Chelate Complexes with Aliphatic Tripodal Triisocyanide Ligands: Synthesis and Crystal Structures of *fac*-{[HC($CH_2CH_2CH_2NC$)$_3$]W(CO)$_3$}, *fac*-{[N($CH_2CH_2CH_2NC$)$_3$]W(CO)$_3$}, and the Dimer *fac,fac*-{[N($CH_2CH_2CH_2NC$)$_3$]W(CO)$_3$}$_2$

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The aliphatic tripodal triisocyanide ligands 3,3′,3″-Nitrilotripropyl isocyanide (**5**) and 3,3′,3″-Methylidynetripropyl isocyanide (**9**) react with (cycloheptatriene)metal carbonyls (M = Cr, W) to give the chelate complexes *fac*-{[HC($CH_2CH_2CH_2NC$)$_3$]M(CO)$_3$} [**10**; M = Cr (**a**), W (**b**)], and *fac*-{[N($CH_2CH_2CH_2NC$)$_3$]W(CO)$_3$} (**11**). If the reaction of **5** with (C_7H_8)W(CO)$_3$ is carried out at a high concentration of the reactants, the dimer *fac,fac*-{[N($CH_2CH_2CH_2NC$)$_3$]W(CO)$_3$}$_2$ (**12**) can be isolated in a small (up to 5%) yield together with **11**. **10b**, **11**, and **12** have been characterized by single-crystal X-ray structure analyses. Crystallographic data for **10b** [**11**] {**12**} are as follows: formula $C_{16}H_{19}N_3O_3W$ [$C_{15}H_{18}N_4O_3W$] {$C_{30}H_{36}N_8O_6W_2$}, crystal system monoclinic [monoclinic] {monoclinic}, space group $P2_1$ [$P2_1$] {$P2_1/c$}, a = 7.974(2) [7.8685(12)] {8.557(3)} Å, b = 13.588(2) [13.468(3)] {11.269(6)} Å, c = 8.104(2) [8.1525(11)] {19.004(7)} Å, β = 99.52(3) [98.501(12)] {99.51(3)}°, and Z = 2 [2] {2} The monomeric complexes of **5** and **9** contain three 12-membered chelate rings, the smallest rings observed so far for facially coordinated tripodal triisocyanides. The central nitrogen atoms of the ligand **5** in the complexes **11** and **12** are not protonated and assume the "*in*" conformation. In **10b** the central methine unit is also found in the *in* configuration, with the C–H vector pointing toward the tungsten atom. This behavior could be predicted from the signal for the methine proton in the ^{1}H NMR spectrum of **10**. This signal is shifted downfield by approximately 1 ppm compared to the corresponding signal for the free ligand due to deshielding of the proton by the NC triple bonds, which is indicative of the *in* configuration.

Introduction

The chemistry of multidentate isocyanides has recently attracted some interest due to their potential use in nuclear medicine for the complexation of ^{99m}Tc[1,2] and their interesting coordination chemistry.[3] Recently, we reported on the coordination chemistry of the tripodal aromatic isocyanide ligands **1**–**4** (Figure 1), which are all capable of forming chelate complexes in which all three isocyanide groups of one ligand coordinate to the same metal center in spite of the linear M–C≡N–R unit and the formation of large chelate rings. The monomeric W(0) complex of **1** contains three 20-membered organometallic chelate rings[4] while **2** and **3** form monomeric complexes with three 18-membered rings.[4–6] A dimeric complex of the type *fac,fac*-[(**2**)W(CO)$_3$]$_2$·2HCl, possessing a 36-membered chelate ring is also known.[7] In order to find the smallest possible ring size for chelate formation, we developed the ligand **4** and showed that this ligand is also capable of forming complexes of the type *fac*-[(**4**)W(CO)$_3$] with three 14-membered chelate rings.[6]

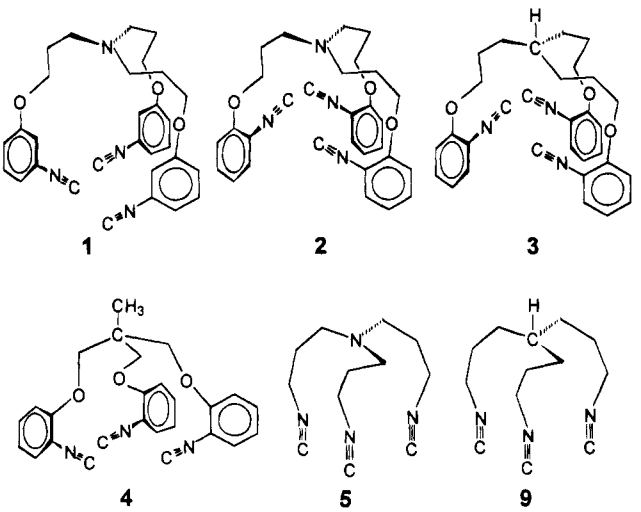

Figure 1. Tripodal triisocyanide ligands.

Our attempts to use tripodal aliphatic triisocyanides for complex formation met initially with little success.

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(1) Abrams, M. J.; Davison, A.; Jones, A. G.; Costello, C. E.; Pang, H. *Inorg. Chem.* **1983**, *22*, 2798.

(2) Hahn, F. E.; Tamm, M.; Dittler-Klingemann, A.; Neumeier, R. *Chem. Ber.* **1991**, *124*, 1683.

(3) For a recent review on the coordination chemistry of multidentate isocyanides see: Hahn, F. E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 650.

(4) Hahn, F. E.; Tamm, M. *Organometallics* **1992**, *11*, 84.

(5) Hahn, F. E.; Tamm, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 203.

(6) Hahn, F. E.; Tamm, M. *J. Organomet. Chem.* **1994**, *467*, 103.

(7) Hahn, F. E.; Tamm, M. *J. Organomet. Chem.* **1990**, *398*, C19.

