

Table 1. Molar masses and optical rotation of the newly prepared polymers.

Polymer[a]	No.	M_n [b]			Styrene part	$[\alpha]_{546}^{20}$ [°]		R=methyl as stereocomplex [d]
		R=trityl PTMA part	R=methyl PMMA part	R=trityl[c]		R=methyl[c]		
(+) 2	1	15 000	4700	–	+422	0.9 ± 0.2	–3.0 ± 0.1	
(–) 2	2	17 800	5600	–	–412	–0.7 ± 0.2	+1.6 ± 0.2	
(+) 2	3	20 000	6300	–	+429	+0.6 ± 0.2	–2.7 ± 0.2	
(+) 2	4	24 300	7600	–	+439	+0.6 ± 0.2	–2.5 ± 0.2	
(+) 2	5	26 800	8300	–	+422	+0.4 ± 0.2	–1.7 ± 0.1	
3	1	19 400	5900	5800	0	0 ± 0.2	0 ± 0.2	
(–) 3	2	12 500	3800	7500	–402	–1.4 ± 0.4	–7.4 ± 0.3	
(+) 3	3	14 800	4500	6800	+438	+1.4 ± 0.2	+9.9 ± 0.3	
(+) 3	4	15 700	4800	6800	+453	+0.7 ± 0.3	+9.9 ± 0.3	
(–) 3	5	16 100	4900	8300	–389	–1.9 ± 0.4	–11.6 ± 0.3	

[a] In the table and in the text, polymers **2** and **3** with R = methyl are indicated by the letter **a**, those with R = trityl by the letter **b**. Polymer **2b** was prepared by anionic polymerization of trityl methacrylate with diphenylmethyl lithium/(+) or (–)-2,3-dimethoxy-1,4-bis(dimethylamino)butane ((+) or (–)-DDB) in toluene at –78 °C. The block copolymers **3** [7] were obtained by anionic polymerization of styrene with *n*-butyllithium/(+) or (–)-DDB in toluene at –20 °C followed by further polymerization at –78 °C after addition of trityl methacrylate [7]. In the case of **3** (No. 1), the reaction was initiated with *n*-butyllithium/tetramethylethylenediamine. [b] The molar masses refer to the poly(trityl methacrylate) (PTMA), the poly(methyl methacrylate) (PMMA), and the polystyrene moieties. The values were determined for the methyl esters by NMR investigation and gel permeation chromatography (versus polystyrene as standard). [c] The values given are the specific optical rotations based on the weight percent of PTMA or PMMA. **2b** and **3b** in THF, $c = 0.4$ – 0.6 ; **2a** in benzene, $c = 0.33$; **3a** in benzene, $c = 0.15$. The limits of error refer to the accuracy of the polarimeter. [d] The stereocomplexes were prepared with syndiotactic PMMA ($M_n = 35000$) according to [6]. Weight ratio of syndiotactic PMMA to **2a** or to **3a** 4:1. Total concentration in benzene 2 wt %.

Poly(methyl methacrylates) (PMMA) (see Table 1) with diphenylmethyl and hydrogen (**2a**) as well as with atactic polystyrene and hydrogen (block copolymer **3a**) as end groups were prepared from the corresponding optically active poly(trityl methacrylates) (PTMA). In both cases, the tritylated polymers **2b** and **3b** exhibited strong optical rotations ($[\alpha]_{546}^{20}$ 389–453°), whereas the methyl esters **2a** and **3a** showed only residual rotations of 0.4–1.9°. These rotations are in part near the limits of detection and are due to the configuration of the chains. By appropriate choice of the catalyst (+) and (–)-2,3-dimethoxy-1,4-bis(dimethylamino)butane ((+) and (–)-DDB), polymers **2** and **3** with either positive or negative rotation could be obtained.

