Table I. Polymerizations of IV Using Cyanide-Modified Versions of R-I and S-I[a]

catalyst	yield (%)	$\bar{M}_n$	PDI[d]	$[\alpha]^{23}_D$
R-I	80	880	1.10	+10
R-I-(CN)-Bu[b]	88	680	1.23	+13
R-I-$(CN)_2$-Bu	50	550	1.24	+23
S-I	81	820	1.10	−10
S-I-(CN)-Bu[c]	74	680	1.23	−13
S-I-$(CN)_2$-Bu	54	630	1.20	−23

[a] Polymerizations were all run under N_2 atmosphere for 36 h. [b] **R-I**-(CN)-Bu is the monocyanide adduct of **R-I**, $N(Bu)_4^+$ salt. [c] **S-I**-(CN)-Bu is likewise a monocyanide adduct of **S-I**, $N(Bu)_4^+$ salt. [d] PDI = polydispersity index, as determined by GPC = $\bar{M}_w/\bar{M}_n$.

$k_S = 6.2\ (2) \times 10^{-3}\ s^{-1}$ with $k_R/k_S = 2.5\ (5)$. Finally, **S-II** polymerizes **S-V** and **R-V** under O_2 at 298 K to yield the rate constants $k_R = 6.8\ (2) \times 10^{-3}\ s^{-1}$ and $k_S = 6.5\ (2) \times 10^{-3}\ s^{-1}$ with $k_R/k_S = 1.05\ (5)$. These kinetic experiments show that the chiral ligands on **S-I**, **R-I**, and **S-II** do have a significant effect at the active site.

We then polymerized *tert*-butyl isocyanide (**III**), a sterically hindered monomer known to form a kinetically controlled helical polymer as evidenced by its resolution on a chiral column.[9] Neat **III** was reacted with **S-I**, **R-I**, and **S-II** under O_2 at 298 K to prepare polymer samples in moderate yield (25–30%). Cleavage of the optically active catalyst from the polymer chains was evidenced by spectroscopic as well as elemental analysis. **III**/**R-I** gave poly(**III**) which had a specific rotation of $[\alpha]^{20}_D = +12$ ($\bar{M}_n$ = 880;[12] M helix). (The helix sense of the poly(**III**) has been assigned previously using circular dichroism.)[13] In contrast, **III**/**S-I** gave poly(**III**) which had a specific rotation of $[\alpha]^{20}_D = -12$ ($\bar{M}_n$ = 800; P helix). Finally, **III**/**S-II** gave poly(**III**) which had a specific rotation of $[\alpha]^{20}_D = -18$ ($\bar{M}_n$ = 1100; P helix). These polymerizations have shown that chiral catalysts **S-I**, **R-I**, and **S-II** do display diastereotopic interactions between the optically active catalyst and helical polymer chains. Furthermore, the presence of such interactions proves that helical poly(**III**) is formed kinetically at the active catalytic site. In contrast, polymerizations of less hindered monomers, e.g., *p*-methoxyphenyl isocyanide (**VI**), using **S-I**, **R-I**, and **S-II** gave only optically inactive polymers, suggesting that their presumed helical conformations are either readily racemized at room temperature[14] or are nonexistent.[5g,h]

Since **III**, a tertiary isocyanide, polymerizes very slowly and gives only low yields of polymer, we prepared a secondary, but also sterically hindered, achiral monomer, diphenylmethyl isocyanide (**IV**) and studied its polymerization chemistry with **S-I** and **R-I**. This monomer polymerizes homogeneously in toluene under N_2 or O_2 at 298 K and forms polymer in high yields (73–98%). The **IV**/**R-I** system gave poly(**IV**) which had a specific rotation of $[\alpha]^{20}_D = +10$ ($\bar{M}_n$ = 880), and **IV**/**S-I** gave poly(**IV**) which had a specific rotation of $[\alpha]^{20}_D = -10$ ($\bar{M}_n$ = 820). In an effort to increase our catalyst's helix-sense selectivity, we sought to block some of the many (up to 3) open coordination positions on **S-I** and **R-I**, which should lower some of the degrees of freedom at the active site. To accomplish this task we used anionic cyanide ligands which should not dissociate under polymerization conditions. Indeed, when 3 equiv of CN^- was added to either **S-I** or **R-I**, the resulting complexes were completely ineffective as polymerization catalysts. Mono- and biscyanide complexes of **S-I** and **R-I** were prepared with $N(Bu)_4^+$ counterions, and the results of polymerizations with **IV** are presented in Table I.