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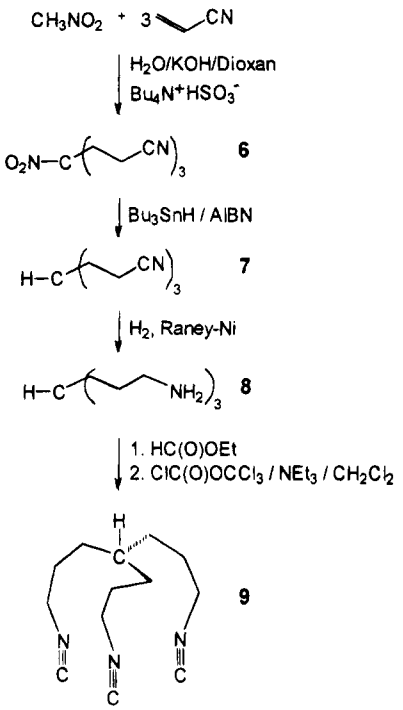
Scheme 1



The ligand **5** reacts with (cycloheptatriene)tungsten tricarbonyl to give a complex of the composition [(**5**)W(CO)$_3$]. This complex was insoluble in most common solvents and therefore we assumed that polymers and not monomeric chelates had formed.[4] However, there are two possible reasons for the insolubility of the tungsten complex of **5**: (i) polymer formation and (ii) protonation of the central nitrogen atom of the ligand, resulting in in formation of an insoluble hydrochloride, as observed for the tungsten complexes of **2**.[4-5] In an attempt to separate the possible reasons for the insolubility we synthesized the ligand **9**[8] with an all carbon backbone but with a geometry and size identical to that of **5**. **9** cannot be protonated at the central backbone atom and allows the study of the coordination chemistry of tripodal aliphatic isocyanides with fewer backbone atoms than found in the aromatic derivatives **1**–**4**. These studies were encouraged by reports that at least for bidentate aliphatic[9] or aromatic[10] diisocyanides eight backbone atoms between the isocyanide groups are sufficient for chelate formation. In this contribution we describe the synthesis of the ligand **9** and the coordination chemistry of **5** and **9** together with the crystal structures of the chelate complexes *fac*-[(**9**)W(CO)$_3$] (**10b**), *fac*-[(**5**)W(CO)$_3$] (**11**), and the dimer *fac,fac*-[(**5**)W(CO)$_3$]$_2$ (**12**).

Results and Discussion

Synthesis of 9. Ligand **9** was synthesized according to the reaction sequence depicted in Scheme 1. The key step in the synthesis of **9** was the preparation of the triamine **8** by Michael addition of 3 equiv of acrylonitrile to nitromethane[11] followed by radical denitrification[12] with tributyltin hydride and reduction of the nitrile functions with H_2/Raney nickel.[13] This procedure is superior to previously described methods employing a C_1 chain extension[14] and has meanwhile been patented.[15] The triamine **8** was then formylated and subsequently dehydrated by the method of Ugi,[16] giving **9** as a colorless oil.

Complexes of 9. As indicated earlier, **9** was developed in order to study the coordination chemistry of "small" aliphatic tripodal triisocyanides which cannot be protonated at the central backbone atom like **2**[4] and therefore should, in the case of formation of monomeric chelates, lead to complexes soluble in aprotic solvents. The reaction of equimolar amounts of **9** and [(C_7H_8)M(CO)$_3$][17] (M = Cr, W; C_7H_8 = cycloheptatriene) affords indeed the dichloromethane soluble complexes *fac*-[(**9**)M(CO)$_3$] [**10**; M = Cr (**a**), W (**b**)]. The good solubility indicated that monomeric complexes had formed. However, two configuration isomers, depicted in Figure 2 for **10a**, are possible for these complexes. A comparison of the ^{1}H NMR spectra of the ligand **9** and the complex **10a** (Figure 2) allows us to distinguish between the possible "*in*" and "*out*" configuration isomers.

Uncoordinated **9** exhibits $^2J(^{14}N,^1H)$ coupling of the isocyanide nitrogen in the ^{1}H NMR spectrum.[18] Consequently, the signals for the methylene protons D and C appear as a triplet of triplets and an unresolved multiplet at δ = 3.41 and 1.69 ppm, respectively. Upon metal coordination the coupling constants involving the isocyanide nitrogen diminish.[19] This behavior can serve as an indicator for complex formation, and indeed, the multiplicity of the signal for the protons D is reduced from a triplet of triplets in **9** to a triplet in **10a** (Figure 2). Most remarkable, however, is the chemical shift of the proton A at the central methine group. In the free ligand the signal for this proton is observed together with that for the protons B as a multiplet at δ = 1.45 ppm. In the metal complex **10a** a downfield shift of almost 1 ppm occurs for the signal of proton A which now appears as the expected septet at δ = 2.43 ppm. This behavior is only consistent with complex **10a** assuming the *in* configuration. Only in this case would the proton A penetrate into the deshielding area of the N≡C triple bond and would its ^{1}H NMR signal experience the observed downfield shift. The signal for the proton A in a complex assuming the *out* configuration should be found in the region typical for a methine proton in a saturated aliphatic hydrocarbon around δ = 1.5 ppm.

The opposite effect, induction of a high-field shift by interaction of methine hydrogens with the shielding

(8) Hahn, F. E.; Tamm, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1212.
(9) (a) Kawakami, K.; Okajima, M.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2327. (b) Yaneff, P. V.; Powell, J. *J. Organomet. Chem.* **1979**, *179*, 101.
(10) (a) Angelici, R. J.; Quick, M. H.; Kraus, G. A.; Plummer, D. T. *Inorg. Chem.* **1982**, *21*, 2178. (b) Plummer, D. T.; Karcher, B. A.; Jacobson, R. A.; Angelici, R. J. *J. Organomet. Chem.* **1984**, *260*, 347.
(11) (a) Bruson, H. A.; Riener, T. W. *J. Am. Chem. Soc.* **1943**, *65*, 23. (b) Newkome, G. R.; Moorefield, C. N.; Theriot, K. J. *J. Org. Chem.* **1988**, *53*, 5552.
(12) Ono, N.; Kaji, A. *Synthesis* **1986**, 693.
(13) Chin, J.; Banaszczyk, M.; Jubian, V.; Zou, X. *J. Am. Chem. Soc.* **1989**, *111*, 186.
(14) Ricci, A.; Danieli, R.; Rossini, S. *J. Chem. Soc., Perkin Trans.* **1976**, 1691.
(15) Yotsui, K.; Hayashi, K.; Haseyama, R.; Sasagawa, K.; Yamaguchi, T. *Chem. Abstr.* **1990**, *113*, 192788j.
(16) Ugi, I.; Fetzer, U.; Eholzer, U.; Knupfer, H.; Offermann, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 472.
(17) M = Cr: King, R. B. *Organometallic Syntheses: Volume I, Transition Metal Compounds*; Academic Press: New York, 1965; p 123. M = W: King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.
(18) Kuntz, I. D., Jr.; von Schleyer, P.; Allerhand, A. *J. Chem. Phys.* **1961**, *35*, 1533.
(19) Yamamoto, Y.; Yamazaki, H. *J. Coord. Chem.* **1977**, *6*, 241.