In order to transform the chains into helices to an appreciable extent, “stereocomplexes” with achiral syndiotactic PMMA chains were prepared. In such stereocomplexes, the isotactic PMMA chain is present as a tightly folded inner helix in a 9/1 double helix with syndiotactic PMMA.^[5] The complex formation in benzene or toluene could be detected by NMR spectroscopy^[6] (about 40% of isotactic PMMA complexed) and showed the expected temperature dependence. The optical activity due to complex formation gradually disappears as the temperature is raised to about 70 °C, leaving only the residual rotation due to the configuration.

Table 1 shows the optical rotations obtained by complex formation. For polymers **2a** (R = methyl), the absolute values are a factor of 2.3 to 4.5 larger than for the uncomplexed polymers, whereas they are enhanced up to tenfold for the block copolymer **3a**. Noteworthy is the fact that, for the same absolute configuration in the chains of **2a** and **3a** (R = methyl) as well as for the same sign of optical rotation of **2b** and **3b** and of the uncomplexed polymers **2a** and **3a**, the sign of the rotation reverses only for the homopolymers **2a** on complexation. This means that the complexed polymers **2a** and **3a** must exist as helices of opposite screw sense; for example, helix formation might begin at the diphenyl end in **2a** and at the H end in **3a**.

The investigations show, therefore, that even a large difference in the chain ends of isotactic polymers is not sufficient to cause significant optical activity due to the configuration of the main chain. However, the chirality inherently present in the polymer structure (cryptochirality) can be revealed by complexing the polymer with a chiral superstructure. Unfortunately, the method described here does not

allow the preparation of polymers with appreciably higher molar masses, which would allow more detailed study of the dependence of the optical activity on molar mass.

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cyclo-As₈ as Complex Ligand**

By Otto J. Scherer,* Rainer Winter, Gert Heckmann,
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Dedicated to Professor Hans Georg von Schnering
on the occasion of his 60th birthday

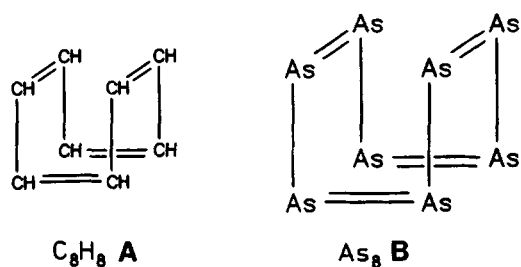
In the complex chemistry of substituent-free E_n units (E = P, As, Sb, Bi), the following arsenic species have been stabilized by coordination: *cyclo*-As₃, *cyclo*-As₄, *cyclo*-As₅[⊖], and *cyclo*-As₆.^[1] The largest rings found for the polyarsenides are the As₇[⊖] unit, a norbornadiene analogue, and the crown-shaped *cyclo*-As₈^{8⊖} unit in the ionic compounds [As₇{Cr(CO)₃}]₃^{3⊖} (**1**)^[2] and ¹_∞[Rb{NbAs₈}]₂^{2⊖} (**2**), respectively.^[3] In analogy to cyclooctatetraene (**A**), structure **B** can formally be postulated for a *cyclo*-As₈ unit.

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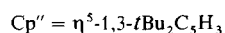
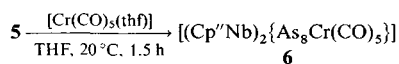
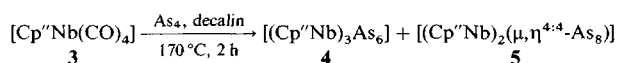
[*] X-ray structure analyses

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Reaction of the tetracarbonylniobium compound **3** with yellow arsenic (As₄) in excess results in formation of the binuclear niobium complex **5** in about 17% yield together



with small amounts of the trinuclear complex **4**,^[4] whose structure has not yet been established. Complex **5** reacts with [Cr(CO)₃(thf)] to give **6**.



Complex **4** forms a brown, microcrystalline powder, **5** mahogany-colored crystalline needles with metallic luster, and **6** red crystals, which are sparingly soluble in petroleum ether, moderately soluble in benzene, and readily soluble in dichloromethane; **4** exhibits the best solubility.

