	0.0797 (3)	0.0186 (8)
C9	−0.1121 (3)	0.2998 (2)	−0.0476 (3)	0.0261 (10)
C10	−0.2397 (3)	0.2697 (2)	−0.1092 (3)	0.0309 (10)
C11	−0.2500 (3)	0.2039 (2)	−0.0447 (3)	0.0300 (10)
C12	−0.1316 (3)	0.1679 (2)	0.0808 (3)	0.0246 (9)
C31	0.4785 (3)	0.14735 (14)	0.5571 (3)	0.0260 (9)
O31	0.5387 (2)	0.10522 (11)	0.6637 (2)	0.0461 (9)
C32	0.5102 (3)	0.28813 (14)	0.4386 (3)	0.0249 (9)
O32	0.5919 (2)	0.33095 (12)	0.4777 (3)	0.0419 (9)
C33	0.2871 (3)	0.28387 (14)	0.5328 (3)	0.0244 (9)
O33	0.2412 (2)	0.32186 (12)	0.6228 (2)	0.0414 (9)
C13	0.6038 (3)	0.1332 (2)	0.2505 (4)	0.0314 (11)
AC1	0.1294 (2)	0.40453 (7)	0.2145 (2)	0.0203 (9)
AC2	0.2335 (2)	0.45166 (7)	0.2457 (2)	0.0320 (11)
AC3	0.2077 (2)	0.52880 (7)	0.3008 (2)	0.0391 (12)
AC4	0.0777 (2)	0.55882 (7)	0.3247 (2)	0.0391 (12)
AC5	−0.0264 (2)	0.51169 (7)	0.2935 (2)	0.0398 (13)
AC6	−0.0006 (2)	0.43454 (7)	0.2384 (2)	0.0311 (11)
BC1	0.0812 (2)	0.14159 (9)	0.4577 (2)	0.0190 (8)
BC2	−0.0240 (2)	0.20240 (9)	0.4802 (2)	0.0324 (11)
BC3	−0.0799 (2)	0.19759 (9)	0.5968 (2)	0.0359 (11)
BC4	−0.0306 (2)	0.13198 (9)	0.6908 (2)	0.0335 (11)
BC5	0.0746 (2)	0.07117 (9)	0.6683 (2)	0.0390 (13)
BC6	0.1305 (2)	0.07598 (9)	0.5517 (2)	0.0316 (11)
TC1	0.4540 (5)	0.5003 (3)	0.8852 (3)	0.046 (2)
TC2	0.4696 (5)	0.5660 (3)	0.9881 (3)	0.048 (2)
TC3	0.5381 (5)	0.5570 (3)	1.1527 (3)	0.065 (2)
TC4	0.5910 (5)	0.4824 (3)	1.2144 (3)	0.064 (2)
TC5	0.5755 (5)	0.4167 (3)	1.1114 (3)	0.052 (2)
TC6	0.5070 (5)	0.4257 (3)	0.9468 (3)	0.0359 (13)
TC7	0.3890 (10)	0.5034 (5)	0.7111 (11)	0.071 (2)

[a] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*A_{ij}$, where A_{ij} is the dot product of the *i*th and *j*th direct-space unit cell vectors.

Table V. Fractional Coordinates and Isotropic or Equivalent Isotropic[a] Thermal Parameters (Å^2) for Non-Hydrogen Atoms of **3b**