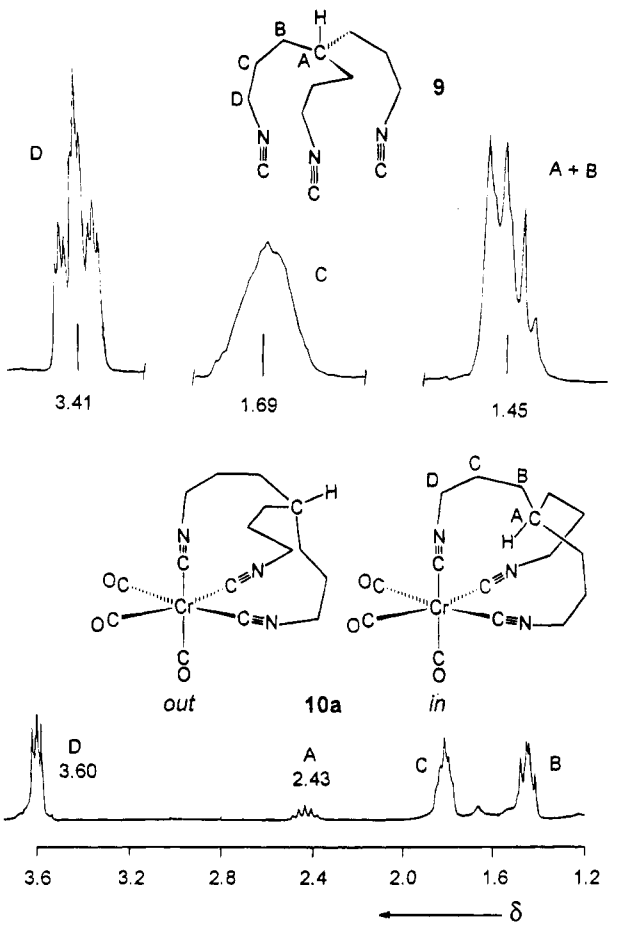


Figure 2. ^{1}H NMR spectra of the ligand **9** (top, 400 MHz) and its chromium(0) complex **10a** (bottom, 270 MHz).

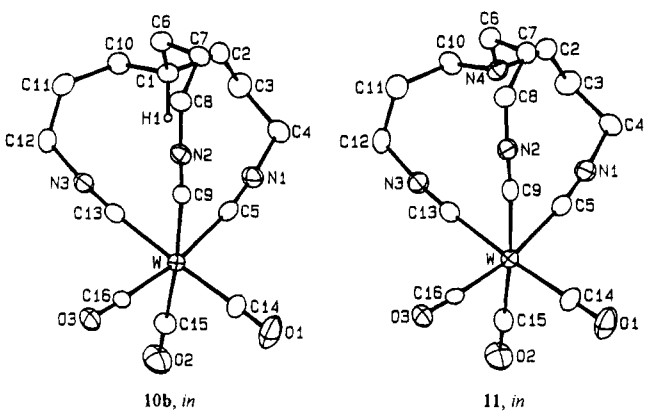


Figure 3. Molecular structures of the complexes *fac*-[(**9**)W(CO)$_3$] (**10b**) (left) and *fac*-[(**5**)W(CO)$_3$] (**11**) (right), showing the employed numbering scheme.

area of an aromatic ring systems, has been described. The ^{1}H NMR signal for the apical methine hydrogen in certain cyclophanes can be observed as low as $\delta = -4.03$ ppm.[20]

The tungsten derivative **10b** is presumably isostructural with **10a** and shows a similar behavior in the ^{1}H NMR spectrum. Crystal of **10b** can be grown from a dichloromethane/hexane solution. Their X-ray structure analysis (Figure 3, left) shows that the assumptions made above about the configuration of the central methine group are correct. The tungsten atom in **10b**

(20) Pascal, R. A., Jr.; Winans, C. G.; Van Engen, D. *J. Am. Chem. Soc.* **1989**, *111*, 3007.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 10b, 11, and 12[a]

	10b	11	12
W–C5	2.138(3)	2.130(4)	2.116(12)
W–C9	2.131(3)	2.125(4)	2.144(13)[b]
W–C13	2.119(3)	2.114(4)	2.120(13)
W–C14	2.005(3)	1.999(4)	1.991(13)
W–C15	1.994(3)	1.996(4)	1.995(12)
W–C16	1.989(3)	1.983(4)	2.017(13)
O1–C14	1.153(4)	1.157(5)	1.168(12)
O2–C15	1.158(4)	1.157(5)	1.158(11)
O3–C16	1.152(4)	1.160(5)	1.141(12)
N1–C5	1.159(4)	1.158(5)	1.146(12)
N2–C9	1.151(4)	1.165(5)	1.143(11)
N3–C13	1.152(4)	1.157(5)	1.160(13)
C1–H1	1.11(5)		
C5–W–C9	81.7(1)	79.9(1)	90.0(5)[b]
C5–W–C13	83.1(1)	81.5(1)	84.4(4)
C5–W–C14	93.9(1)	95.2(2)	91.8(4)
C5–W–C15	98.1(1)	99.1(2)	90.1(6)
C5–W–C16	170.5(1)	169.2(1)	176.1(4)
C9–W–C13	82.2(1)	81.2(1)	86.9(4)[b]
C9–W–C14	95.8(1)	96.3(2)	90.6(4)[b]
C9–W–C15	174.6(1)	174.3(1)	179.7(6)[b]
C9–W–C16	90.3(1)	91.0(1)	91.7(4)[b]
C13–W–C14	176.7(1)	176.2(1)	175.5(4)
C13–W–C15	92.4(1)	93.1(2)	92.8(4)
C13–W–C16	90.9(1)	91.5(1)	92.2(4)
C14–W–C15	89.6(2)	89.3(2)	89.7(4)
C14–W–C16	91.8(1)	91.5(2)	97.1(4)
C15–W–C16	89.5(1)	89.4(2)	88.1(6)
C4–N1–C5	174.7(3)	174.8(4)	167(2)
C8–N2–C9	173.4(3)	174.6(4)	175.6(13)
C12–N3–C13	174.1(3)	171.6(4)	169.2(12)
C2–N4–C6		107.9(4)	113.3(9)
C2–N4–C10		107.8(3)	112.6(9)
C6–N4–C10		109.4(4)	113.6(10)
W–C5–N1	170.3(3)	170.1(3)	175.8(12)
W–C9–N2	171.6(2)	171.3(3)	177.5(11)[c]
W–C13–N3	174.5(3)	173.6(3)	178.1(10)
W–C14–O1	177.9(3)	179.2(4)	177.2(10)
W–C15–O2	177.2(3)	177.4(4)	177.4(13)
W–C16–O3	177.8(3)	177.2(3)	176.1(10)

[a] Estimated standard deviations are given in parentheses in this and all subsequent tables. [b] Distances and angles involving C9* (see Figure 4) are listed; symmetry code (*) $1-x, 1-y, 1-z$. [c] Angle involving W* is listed (see Figure 4); symmetry code (*) $1-x, 1-y, 1-z$.

is coordinated in a distorted octahedral fashion by three isocyanide groups of one ligand **9** and three carbonyl groups. The central methine group assumes the *in* configuration. This brings the central hydrogen atom H1 into the deshielding area of the anisotropy cones of the N≡C triple bonds. The distances from H1 (the coordinates of H1 were take from a difference Fourier map and refined in the least-squares procedure) to the nitrogen atoms N1–N3 fall in the range from 2.69(4) to 2.78(5) Å. The C1–H1 vector points toward the tungsten atom [angle C1–H1–W 177(3)°]. This geometry explains perfectly well the observed downfield shift for the ^{1}H NMR signal of proton A. The IR absorptions for the NC vibration in **10b** were observed at 2167 and 2122 cm^{-1}. These values are significantly higher than in the similar complexes with tripodal aromatic isocyanides[4–6] and reflect the reduced ability of the aliphatic isocyanides to function as effective π-acceptors. This leads also to lower wavenumbers for the CO vibrations in **10b** when compared to the values for complexes with aromatic triisocyanides.[4] These effects, however, are not reflected in the W–CO, W–CN, C≡O, and C≡N bond lengths (Table 1). Within experimental

error (3σ) identical values are observed for these parameters in complexes with aromatic and aliphatic ligands.