The ¹H NMR spectrum^[4] of **4** reveals only one kind of Cp'' ligand even at low temperatures. For **5** and **6**, the signal pattern expected on the basis of symmetry^[4] is observed.

X-ray crystal structure analyses^[5] show that, for both **5** and **6**, the arsenic analogue **B** of cyclooctatetraene forms a puckered, strongly distorted eight-membered ring (Figs. 1

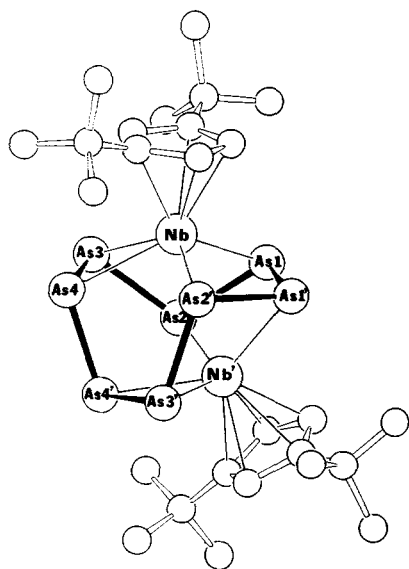


Fig. 1. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: Nb-As1 2.585(2), Nb-As2' 2.545(2), Nb-As3 2.642(2), Nb-As4 2.744(2), As1-As1' 2.530(3), As1-As2 2.402(2), As2-As3 2.422(2), As3-As4 2.355(3), As4-As4' 2.429(3), Nb-Cp''(center) 2.13; As1'-As1-As2 106.3(3), As1-As2-As3 107.9(1), As2-As3-As4 96.9(1), As3-As4-As4' 99.9(1), Cp''(center)Nb-Nb' 158.3.

and **2**, respectively). To our knowledge, such a coordination geometry has not yet been observed for cyclooctatetraene complexes.^[6] Possibly, the two ten-valence-electron fragments Cp''Nb are largely responsible for this *cyclo*-As₈ distortion. Together with the two sets of four arsenic atoms As1, As2', As4, As3 and As1', As2, As4', As3' in **5** (Fig. 1) as well as As3, As5, As7, As8 and As1, As2, As4, As6 in **6** (Fig. 2), they define two distorted tetragonal pyramids. The corresponding bond lengths and angles in the Nb₂As₈ framework, which consists of annelated three-, four-, and five-membered rings, differ only slightly in **5** and **6**. The average

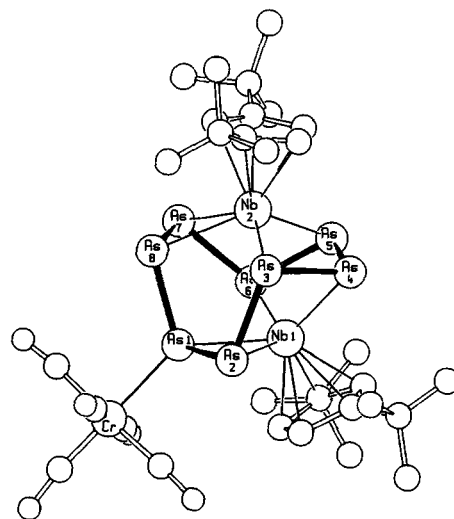


Fig. 2. Molecular structure of **6**. Selected bond lengths [Å] and angles [°]: Nb2-As5 2.573(6), Nb2-As3 2.533(5), Nb2-As7 2.637(6), Nb2-As8 2.735(6), Nb1-As4 2.576(6), Nb1-As6 2.539(5), Nb1-As2 2.669(5), Nb1-As1 2.714(5), As5-As4 2.546(6), As4-As3 2.393(6), As3-As2 2.380(6), As2-As1 2.361(6), As1-As8 2.432(6), As8-As7 2.360(7), As7-As6 2.390(6), As6-As5 2.380(6), As1-Cr 2.508(8), Nb1-Cp''(center) 2.09, Nb2-Cp''(center) 2.08; As5-As4-As3 106.1(2), As4-As3-As2 107.1(2), As3-As2-As1 94.6(2), As2-As1-As8 102.6(2), As1-As8-As7 98.0(2), As8-As7-As6 99.1(2), As7-As6-As5 108.0(2), As6-As5-As4 106.6(2), Cp''(center)Nb1-Nb2 162.4, Cp''(center)Nb2-Nb1 156.3.