atom	*x*	*y*	*z*	*U*
W	0.238281 (15)	0.24876 (2)	0.877466 (11)	0.02048 (6)
P1	0.04433 (13)	0.22350 (10)	0.80267 (9)	0.0247 (4)
P2	0.26816 (15)	0.13634 (11)	0.78225 (10)	0.0221 (5)
P3	0.2543 (2)	0.36065 (11)	0.77407 (10)	0.0258 (6)
C1	−0.0290 (5)	0.3086 (5)	0.7341 (4)	0.036 (2)
C2	0.0330 (6)	0.3352 (5)	0.6696 (4)	0.039 (2)
C3	0.1290 (7)	0.3989 (5)	0.6995 (5)	0.034 (2)
C4	0.3474 (7)	0.3284 (5)	0.7080 (5)	0.035 (3)
C5	0.3138 (5)	0.2453 (6)	0.6587 (3)	0.035 (2)
C6	0.3459 (7)	0.1621 (5)	0.7050 (5)	0.032 (3)
C7	0.1349 (6)	0.0966 (4)	0.7200 (4)	0.026 (2)
C8	0.0362 (5)	0.1333 (4)	0.7300 (3)	0.027 (2)
C9	−0.0647 (5)	0.1052 (5)	0.6810 (4)	0.037 (2)
C10	−0.0683 (6)	0.0422 (5)	0.6226 (4)	0.043 (2)
C11	0.0292 (6)	0.0049 (5)	0.6121 (4)	0.038 (2)
C12	0.1307 (5)	0.0323 (4)	0.6604 (4)	0.033 (2)
C31	0.4013 (5)	0.2630 (4)	0.9214 (3)	0.032 (2)
O31	0.4966 (4)	0.2699 (3)	0.9447 (3)	0.051 (2)
C32	0.1930 (6)	0.3320 (4)	0.9531 (4)	0.033 (2)
O32	0.1681 (5)	0.3779 (3)	1.0001 (3)	0.062 (2)
C33	0.2315 (5)	0.1568 (4)	0.9584 (4)	0.028 (2)
O33	0.2288 (4)	0.1026 (3)	1.0056 (3)	0.044 (2)
C13	−0.0574 (3)	0.1937 (3)	0.8610 (3)	0.0356 (14)
C14	−0.1416 (3)	0.2501 (3)	0.8704 (3)	0.061 (2)
C15	−0.2152 (3)	0.2253 (3)	0.9173 (3)	0.074 (3)
C16	−0.2045 (3)	0.1442 (3)	0.9548 (3)	0.066 (2)
C17	−0.1203 (3)	0.0878 (3)	0.9454 (3)	0.057 (2)
C18	−0.0468 (3)	0.1126 (3)	0.8985 (3)	0.040 (2)
C19	0.3398 (3)	0.0384 (2)	0.8299 (2)	0.0294 (13)
C20	0.4532 (3)	0.0457 (2)	0.8667 (2)	0.0348 (14)
C21	0.5117 (3)	−0.0255 (2)	0.9064 (2)	0.040 (2)
C22	0.4569 (3)	−0.1040 (2)	0.9093 (2)	0.044 (2)
C23	0.3435 (3)	−0.1113 (2)	0.8724 (2)	0.045 (2)
C24	0.2849 (3)	−0.0401 (2)	0.8327 (2)	0.0380 (15)
C25	0.3174 (3)	0.4667 (2)	0.8110 (2)	0.0270 (13)
C26	0.3574 (3)	0.4815 (2)	0.8945 (2)	0.0378 (15)
C27	0.3986 (3)	0.5629 (2)	0.9224 (2)	0.046 (2)
C28	0.3998 (3)	0.6296 (2)	0.8668 (2)	0.045 (2)
C29	0.3597 (3)	0.6149 (2)	0.7833 (2)	0.040 (2)
C30	0.3185 (3)	0.5334 (2)	0.7554 (2)	0.0350 (14)

[a] For anisotropic atoms, the *U* value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*A_{ij}$, where A_{ij} is the dot product of the *i*th and *j*th direct-space unit cell vectors.

isomers[2b]) and tungsten hexacarbonyl (50.5 mg, 0.144 mmol) in degassed mesitylene (10 mL) was heated at 165 °C for 16 h. An IR spectrum of the reaction solution taken at 10 h exhibited the following absorptions: 2113 (w), 1945 (s), 1925 (vw), 1900 (w), 1870 (s), 1850 cm^{-1} (s). After the 16-h heating period, the solution was filtered while hot and allowed to cool to room temperature to deposit analytically pure, light yellow crystals of X-ray quality of **3b** (38 mg, 41%): mp 320–325 °C (dec); ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.9 (m, 2 H), 7.5–7.2 (complex m, 12 H), 3.35 (m, 2 H), 2.70 (m, 2 H), 2.40 (m, 2 H), 2.25 (m, 2 H), 2.05 (m, 2 H), 1.85 (br m, 2 H); ^{13}C NMR (CD_2Cl_2) δ 132.6–128.5 (complex absorptions), 32.9 (d, J = 22.1 Hz), 30.0 (d, J = 23.5 Hz), 22.2 (s); ^{31}P{H} NMR (C_6D_6) δ 22.9 (t, J_{P-P} = 19 Hz), −31.6 (d, J_{P-P} = 19 Hz); IR (CH_2Cl_2) ν_{CO} 1945, 1860 cm^{-1}.