The crystal structure of **10b** shows that aliphatic tripodal triisocyanides are also capable of forming chelate complexes. The number of backbone atoms between the isocyanide functions can be reduced to only seven without impairing the ligands ability to form chelates. In comparison with complexes of ligands with larger backbones[4-7] it should be noted that the smaller chelate rings fromed in **10b** do not require the isocyanide functions to deviate from linearity significantly more than the deviation observed for ligands with a larger backbone.

Complexes of 5. In light of the results obtained with ligand **9**, we reinvestigated the coordination chemistry of **5**. Early experiments to coordinate this ligand to a $W(CO)_3$ fragment exclusively led to insoluble materials, and we therefore assumed, wrongly, that the ligand for geometric reasons (size of backbone) was not capable of forming chelates.[4] Since **5** and **9** are almost identical in size, this conclusion was reconsidered. Reaction of **5** with $[(C_7H_8)W(CO)_3]$ in dichloromethane at high dilution leads indeed to a soluble complex. After chromatographic purification this complex exhibited spectroscopic and microanalytical data consistent with the formulation $[(\mathbf{5})W(CO)_3]$. Single crystals of this complex can be grown from a dichloromethane/hexane solution. Their X-ray structure analysis shows (Figure 3, right), that indeed a chelate complex *fac*-$[(\mathbf{5})W(CO)_3]$ (**11**) had formed. The only difference between **10b** and **11** is the substitution of the CH unit in **10b** for a nitrogen in **11**. Consequently, the molecular structures of the complexes are very similar. Indeed, comparable bond distances and angles are identical within experimental error in **10b** and **11** (Table 1). The central nitrogen atom in **11** is not protonated and assumes the *in* conformation.

A comparison of the N≡C bond length in the free ligand **5**[5] and complex **11** shows that even the aliphatic isocyanide ligand experiences some back-bonding which results in a slight lengthening of this bond in the metal complex [*d*(N≡C) 1.135(3) Å in **5**,[5] 1.157(5)−1.165(5) Å in **11**]. This lengthening is only observed in tricarbonyl complexes. In pentacarbonyl complexes like $\{H_3C(CH_2NC)_2[CH_2NCCr(CO)_5]\}$ with coordinated and noncoordinated isocyanide functions in the same molecule the isocyanide loses out in the competition for back-bonding with the five carbonyl and no difference in the N≡C bond lengths between coordinated and noncoordinated isocyanides is observed.[21]

Ligand **5** shows a tendency to form higher oligomers, similar to the behavior we observed for the aromatic ligand **2**.[7] While **11** is the main product in the reaction of **5** with $(C_7H_8)W(CO)_3$ the chromatographic purification of the reaction mixture allows isolation of the dimeric complex *fac,fac*-$[(\mathbf{5})W(CO)_3]_2$ (**12**) in a small (up to 5%) yield. Crystals of **12** can be grown from a dichloromethane/hexane solution. Their X-ray structure analysis (Figure 4) shows that an isocyanide bridged, centrosymmetric dimer had formed. Two isocyanide functions of one ligand coordinate to one tungsten atom, while the third group bridges to another tungsten atom.

(21) Hahn, F. E.; Tamm, M. *Chem. Ber.* **1992**, *125*, 119.

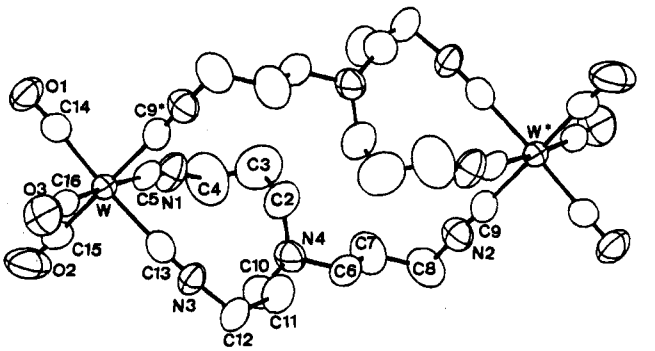


Figure 4. Molecular structure of the dimer *fac,fac*-$\{[(\mathbf{5})W(CO)_3]_2\}$ (**12**) with the employed numbering scheme. The molecule is located on an inversion center in the unit cell. The asymmetric unit contains one half molecule of **12**; symmetry code (*) $1-x, 1-y, 1-z$.

This leads to the formation of 12- and 24-membered chelate rings.

Both tungsten atoms are coordinated in a slightly distorted octahedral fashion. Bond lengths and angles in **12** (Table 1) are very similar to the equivalent parameters in **11**. The only noticeable differences are the larger C−N4−C angles in **12** when compared to the angles at N4 in **11**. In both **11** and **12** the central nitrogen atom of the ligand is not protonated and assumes the *in* conformation. A similar behavior has been observed for the tungsten complexes of the ligand **2**. This ligand forms the monomeric complex *fac*-$[(\mathbf{2})W(CO)_3]\cdot HCl$[4] and in a small yield the dimeric *fac,fac*-$[(\mathbf{2})W(CO)_3]_2\cdot 2HCl$.[7] However, in these complexes the central nitrogen atoms are both protonated and assume the *out* configuration.

Conclusions

Tripodal triisocyanides like **5** and **9** with only seven atoms between the isocyanide functions can form monomeric chelates with group VI tricarbonyls. This leads to the smallest chelate rings involving multidentate isocyanides observed so far. Higher oligomers are obtained in small yields with these ligands. The central backbone group of the ligand in the complexes (CH or N) assumes exclusively the *in* conformation or configuration, respectively. We assume that the reduced number of backbone atoms in the ligands **5** and **9** compared to **1**−**3** enforces the *in* geometry.