values of the very different As-As and Nb-As distances are 2.415 and 2.629 Å, respectively, for **5** and 2.405 and 2.622 Å, respectively, for **6**; these bond lengths are 2.405 Å for **1**^[2] and 2.434 as well as 2.619 Å for **2**^[3] and are also comparable to $\bar{d}(\text{As-As})$ in complexes with (RAs)_n ligands.^[7] The average value of the As-As-As angle is 102.8° in **5** and **6**. Noteworthy are the following transannular distances, some of them very short: Nb...As1' = 3.022(2) and Nb...As2 = 2.861(2) Å in **5**; Nb1...As3 = 2.882(5), Nb1...As5 = 2.999(5), Nb2...As4 = 3.010(5), and Nb2...As6 = 2.854(5) Å in **6**. The Nb...Nb distance in **5** (3.326(2) Å) and **6** (3.311(5) Å) lies at the limits of bonding interactions.^[8]

Experimental Procedure

4, 5: Complex **3**[9] (765 mg, 2.00 mmol), dissolved in 10 mL of decalin, and 150 mL of a freshly prepared decalin solution of As₄ (ca. 862 mg = 2.9 mmol) were stirred at about 170°C and the reaction was monitored by IR (after ca. 2 h, CO bands were no longer observed). After removal of the solvent under oil-pump vacuum (ca. 50°C bath temperature), the black-brown, oily residue was treated with 3 mL of CH₂Cl₂ and about 2.5 g of Al₂O₃ (basic, 3% H₂O) and the mixture was then dried under oil-pump vacuum until it was free-flowing. Unreacted, red **3** (20 mg, 2.6%) was eluted with petroleum ether (column: 30 × 2.5 cm, Al₂O₃). Complex **4** (106 mg, 4.3% based on reacted **3**) was eluted with petroleum ether-toluene (20:1). Recrystallization from toluene-hexane (1:2) afforded 88 mg (3.6%) of brown, microcrystalline **4**. Complex **5** was eluted as a mahogany-colored fraction with petroleum ether-toluene (10:1). Concentration of the solution to about 5 mL followed by two-day crystallization gave 196 mg (8.8% based on reacted **3**) of **5**. An additional 177 mg (8.0%) could be isolated from the mother liquor. Suitable single crystals were obtained

by dissolving **5** in diethyl ether, adding petroleum ether, gently concentrating the solution until the onset of crystallization, and allowing the solution to stand for two days at room temperature. Complex **5** forms mahogany-colored crystalline needles.

6: A solution of $[\text{Cr}(\text{CO})_5(\text{thf})]$, prepared photochemically from freshly sublimed $[\text{Cr}(\text{CO})_5]$ (11.7 mg, 0.053 mmol), in 50 mL of THF was added to **5** (61 mg, 0.053 mmol). The reaction mixture was stirred for about 1.5 h at room temperature (IR monitoring showed no further increase in the newly appeared CO bands) and then worked up as described for **5**. Unreacted **5** (8 mg, 13.1 %) was eluted as a mahogany-colored fraction with petroleum ether–diethyl ether (15:1), followed by a red-brown fraction of **6**. The fraction of **6** was concentrated to about 10 mL and allowed to stand at room temperature. Ruby-red, cube-shaped crystals of **6** (48 mg, 71 % based on reacted **5**) formed within 20 h. An additional 3 mg of product was isolated from the mother liquor (total yield 51 mg (76 %)).