In summary, we have demonstrated that, by modifications in optically active catalyst as well as in monomer, both helix-sense selectivity and yield (30 to >90%) in isocyanide polymerizations were increased. The actual extent of enantiomeric excess in these samples remains unknown due to the dependence of optical rotation on molecular weight as well as helical excess.[5b,f] By comparison of optical rotations of our poly(**III**) samples with that of a resolved polymer of **III** of "low molecular weight"[5f] ($\bar{M}_n < 1800$, $n < 20$, $[\alpha]^{20}_D = +26$), we can, ignoring molecular weight effects, set a minimum on percent ee at 46% for **R-I**, 46% for **S-I**, and 69% for **S-II** for polymerizations of **III**. At present, we are working on developing the necessary calibration curves to determine true enantiomeric excess values.

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Supplementary Material Available: Experimental procedures for the preparation of **R-I**, **S-I**, and **S-II** and for all of the polymerization reactions (9 pages). Ordering information is given on any current masthead page.

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[12] Molecular weights were determined by GPC relative to polystyrene standards using chloroform as eluent (see the supplementary material for more details).

[13] van Beijnen, A. J. M.; Nolte, R. J. M.; Drenth, W.; Hezemans, A. M. F. *Tetrahedron* **1976**, *32*, 2017.

[14] Similar results were obtained earlier.[8]

[15] Ugi, I.; Fetzer, U.; Eholzer, U.; Knupfer, H.; Offermann, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 472.

Evidence for Aryne-Ring Rotation in Isomeric 4,5-Dehydro[2.2](1,4)naphthalenoparacyclophanes

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There are a few reports on the reactions of dehydrocyclophanes generated from [*n.n*]paracyclophane compounds.[1-3] However, it is not known whether the aryne ring in dehydrocyclophanes can rotate through 180° without reaction. We have now obtained evidence for such aryne-ring rotation by examining adducts from isomeric 4,5-dehydro[2.2](1,4)naphthalenoparacyclophanes **2a** and **2s** generated from the corresponding *anti*- and *syn*-4-bromocyclophanes **1a** and **1s**.

The experimental procedure was as follows. To 0.20 g of **1** in 15 mL of *tert*-butylbenzene was added 1.32 g (20 equiv) of potassium *tert*-butoxide. The mixture was refluxed at 175–180 °C for 3.5 h, worked up in the usual manner,[1] and then subjected to preparative TLC on silica gel using hexane–ethyl acetate (10:1) and dichloromethane–hexane (1:2). In this manner, both **1a** and **1s** gave a bridged dibenzobarrelene **3**, as well as *anti*- and *syn*-4-hydroxy[2.2](1,4)naphthalenoparacyclophanes **4a** and **4s** and their *tert*-butyl ethers **5a** and **5s**, as shown in Table I. The products **3**, **4a**, and **4s**, known substances, showed the same melting points and ^1H NMR spectra as those reported.[4] The structures of unknown ethers **5a** and **5s** were determined by ^1H NMR and mass spectroscopy.

Interestingly, **1a** gives anti products **4a** and **5a** in preference to the others, and **1s** gives syn products **4s** and **5s**, similarly. The formation of phenolic products **4a** and **4s** results from butoxide anion addition[3] to *anti*- and *syn*-4,5-dehydrocyclophanes **2a** and **2s**, whose 4,5-dehydro bond is arranged anti and syn, respectively, to the bridge-free benzo ring of the naphthalene moiety. The above results can be explained by an aryne route involving aryne-ring rotation, as shown in Scheme I.

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[1] Longone, D. T.; Gladysz, J. A. *Tetrahedron Lett.* **1976**, 4559.

[2] Longone, D. T.; Chipman, G. R. *J. Chem. Soc., Chem. Commun.* **1969**, 1358.

[3] Cram, D. J.; Day, A. C. *J. Org. Chem.* **1966**, *31*, 1227. Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3527.