Experimental Section

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. ^1H NMR spectra were recorded on Bruker WP 80 (80-MHz) or WH 400 (400-MHz) instruments, and ^{13}C NMR spectra on a Bruker WP 80 SY (20.15-MHz) spectrometer. Infrared spectra were taken in KBr on a Perkin-Elmer 580 B instrument. Elemental analyses (C, H, N) were performed at the Technische Universität Berlin on a Perkin-Elmer 240 C elemental analyzer. Mass spectra (EI, 70 eV) were recorded on a Varian MAT 311 instrument. Ligand **5** was prepared by literature methods.[5]

3,3′,3″-Nitromethylidynetripropionitrile (6). Nitromethane (20 g, 328 mmol) was dissolved in a mixture of 100 mL of acrylonitrile, 100 mL of dioxane, and 20 mL of water in a three necked round bottom flask equipped with a condenser and dropping funnel. The dropping funnel was charged with

a solution of 4.5 g of KOH dissolved in 10 mL of water. The contents of the dropping funnel was added dropwise with stirring to the round bottom flask. The reaction is strongly exothermic. After all KOH/H_2O was added, the reaction mixture was stirred for 18 h at room temperature. Then diluted HCl was added until the pH was neutral. Dichloromethane (500 mL) was added, and the organic phase was separated out, washed with water, and dried. The solvent was removed in vacuo and the residue was recrystallized from ethanol giving **6** as colorless needles (51.4 g, 71% relative to nitromethane). Anal. Calcd for $C_{10}H_{12}N_4O_2$ (M_r = 220.23): C, 54.54; H, 5.49; N, 25.44. Found: C, 54.67; H, 5.71; N, 26.02. ^{1}H NMR (80 MHz, acetone-d_6): δ 2.80–2.35 (m, 12 H, AA'BB' system). ^{13}C{H} NMR (acetone-d_6): δ 119.18 (*C*N), 91.82 (O_2N–*C*), 30.76 (O_2N–C–*C*H_2), 12.50 (H_2*C*–CN).

3,3',3''-Methylidynetripropionitrile (7). A mixture made from **6** (28 g, 127 mmol), tributyltin hydride (42 mL, 156 mmol), and AIBN (4.4 g, 27 mmol, AIBN = azabis(isobutyronitrile)) was refluxed for 12 h in 350 mL of dry benzene. Initially, **6** was only suspended but it dissolved during the reaction. The solvent was then removed in vacuo, leaving a crystalline mass. This was washed with benzene and recrystallized from ethanol, giving **7** as colorless crystals (19.83 g, 89%). Anal. Calcd for $C_{10}H_{13}N_3$ (M_r = 175.23): C, 68.54; H, 7.48; N, 23.98. Found: C, 67.44; H, 7.49; N, 23.30. ^{1}H NMR (80 MHz, acetone-d_6): δ 2.53 (t, 6 H, C*H*$_2$–CN), 1.75 (m, 7 H, HC–C*H*$_2$ and *H*–C). ^{13}C{H} NMR (acetone-d_6): δ 120.45 (*C*N), 36.36 (H*C*–CH$_2$), 28.34 (HC–*C*H$_2$), 14.36 (H_2*C*–CN).

3,3',3''-Methylidynetris(propylamine) (8). A 5-g (29-mmol) sample of **7** was dissolved in a Raney nickel suspension (prepared by dissolving 10 g of Ni/Al alloy together with 2.8 g of NaOH in 100 mL of dry ethanol[22]). The mixture was hydrogenated at 3 bars of hydrogen pressure. Hydrogen uptake was complete after 3 h. The catalyst was removed by filtration and washed with ethanol. The combined ethanol fractions were stripped of the solvent, and the residue was extracted with dichloromethane. The dichloromethane solution was then filtered through neutral aluminum oxide. After removal of the solvent the oily residue was distilled (bp 110 °C at 0.04 mbar), giving **8** as a colorless oil (4.53 g, 83%). Anal. Calcd for $C_{10}H_{25}N_3$ (M_r = 187.33): C, 64.12; H, 13.45; N, 22.43. Found: C, 65.25; H, 12.88; N, 21.28. ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.52 (t, 6 H, C*H*$_2$–NH$_2$), 1.16 (m br, 13 H, HC–C*H*$_2$, *H*–C, and CH$_2$–C*H*$_2$–CH$_2$), 0.94 (s, N*H*$_2$). ^{13}C{H} NMR ($CDCl_3$): δ 41.74 (*C*H$_2$–NH$_2$), 36.17 (H*C*–CH$_2$), 30.00 (CH$_2$–*C*H–CH$_2$), 29.83 (HC–*C*H$_2$). The triamine **8** is hygroscopic, and therefore it was difficult to obtain analytically pure samples of the free amine. The hydrochloride **8**·3HCl is easlier to purify, and a small sample was prepared for analytical reasons by addition of aqueous HCl to an ethanol solution of **8** and recrystallization of the trihydrochloride from ethanol. Anal. Calcd for $C_{10}H_{28}N_3Cl_3$ (M_r = 296.71): C, 40.48; H, 9.51; N, 14.16. Found: C, 40.17; H, 9.23; N, 14.07. ^{1}H NMR (80 MHz, D_2O): δ 2.91 (t, 6 H, C*H*$_2$–NH$_3$), 1.80–1.60 (m br, 13 H, HC–C*H*$_2$, *H*–C, and CH$_2$–C*H*$_2$–CH$_2$). ^{13}C{H} NMR (D_2O/CD_3OD): δ 40.90 (*C*H$_2$–NH$_3$), 37.00 (H*C*–CH$_2$), 30.31 (CH$_2$–*C*H$_2$–CH$_2$), 25.10 (HC–*C*H$_2$).