Anal. Calcd for $C_{33}H_{31}O_3P_3W$: C, 52.68; H, 4.15. Found: C, 52.59; H, 4.00.

Dichloro[*meso-cis*-2,10-diphenyl-6-aza-κ*N*-2,10-diphospha-κ^2*P*-bicyclo[9.4.0]pentadeca-11(1),12,14-triene]nickel(II) (4). A solution of $NiCl_2{\cdot}2DME$[15] complex (280 mg, 1.27 mmol) in THF (10 mL) was treated at room temperature with a solution of **1g** (498 mg, 1.27 mmol) in THF (2 mL). The solution turned from yellow to brown, and a brown solid precipitated (652 mg, 98%). Crystals of analytical and X-ray quality were grown from dichloromethane/hexane solution: mp 300–305 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.6–7.2 (m, 14 H), 2.9–2.5 (m, 2 H), 2.5–2.2 (m, 4 H), 2.2–1.7 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 133.3, 131.8 (t, J = 8 Hz), 128.4, 128.1, 127.0, 48.7, 28.2 (m); ^{31}P{H} NMR ($CDCl_3$) δ 53.7.

Anal. Calcd for $C_{24}H_{27}Cl_2NNiP_2$: C, 55.32; H, 5.22. Found: C, 55.14; H, 5.22.

Crystallographic Analysis. Crystals were grown by cooling or evaporation from the solvents indicated in Table III. For each compound a single crystal was affixed to a glass fiber attached to a goniometer head and then transferred to a Syntex P2$_1$ autodiffractometer, where it was maintained in a cold (−110 °C for **3a** and **4** and −35 °C for **3b**) stream of dry nitrogen for the duration of the diffraction experiments. Preliminary diffraction studies allowed determination of crystal symmetry and verification of the suitable quality of the crystals for intensity data collection. A summary of the pertinent crystal data and details of the X-ray diffraction data collection and processing are presented in Table III. The measured intensities were reduced and assigned standard deviations as described elsewhere,[16] including corrections for absorption based on measured crystal shape.

Solution and Refinement of the Structures.[17] Each structure was

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(15) Ward, L. G. L.; Pipal, J. R. *Inorg. Synth.* **1972**, *13*, 154.

(16) Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 381.

(17) Principal computer programs: least-squares lattice parameters, LSLAT by K. N. Trueblood; absorption correction, SYABS, a local version of ORABS by W. R. Busing and H. A. Levy as modified by J. M. Williams; full-matrix least-squares and Fourier calculations, SHELX-76 by G. M. Sheldrick; least-squares planes, PLANES by A. W. Cordes; thermal ellipsoid plots, ORTEP-II by C. K. Johnson. Various data processing programs were of local origin, including the following: statistical analysis of check reflections, SYSTD by T.-H. Hseu; data reduction, INCON by R. E. Davis; preparation of computer-typed tables of atomic parameters, bond lengths, bond angles, and torsion angles for publication, FUER by S. B. Larson; listings of structure factor amplitudes, FTABLE by R. E. Davis and XLFC by S. B. Larson.

Table VI. Fractional Coordinates and Isotropic or Equivalent Isotropic[a] Thermal Parameters (Å^2) for Non-Hydrogen Atoms of **4**