[4] Takada, Y.; Tsuchiya, K.; Takahashi, S.; Mori, N. *J. Chem. Soc., Perkin Trans. 2* **1990**, 2141. The melting point (137–139 °C) of **6a** (**3** in the present text) described therein should be replaced by 177–179 °C.

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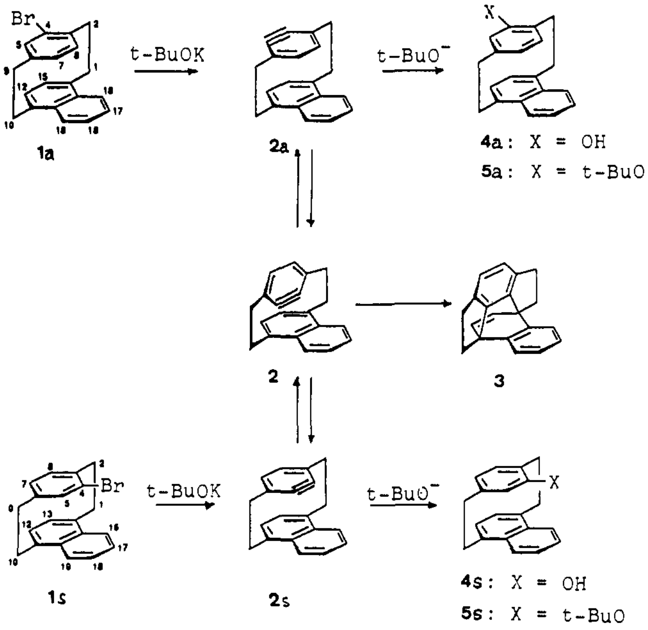
Table I. Reaction of *anti*- and *syn*-4-Bromo[2.2](1,4)naphthalenoparacyclophanes with Potassium *tert*-Butoxide

	isolated yields (%)				
substrate	**3**	**4a**	**5a**	**4s**	**5s**
1a	7.7	21.0	20.2	15.3	*a*
1s	2.6[b]	16.6	*a*	27.8	8.2[b]

[a] A minor amount of the compound was formed, as confirmed on silica gel TLC. [b] **3** and **5s** were obtained as a mixture, and the yields were determined by ^{1}H NMR spectroscopy.

Scheme I



In the reaction of **1a**, **2a** is first generated. Only a portion of **2a** traps butoxide anion to give **4a** and **5a**, and the remainder is converted into **2s** by way of dehydrocyclophane **2**, whose aryne ring is arranged perpendicularly to the facing ring. This **2** can itself undergo internal cycloaddition to give **3**. The resulting **2s** undergoes similar butoxide anion trapping to give **4s** and **5a** and also conversion into **2a**. This interconversion of **2a** and **2s** (or aryne-ring rotation, **2a** ⇄ **2** ⇄ **2s**) continues without reaction until all dehydrocyclophane molecules are consumed. As a result, **4a** and **5a** are formed in preference to the other products. In clarifying the reaction mechanism, it is also important to know whether retro Diels–Alder reaction of **3** reverting to **2** takes place. Considering the large bond-angle distortion observed around the bridgehead,[5] one may suppose the reaction to occur. However, **3** did not give any external adducts under the same reaction conditions as described above, indicating that **3** did not revert to **2**.

The reaction of **1s** proceeds via the reverse aryne route starting from **2s**, leading to the preferred formation of **4s** and **5s**.

Previous work by Longone et al. demonstrated that 5,6-dehydro[3.3]paracyclophane, generated from 5-bromo[3.3]-paracyclophane and a large excess of potassium *tert*-butoxide, gives an internal cycloadduct similar to **3** but does not give adducts arising from *tert*-butoxide addition to the dehydrocyclophane.[1] This is in sharp contrast to similarly generated 4,5-dehydro-[2.2]paracyclophane, where such external adducts dominate.[2,3] Dehydrocyclophanes **2a** and **2s** give not only external adducts but also an internal one, probably by way of aryne-ring rotation. This suggests that the aryne ring in **2a** and **2s** has a sufficiently long lifetime to rotate without reaction occurring at a temperature of 180 °C, despite the 20-fold excess of base used.