3,3',3''-Methylidynetripropyl isocyanide (9). Two reactions must be carried out for the preparation of **9** from **8**. First the the primary amine groups were formylated by refluxing a mixture of 4.5 g (24 mmol) of **8** in formic acid ethyl ester for 2 h. Upon removal of the solvents in vacuo a viscous oil (6.5 g, 99%) of 3,3',3''-[methylidynetris(trimethylene)]triformamide was obtained. This material crystallized upon storage for 1 week. It was not further purified and was characterized by its ^{1}H NMR spectrum (80 MHz, CD_3OD): δ 8.02 (s, 3 H, NHC(O)*H*), 3.19 (t, 6 H, C*H*$_2$–NH), 1.67–1.16 (m br, 13 H, HC–C*H*$_2$, *H*–C, and CH$_2$–C*H*$_2$–CH$_2$). The triformamide (3.18 g, 12 mmol) was suspended with stirring in 50 mL of dichloromethane in a three necked round bottom flask equipped with gas inlet, cooler, and septum. Triethylamine (10 mL) was added, and the suspension was cooled to 0 °C. Then 2.2 mL of diphosgene [Cl_3C–O–C(O)Cl] was added dropwise over the period of 1 h with a syringe via the septum. The reaction mixture was then allowed to warm to room temperature and was stirred for another 30 min. The organic layer was separated out, washed once with water (50 mL) and twice with an aqueous solution of soda (50 mL, 10% Na_2CO_3), and dried over Na_2SO_4. After the solvent was removed in vacuo a brown oil was obtained. This was purified by chromatography on neutral aluminum oxide (4% water) with dichloromethane, giving **9** as an odorless colorless oil (1.25 g, 48%). Anal. Calcd for $C_{13}H_{19}N_3$ (M_r = 217.32): C, 71.85; H, 8.81; N, 19.34. Found: C, 71.32; H, 8.27; N, 20.46. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.41 (tt, $^2J(^{14}N,^1H)$ = 1.6 Hz, 6 H, C*H*$_2$–NC), 1.69 (m, 6 H, CH$_2$–C*H*$_2$–CH$_2$), 1.49–1.43 (m, 7 H, HC–C*H*$_2$ and *H*–C). ^{13}C{H} NMR ($CDCl_3$): δ 156.07 (t, $^1J(^{14}N,^{13}C)$ = 5.6 Hz, CH$_2$–N*C*), 41.52 (t, $^1J(^{14}N,^{13}C)$ = 6.7 Hz, *C*H$_2$–NC), 35.35 (H*C*–CH$_2$), 29.60 (CH$_2$–*C*H$_2$–CH$_2$), 25.82 (HC–*C*H$_2$). IR: $\tilde{\nu}$ 2148 (st, CN).

***fac*-{[HC(CH$_2$CH$_2$CH$_2$NC)$_3$]Cr(CO)$_3$} (10a).** In a 100-mL three necked round bottom flask equipped with a condenser and two rubber seals was placed 20 mL of benzene. The benzene was heated to reflux and 0.3 g of **9** (1.4 mmol dissolved in 10 mL of benzene) and 0.315 g of (C_7H_8)Cr(CO)$_3$ (1.4 mmol dissolved in 10 mL of benzene) were added simultaneously with two syringes at a rate that the deep red chromium starting material always decolorized upon addition (ca. 2 h). Insoluble materials were separated by filtration. Thin layer chromatography still showed the presence of higher oligomers. Chromography on neutral aluminum oxide (4% water) with dichloromethane/hexane 1:1 (v:v) gave **10a** as a white powder (0.11 g, 23%). Anal. Calcd for $C_{16}H_{19}CrN_3O_3$ (M_r = 353.34): C, 54.39; H, 5.42; N, 11.89. Found: C, 54.64; H, 5.67; N, 11.94. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 3.60 (t, 6 H, C*H*$_2$–NC) 2.43 (septet, 1 H, *H*–C), 1.82 (quintet, 6 H, CH$_2$–C*H*$_2$–CH$_2$), 1.44 (dt, 6 H, HC–C*H*$_2$). ^{13}C{H} NMR (CD_2Cl_2, 67.89 MHz): δ 206.57 (Cr–*C*O), 151.00 (br, Cr–*C*N), 46.09 (*C*H$_2$–NC), 35.49 (H*C*–CH$_2$), 34.88 (CH$_2$–*C*H$_2$–CH$_2$), 25.61 (HC–*C*H$_2$). IR: $\tilde{\nu}$ 2162 (s, CN), 2120 (s, CN), 1933 (vs, CO) 1859 (vs, CO).

***fac*-{[HC(CH$_2$CH$_2$CH$_2$NC)$_3$]W(CO)$_3$} (10b).** Solutions of the ligand **9** (1.52 g, 7.0 mmol, in 20 mL of dichloromethane) and (C_7H_8)W(CO)$_3$ (2.52 g, 7.0 mmol, in 50 mL of dichloromethane) were added simultaneously from two dropping funnels over a period of 12 h to 100 mL of dichlormethane in a round bottom flask. The reaction mixture was then stirred for an additional 12 h. A clear yellow solution was then separated from insoluble material (probably oligomers) by filtration and the solvents were stripped in vacuo, giving a yellow powder. HPLC (reversed phase RP-18, eluent methanol) showed the presence of four products with a retention time in minutes (area) of 1.16 (69.5), 1.35 (20.0), 1.68 (7.4), and 2.04 (2.8). Reference chromatograms indicated the absence of both starting materials. Preparative chromatography on neutral aluminum oxide (4% water) with dichloromethane/hexane (1:1, v:v) produced an off-white microcrystalline powder. This can be recrystallized by evaporation of the dichloromethane from a dichloromethane/hexane solution to give colorless crystals (0.44 g, 13%). Anal. Calcd for $C_{16}H_{19}N_3O_3W$ (M_r = 485.25): C, 39.61; H, 3.95; N, 8.66. Found: C, 38.71; H, 3.83; N, 8.36. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 3.65 (t, 6 H, C*H*$_2$–NC) 2.48 (septet, 1 H, *H*–C), 1.86 (quintet, 6 H, CH$_2$–C*H*$_2$–CH$_2$), 1.50 (dt, 6 H, HC–C*H*$_2$). ^{13}C{H} NMR (CD_2Cl_2, 67.89 MHz): δ 206.57 (W–*C*O), 150.78 (br, W–*C*N), 46.09 (*C*H$_2$–NC), 35.49 (H*C*–CH$_2$), 34.87 (CH$_2$–*C*H$_2$–CH$_2$), 25.60 (HC–*C*H$_2$). IR: $\tilde{\nu}$ 2167 (s, CN), 2122 (s, CN), 1930 (vs, CO) 1849 (vs, CO). MS (LR, 70 eV, *m/z*): 485 (M^+, 27.3), 457 (M^+ – CO, 17.0), 429 (M^+ – 2CO, 100.0), 401 (M^+ – 3CO, 95.5).

***fac*-{[N(CH$_2$CH$_2$CH$_2$NC)$_3$]W(CO)$_3$} (11) and *fac,fac*-{[N(CH$_2$CH$_2$CH$_2$NC)$_3$]W(CO)$_3$}$_2$ (12).** The preparation of complexes **11** and **12** was carried out like the synthesis of **10b** from **5** (0.89 g, 4 mmol, in 25 mL of dichloromethane) and

(22) Billica, H. R.; Adkins, H. *Org. Synth.* **1955**, *3*, 176.