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3, 133887-27-1; **4**, 133887-28-2; **5**, 133887-29-3; **6**, 133887-30-6; As_4 , 12187-08-5; $[\text{Cr}(\text{CO})_5(\text{thf})]$, 15038-41-2.

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[4] ^1H NMR (400 MHz for **4** and **5**, 298 K), **4** (C_6D_6): δ = 5.87(br, 2H), 4.76(br, 1H), 1.29(s, 18H), ^{13}C NMR (400 MHz, CD_2Cl_2 , 298 K): δ = 123.1(s), 91.9(d, $^1J(\text{CH})$ = 165 Hz), 88.0(d, $^1J(\text{CH})$ = 172 Hz), 32.7(q, $^1J(\text{CH})$ = 126 Hz), 32.1(s). **5** (CD_2Cl_2): δ = 4.78(t, 1H), 4.74(t, 1H), 4.24(t, 1H), each $^3J(\text{HH})$ = $^4J(\text{HH})$ = 2.4 Hz, 1.14(s, 9H), 0.97(s, 9H). **6** (200 MHz, C_6D_6 , 298 K): δ = 4.97(t, $^4J(\text{HH})$ = 2.20 Hz), 4.73(dd, $^3J(\text{HH})$ = 3.08, $^4J(\text{HH})$ = 2.20 Hz), 4.48(dd, $^3J(\text{HH})$ = 2.94, $^4J(\text{HH})$ = 2.35 Hz), 4.30(dd, $^3J(\text{HH})$ = 2.94, $^4J(\text{HH})$ = 2.35 Hz), 4.20(dd, $^3J(\text{HH})$ = 3.08, $^4J(\text{HH})$ = 2.20 Hz), 4.17(t, $^4J(\text{HH})$ = 2.35 Hz), 1.33(s, 9H), 1.16(s, 9H), 0.99(s, 9H), 0.90(s, 9H). IR(hexane): $\tilde{\nu}(\text{CO})$ [cm^{-1}] = 2049(s), 1977(m), 1938(vs), 1928(vs), 1919(s). MS (70 eV), **4**: m/z 1259.4 (M^+ , 100%), 630.0 (M^{2+} , 31 %), and further fragments. Correct C,H analyses.

[5] a) Complex **5** forms monoclinic crystals, $C2/c$; a = 25.103(3), b = 8.067(3), c = 17.699(3) Å, β = 99.53(1)°, Z = 4, 3099 unique reflections ($M_{\text{O}_{\text{K}\alpha}}$: $1.5^\circ \leq \theta \leq 25^\circ$), 1748 observed with $I \geq 2\sigma(I)$; 183 parameters, R = 0.053, R_w = 0.049[5c]; b) Complex **6** forms orthorhombic crystals, P_{ccca} ; a = 17.319(3), b = 20.027(2), c = 24.343(17), Z = 8, 3946 unique reflections ($M_{\text{O}_{\text{K}\alpha}}$: $1.5^\circ \leq \theta \leq 25^\circ$), 1711 observed with $I \geq 2\sigma(I)$; 221 parameters, R = 0.068, R_w = 0.0635[5c]; c) The structures were solved and refined using the programs SHELXS-76, SHELX-86. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depositor number CSD-55255, the names of the authors, and the journal citation.