atom	x	y	z	U
Ni	0.21429 (4)	0.18583 (2)	0.35702 (4)	0.01384 (13)
P1	0.17974 (8)	0.21933 (4)	0.11671 (7)	0.0118 (2)
P2	−0.05168 (8)	0.23078 (4)	0.27943 (7)	0.0129 (2)
N	0.2243 (3)	0.0298 (2)	0.3029 (3)	0.0193 (9)
C1	0.3060 (3)	0.1259 (2)	0.0366 (3)	0.0177 (11)
C2	0.3574 (4)	0.0258 (2)	0.1090 (4)	0.0213 (11)
C3	0.2268 (4)	0.0026 (2)	0.1467 (3)	0.0206 (11)
C4	0.1167 (4)	−0.0044 (2)	0.3516 (3)	0.0228 (12)
C5	−0.0691 (4)	0.0534 (2)	0.2715 (3)	0.0221 (12)
C6	−0.1264 (4)	0.1470 (2)	0.3347 (3)	0.0190 (11)
C7	−0.1468 (3)	0.2473 (2)	0.0599 (3)	0.0137 (9)
C8	−0.0377 (3)	0.2425 (2)	−0.0163 (3)	0.0142 (9)
C9	−0.0969 (3)	0.2543 (2)	−0.1841 (3)	0.0176 (10)
C10	−0.2630 (3)	0.2675 (2)	−0.2748 (3)	0.0199 (11)
C11	−0.3703 (3)	0.2686 (2)	−0.1986 (3)	0.0210 (11)
C12	−0.3134 (3)	0.2589 (2)	−0.0329 (3)	0.0178 (10)
Cl1	0.48164 (8)	0.16684 (5)	0.41700 (8)	0.0237 (3)
Cl2	0.24349 (9)	0.16009 (4)	0.61198 (7)	0.0225 (3)
C13	0.2121 (2)	0.32256 (9)	0.0668 (2)	0.0134 (5)
C14	0.2487 (2)	0.33223 (9)	−0.0670 (2)	0.0178 (5)
C15	0.2610 (2)	0.41497 (9)	−0.1079 (2)	0.0210 (6)
C16	0.2367 (2)	0.48804 (9)	−0.0149 (2)	0.0202 (5)
C17	0.2001 (2)	0.47837 (9)	0.1190 (2)	0.0195 (5)
C18	0.1878 (2)	0.39563 (9)	0.1598 (2)	0.0164 (5)
C19	−0.15496 (14)	0.33851 (10)	0.3502 (2)	0.0153 (5)
C20	−0.05402 (14)	0.37529 (10)	0.4686 (2)	0.0184 (5)
C21	−0.12700 (14)	0.45638 (10)	0.5275 (2)	0.0187 (5)
C22	−0.30093 (14)	0.50070 (10)	0.4680 (2)	0.0198 (5)
C23	−0.40187 (14)	0.46391 (10)	0.3496 (2)	0.0226 (6)
C24	−0.32889 (14)	0.38282 (10)	0.2907 (2)	0.0208 (6)

[a] For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$, where A_{ij} is the dot product of the ith and jth direct-space unit cell vectors.

solved by the heavy-atom method, using heavy-atom positions determined from a sharpened Patterson map. All structures were refined by full-matrix least-squares methods, using the program SHELX-76. Neutral-atom scattering factors[18] for H, C, N, O, P, Cl, Ni, Mo, and W were used, including real and imaginary corrections for anomalous dispersion. In each structure, phenyl rings were treated as rigid groups, constrained with C–C = 1.395 Å, C–H = 1.00 Å, and C–C–C = C–C–H = 120°. Other non-H atoms were refined anisotropically, and H atoms isotropically, except as noted.[19] For each structure, refinement was continued until shifts in all parameters were less than one estimated standard deviation in the respective parameter. Further details of the refinements appear in Table III.

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Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, anisotropic thermal parameters, fractional coordinates and isotropic thermal parameters for hydrogen atoms, and full listings of bond lengths, bond angles, and torsion angles (115 pages). Ordering information is given on any current masthead page.

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(18) Scattering factors for H, C, N, O, P, and Cl were used as programmed in SHELX-76. Values for Ni, Mo, and W were obtained from: "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(19) The structure of **3a** contains one molecule of toluene solvent per unit cell, disordered about the inversion center at $^1/_2$, $^1/_2$, 0. This structure was refined with C atoms of the rigid phenyls anisotropic, H atoms of these rings having each isotropic U fixed to the final U of its C atom, and the toluene solvent treated as two rigid groups (one consisting of idealized phenyl and the other of idealized $-CH_3$, each group with isotropically refined C U values and fixed H U values). The presence of the toluene at the inversion center suggested that the correct space group might be the noncentrosymmetric alternative, $P1$. However, attempted refinement in that space group resulted in highly erratic U values and bond lengths in the macrocycle complex molecule, with no improvement of the density distribution in the toluene region, so the centrosymmetric space group was accepted as the correct choice. The structures of **3b** and **4** were refined with C atoms of the rigid phenyls isotropic. The satisfactory refinement and geometry of **4** indicated the correctness of the centrosymmetric space group.