Table 2. Summary of Crystal Structure Data

	10b	11	12
cryst size, mm	0.62 × 0.45 × 0.40	0.45 × 0.25 × 0.20	0.35 × 0.20 × 0.20
formula	$C_{16}H_{19}N_3O_3W$	$C_{15}H_{18}N_4O_3W$	$C_{30}H_{36}N_8O_6W_2$
fw	485.2	486.2	972.4
space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)	$P2_1/c$ (No. 14)
a, Å	7.974(2)	7.8685(12)	8.557(3)
b, Å	13.588(2)	13.468(3)	11.269(6)
c, Å	8.104(2)	8.1525(11)	19.004(7)
β, deg	99.52(3)	98.50(12)	99.51(3)
V, Å^3	866.0(6)	854.4(5)	1807(1)
Z	2	2	2
d_c, g/cm^3	1.861	1.890	1.787
d_o, g/cm^3	1.88	1.90	1.80
μ_c, cm^{-1}	68.29	69.23	61.29
radiation (λ, Å)		Mo Kα (0.710 73)	
2θ range, deg	$2 \le 2\theta \le 55$	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$
hkl range	$0 \le h \le 10$	$0 \le h \le 9$	$-10 \le h \le 10$
	$-17 \le k \le 17$	$-15 \le k \le 15$	$0 \le k \le 13$
	$-10 \le l \le 10$	$-9 \le l \le 9$	$0 \le l \le 22$
scan speed (θ), deg/min	variable min 1.5, max 5.5	variable min 1.4, max 5.5	variable min 1.5, max 29.3
scan width, $\Delta\theta$, deg	0.75 + 0.35[tan(θ)]	0.70 + 0.35[tan(θ)]	0.60 + 0.60[tan(θ)]
no. of unique data	3981	3015	2853
no. of obsd data, $F_o^2 \ge 3\sigma(F_o^2)$	3882	2930	1871
R, %[a]	1.49	1.51	3.83
R_w, %[a]	2.16	1.99	3.02
p factor[a]	0.04	0.03	
GOF[a]	1.006	1.195	
no. of variables	211	208	209
max shift/error	<0.01	<0.01	0.001
res electr dens, e/Å^3	1.2 near W	1.5 near W	0.682 near W
abs cor	empirical, 5 Ψ-scans	empirical, DIFABS[b]	empirical, DIFABS
min, max cor	0.718, 0.999	0.881, 1.110	0.920, 1.077

[a] See ref 26. [b] See ref 24.

$(C_7H_8)W(CO)_3$ (1.35 g, 4 mmol, in 25 mL of dichloromethane) in 100 mL of dichloromethane. After separation of insoluble oligomers by filtration and removal of the solvents in vacuo, the crude reaction product was subjected to preparative chromatography on neutral aluminum oxide (4% water) with dichloromethane/hexane (2:1, v:v). The first fraction contained the monomer **11** (0.29 g, 15%). A second fraction containing the dimer **12** was subsequently eluted (0.04 g). Air-stable, colorless crystals of **11** can be grown by slow evaporation of the dichloromethane from a dichloromethane/hexane solution (1:1, v:v). The dimer **12** was crystallized by slowly diffusing pentane into a dichloromethane solution. Analytical data for **11** follow. Anal. Calcd for $C_{15}H_{18}N_4O_3W$ (M_r = 486.18): C, 37.06; H, 3.73; N, 11.52. Found: C, 36.6; H, 3.21; N, 11.0. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 3.65 (t, 6 H, CH_2–NC) 2.47 (t, 6 H, N–CH_2–CH_2), 1.94 (quint, 6 H, CH_2–CH_2–CH_2). ^{13}C{H} NMR (CD_2Cl_2, 67.89 MHz): δ 207.40 (W–CO), 151.78 (br, W–CN), 56.77 (N–CH_2), 45.18 (CH_2–NC), 28.33 (CH_2–CH_2–CH_2). IR: $\tilde{\nu}$ 2160 (s, CN), 2115 (s, CN), 1932 (vs, CO) 1854 (vs, CO). MS (LR, 70 eV, *m/z*): 486 (M^+, 73.6), 458 (M^+ − CO, 51.2), 430 (M^+ − 2CO, 55.9), 402 (M^+ − 3CO, 100.0). Complex **12** was only characterized by single crystal X-ray structure analysis.

Crystal Structure Analyses. 10b, **11**, and **12** form air-stable crystals. Suitable specimens of **10b** and **11** were selected in air and mounted in the cold stream [−100(5) °C] of an Enraf-Nonius CAD4 diffractometer. A crystal of **12** was mounted at room temperature on a Syntex $P2_1$ diffractometer. Important crystal and data collection details are listed in Table 2. Data were collected using ω–2Θ scans at −100(5) °C for **10b** and **11** and at room temperature for **12** and reduced structure factors[23] (and their esd's) by correcting for scan speed, Lorentz, and polarization effects. No crystal decay was detected. The data for **10b** were corrected for absorption by means of five ψ scans, while empirical corrections using the program DIFABS[24] were applied to the data for **11** and **12** after all atoms in the asymmetric unit were refined with isotropic thermal parameters. Systematically absent reflections for **10b** and **11** ($0k0$, $k = 2n + 1$) indicated the space group to be either $P2_1$ or $P2_1/m$. $P2_1$ was chosen because the measured density of the crystals showed that Z had to be 2 and, since the

Table 3. Fractional Coordinates for 10b

atom	x	y	z	B_{eq},[a] Å^2
W	0.78974(1)	0.000	0.77703(1)	1.558
O1	0.4393(3)	−0.1040(2)	0.7964(4)	4.14
O2	0.8205(4)	−0.1238(2)	0.4545(3)	4.08
O3	0.6077(3)	0.1672(2)	0.5464(3)	2.53
N1	1.0215(3)	−0.1304(2)	1.0717(3)	2.28
N2	0.8093(3)	0.1448(2)	1.1027(3)	2.01
N3	1.1587(3)	0.1068(2)	0.7897(3)	2.18
C1	1.2260(3)	0.0822(3)	1.2144(3)	2.02
C2	1.2719(3)	−0.0072(3)	1.3312(3)	2.59
C3	1.2992(4)	−0.1074(3)	1.2528(5)	2.75
C4	1.1390(4)	−0.1691(2)	1.2106(4)	2.50
C5	0.9343(4)	−0.0926(2)	0.9612(4)	1.99
C6	1.1726(4)	0.1685(2)	1.3165(4)	2.11
C7	0.9995(4)	0.1618(2)	1.3722(4)	2.18
C8	0.8509(4)	0.2034(2)	1.2513(4)	2.18
C9	0.7892(3)	0.0923(2)	0.9895(3)	1.69
C10	1.3820(4)	0.1098(2)	1.1355(4)	2.24
C11	1.3593(4)	0.1920(2)	1.0032(4)	2.37
C12	1.3195(3)	0.1577(2)	0.8234(4)	2.17
C13	1.0283(4)	0.0686(2)	0.7764(3)	1.93
C14	0.5688(4)	−0.0672(2)	0.7915(4)	2.42
C15	0.8110(4)	−0.0804(2)	0.5756(4)	2.32
C16	0.6727(4)	0.1044(2)	0.6288(3)	1.70
H1	1.124(5)	0.065(3)	1.107(5)	3.1

[a] $B_{eq} = {}^8/_3\pi^2[\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j]$; the positional parameters for H1 were refined in the least-squares procedure with B_{eq} held constant; the z coordinate for W was fixed to define the origin in the polar space group $P2_1$.