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Phosphorus Monoxide (PO) as Complex Ligand**

By Otto J. Scherer*, Jürgen Braun, Peter Walther, Gert Heckmann, and Gotthelf Wolmershäuser

In contrast to the ubiquitous nitrogen monoxide (NO), whose ligand properties also have been investigated in detail,^[1] only a few spectroscopic data^[3] have thus far been

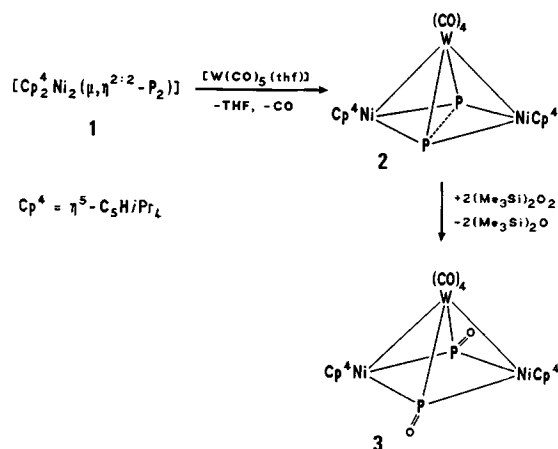
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[†] X-ray structure analyses.

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reported for the phosphorus analogue PO, probably the most abundant phosphorus-containing molecule occurring in interstellar clouds.^[2]

Reaction of diphospha-dinickela-tetrahydrene with $[\text{W}(\text{CO})_5(\text{thf})]$ leads to formation of the Ni_2WP_2 -complex **2**, which can be oxidized with bis(trimethylsilyl) peroxide to give **3**, the first complex with a PO ligand. **1**, **2** and **3** form,



respectively, black, dark green, and black crystals, which are briefly stable in air, readily to moderately soluble in pentane, and very readily to readily soluble in benzene and dichloromethane. Solutions of **2** are extremely sensitive to traces of oxygen. Table 1 lists the most important X-ray structure data^[4] and IR ($\tilde{\nu}(\text{CO})$, $\tilde{\nu}(\text{PO})$) and ^{31}P -NMR^[5] spectroscopic data of the complexes **1–3**.

Table 1. Selected bond lengths [Å] and angles [°] as well as $\tilde{\nu}(\text{CO})$, $\tilde{\nu}(\text{PO})$ [cm^{-1}] and ^{31}P -NMR data of the complexes **1–3**.

	1	2	3
P1-P2	2.053(5)	2.304(4)	2.624(5)
Ni1-P1	2.186(3)	2.178(4)	2.148(4)
Ni2-P1	2.185(3)	2.176(3)	2.135(4)
Ni1-P2	2.182(3)	2.161(3)	2.141(4)
Ni2-P2	2.186(3)	2.174(4)	2.134(4)
Ni1-Cp _(center) ⁴	1.72	1.74	1.735
Ni2-Cp _(center) ⁴	1.73	1.73	1.715
W-P1		2.507(3)	2.524(5)
W-P2		2.512(3)	2.516(4)
Ni1-W		2.849(1)	2.847(2)
Ni2-W		2.848(1)	2.847(2)
Ni1-Ni2	2.571(1)	3.66	3.37
P1-O1			1.480(10)
P2-O2			1.462(9)
P1-Ni1-P2	56.1(1)	64.1(1)	75.4(2)
P1-Ni2-P2	56.0(1)	63.9(1)	75.8(2)
Ni1-P1-Ni2	72.1(1)	115.5(1)	103.7(2)
Ni1-P2-Ni2	72.1(1)	116.2(1)	104.0(2)
Dihedral angle			
Ni1, P1, P2	96.4	176.5	189.6
Ni2, P1, P2			
$\delta(^{31}\text{P}\{^1\text{H}\})$ [a]	288.2 (s)	403.5 (s)	354.0 ("s") $^1J(\text{WP})$ 68 Hz
$\tilde{\nu}(\text{CO})$ [b]		2029 (s), 1958 (s) 1946 (m), 1905 (s)	2043 (s), 1975 (s) 1962 (w), 1925 (s)
$\tilde{\nu}(\text{PO})$ [b]			1260 (s)

[a] In C_6D_6 , 162 MHz, 85% H_3PO_4 ext. [b] In hexane.

If one compares the bond distances and angles in the complexes **1–3** one sees that $\bar{d}(\text{N–P})$ decreases in the transition from the symmetrical diphospha-dinickela-tetrahydrene **1**