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(5) Matsuzawa, H.; Kozawa, K.; Uchida, T.; Tsuchiya, K.; Mori, N. *Acta Crystallogr.* **1989**, *C45*, 1389.

Simple Low-Valent Amido, Imido, and Nitrido Complexes of Tungsten

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Most transition metal imido (or nitrene) complexes are nucleophilic at nitrogen,[1] but certain species exhibit reactivity patterns indicative of electrophilic character.[2-5] For example, high-valent manganese(V)[2a] and iron(V)[2b] derivatives, activated by trifluoroacetyl and tosyl groups, respectively, transfer the nitrene unit to alkenes to produce aziridines. McElwee-White et al. have reported that the putative $(CO)_5W{=}NC_6H_5$ complex can behave as a nucleophile[3a] or an electrophile;[3b] the latter property is illustrated by reaction with PPh_3 to form $PhNPPh_3$. Our work has focused on preparing low-valent metal nitrene complexes containing strong π-acid ligands in the coordination sphere, features which may impart electrophilic character to nitrogen.[6] This communication describes the simple amido (NH_2^-), imido (NH^{2-}), and nitrido (N^{3-}) derivatives of the low-valent tungsten moiety $Tp'(CO)_2W$ (Tp′ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) and their facile interconversions. The nitride complex serves as a convenient precursor to a variety of cationic nitrene complexes.

The preparation and reactions of these complexes are summarized in Scheme I. Treatment of a solution of $Tp'(CO)_2WI$[7] (**1**) with ammonia in CH_2Cl_2 at low temperature affords $Tp'(CO)_2W(NH_2)$ (**2**), a rare example of a metal complex with both carbonyl and amido ligands. Formulation of **2**, which was isolated as a green solid, as an amido complex follows from the spectroscopic data.[8] Two broad signals in the ^{1}H NMR spectrum (13.5 and 11.6 ppm) are assigned as the amido hydrogens and reflect restricted rotation around the $W{=}NH_2$ bond. These signals coalesce at 103 °C and establish the barrier to rotation as $\Delta G^\ddagger = 17$ kcal/mol.

Amido complex **2** shows ambiphilic character and reacts as either a hydride or proton donor. Thus, treatment of **2** with $[Ph_3C][PF_6]$ produces two isolable nitrene products [Tp′-

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(1) (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (c) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (d) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719.

(2) (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073. (b) Mahy, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517.

(3) (a) Arndsten, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871. (b) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007.

(4) The Cu(I) aziridination catalysts reported by Evans may also involve an electrophilic nitrene intermediate: Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726.

(5) Basolo has postulated the intermediacy of the electrophilic nitrene $[Ir(NH_3)_5NH]^{3+}$ from protonation of $[Ir(NH_3)_5N_3]^{2+}$. See: (a) Lane, B. C.; McDonald, J. W.; Basolo, F.; Pearson, F. G. *J. Am. Chem. Soc.* **1972**, *94*, 3786. (b) Gafney, H. D.; Reed, J. L.; Basolo, F. *J. Am. Chem. Soc.* **1973**, *95*, 7998.

(6) Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 8190.

(7) Dicarbonyl **1** was prepared by heating a THF solution of $Tp'(CO)_3WI$[6] at reflux for several hours. The solvent was partially evaporated under vacuum. Orange crystals were obtained in 75% yield upon cooling the resulting red-orange solution overnight (−30 °C).

(8) Spectroscopic data for **2**: IR (CH_2Cl_2) ν(CO) 1915, 1793 cm^{-1}; IR Nujol mull ν(NH) 3395, 3305 cm^{-1}; ν(BH) 2540 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 13.5 (br s, 1 H, N*H*H), 11.6 (br s, 1 H, NH*H*), 6.06, 5.90 (1:2, 3 C*H*), 2.53, 2.48, 2.41, 2.00 (6:3:3:6, 6 CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) 254.7 (2 CO, J_{WC} = 175 Hz), 160.0, 151.2, 146.6, 145.6 (1:2:1:2, 6 *C*CH$_3$), 108.3, 106.6 (1:2, 3 *C*H), 15.5, 15.0, 13.0, 12.6 (1:2:1:2, 6 *C*H$_3$). Attempts to obtain an analytically pure sample were unsuccessful due to decomposition.

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