(23) Neutral scattering factors were used: Cromer, D. T.; Waber, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321. For hydrogen atoms: Stewart, R. F. *J. Chem. Phys.* **1965**, *42*, 3175. Terms of anomalous dispersion from: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(24) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

Table 4. Fractional Coordinates for 11

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
W	0.79039(1)	0.000	0.77712(1)	1.613
O1	0.4322(4)	−0.1009(2)	0.7982(4)	3.91
O2	0.8195(5)	−0.1272(2)	0.4579(4)	3.91
O3	0.6168(3)	0.1709(2)	0.5488(3)	2.48
N1	1.0193(4)	−0.1282(2)	1.0724(4)	2.33
N2	0.8182(4)	0.1449(2)	1.1036(4)	2.12
N3	1.1667(4)	0.1050(2)	0.7935(4)	2.30
N4	1.2299(3)	0.0800(3)	1.2191(3)	2.13
C2	1.2798(4)	−0.0065(4)	1.3283(4)	2.50
C3	1.3006(5)	−0.1050(3)	1.2428(6)	2.80
C4	1.1368(5)	−0.1663(3)	1.2095(5)	2.52
C5	0.9327(5)	−0.0913(3)	0.9618(5)	2.03
C6	1.1833(5)	0.1620(3)	1.3238(5)	2.25
C7	1.0036(5)	0.1560(3)	1.3728(4)	2.13
C8	0.8606(5)	0.2026(3)	1.2515(5)	2.18
C9	0.7941(4)	0.0928(3)	0.9884(4)	1.94
C10	1.3805(5)	0.1090(3)	1.1420(5)	2.37
C11	1.3506(5)	0.1928(3)	1.0123(5)	2.71
C12	1.3237(4)	0.1595(3)	0.8344(5)	2.29
C13	1.0349(5)	0.0653(3)	0.7787(4)	2.02
C14	0.5638(5)	−0.0639(3)	0.7917(5)	2.35
C15	0.8105(5)	−0.0825(3)	0.5774(5)	2.37
C16	0.6789(4)	0.1060(3)	0.6302(4)	1.89

[a] See footnote *a* in Table 3.

Table 5. Fractional Coordinates for 12

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
W1	0.10794(4)	0.16912(5)	0.10737(3)	3.61
O1	−0.2525(10)	0.1379(8)	0.0398(4)	6.58
O2	0.0025(11)	0.1777(13)	0.2563(5)	11.76
O3	0.1543(12)	−0.1062(7)	0.1332(5)	7.80
N1	0.0897(15)	0.4578(9)	0.0977(7)	6.36
N2	0.7824(11)	0.8483(9)	0.0501(5)	5.49
N3	0.4806(12)	0.2236(8)	0.1720(5)	4.98
N4	0.4945(13)	0.5902(8)	0.1444(5)	5.24
C2	0.3957(16)	0.5620(12)	0.0752(7)	7.31
C3	0.2365(21)	0.6188(12)	0.0606(9)	9.67
C4	0.1242(21)	0.5867(11)	0.1051(9)	9.73
C5	0.0915(14)	0.3561(11)	0.0988(6)	4.58
C6	0.6322(13)	0.6636(12)	0.1378(6)	6.00
C7	0.5855(17)	0.7941(10)	0.1249(7)	7.58
C8	0.7308(17)	0.8687(10)	0.1168(6)	7.86
C9	0.8213(12)	0.8394(10)	−0.0044(6)	4.36
C10	0.5337(15)	0.4833(11)	0.1899(6)	6.07
C11	0.6466(16)	0.3974(11)	0.1635(7)	6.38
C12	0.6350(13)	0.2726(10)	0.1960(7)	5.28
C13	0.3493(15)	0.2022(9)	0.1493(6)	4.52
C14	−0.1182(15)	0.1492(10)	0.0630(6)	4.69
C15	0.0443(12)	0.1766(14)	0.2014(6)	6.22
C16	0.1358(14)	−0.0075(11)	0.1212(6)	4.70

[a] See footnote *a* in Table 3. The asymmetric unit contains one half molecule of **12** which is related to the other half by an inversion center (see Figure 4).

molecules had no inversion center were unlikely to reside on a mirror plane. The successful solution and refinement confirmed this choice. The space group for **12** was unambiguously assigned from the systematic absences to be $P2_1/c$. All three structures were solved by standard Patterson methods. The positional parameters for all non-hydrogen atoms were refined by using first isotropic and later anisotropic thermal parameters. Difference Fourier maps calculated at this stage showed for all three molecules the positional parameters of the hydrogen atoms. However, all hydrogens were added on calculated positions [d(C−H) = 0.95 Å[25]] with the exception of H1 in **10b**. The positional parameters of this atom were identified in a difference Fourier map and included in the least-squares refinement. The isotropic temperature factors for hydrogens were fixed to be 1.3 times the B_{eq} of the parent carbon atom for **10b** and **11**. For **12** all isotropic temperature factors for hydrogens were tied to a free variable which was refined in the least-squares procedure to $U_{iso,H}$ = 0.13 Å^2. At this point the residuals for **10b** were R = 0.034 and R_w = 0.057.[26] To determine the correct enantiomer in the acentric space group $P2_1$ all positional parameters were inverted, leading to residuals of R = 0.016 and R_w = 0.026. This allowed the identification of the crystallographically correct enantiomer. A similar procedure was employed to find the correct enantiomer for **11**. Calculations were carried out with the MolEN package[27] (for **10b** and **11**) or the SHELX-76 program[28] (for **12**). ORTEP[29] was used for all molecular drawings. Atomic coordinates and equivalent isotropic thermal parameters for **10b**, **11**, and **12** are listed in Tables 3−5.

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Supplementary Material Available: Tables of all bond distances and angles, anisotropic thermal parameters and hydrogen positions (9 pages). Ordering information is given on any current masthead page.

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(25) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(26) Definition of residuals for **10b** and **11**: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$, GOF = $[\Sigma w||F_o| - |F_c||^2/(n_o - n_p)]^{1/2}$ with n_o = number of structure factors and n_p = number of parameters, $w = 1/[\sigma_F]^2$, $\sigma_F = \sigma_F^2/2F$, $\sigma_F^2 = \{[\sigma_I]^2 + [pF^2]^2\}^{1/2}$. The weights for **12** were calculated as $w = 1.08/[\sigma_F]^2$.

(27) MolEN: Molecular Structure Solution Procedures. Program Descriptions; Enraf-Nonius: Delft, The Netherlands, 1990.

(28) Sheldrick, G. M. SHELX-76, Program for Crystal Structure Determination, Cambridge, England, 1976.

(29) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.