Table I. Internuclear Distances, Vibrational Amplitudes (l), and Valence Angles of WMe$_6$[a]

	r_a, Å	l, Å	angles, deg
W–C	2.146 (3)	0.060 (3)	
C–H	1.119 (4)	0.078 (5)	
W- -H	2.682 (8)	0.151 (18)	
C(1)- -C(2)	2.928 (12)	[0.17][b]	
C(1)- -C(4)	2.645 (16)	[0.13][b]	
C(1)- -C(5)	3.946 (5)	0.161 (12)	
θ[c]			52.0 (3)
∠C(1)WC(2)			86.0 (2)
∠C(1)WC(4)			76.1 (6)
∠WCH			106.1 (7)
R[d]		4.7%	

[a] Molecular symmetry D_{3h}. Estimated standard deviations in parentheses in units of the last digit. [b] See comments in text. [c] The angle between the W–C(1) bond and the 3-fold symmetry axis. [d] $R = [\sum w(I_{\text{obsd}} - I_{\text{calcd}})^2/\sum w I_{\text{obsd}}^2]^{1/2}$.

squares refinement of the four structure parameters along with four root-mean-square vibrational amplitudes yielded the best values listed in Table I. When attempts were made to refine the vibrational amplitudes of the C(1)- -C(2) and C(1)- -C(4) distances, the refinements failed to converge. These amplitudes were therefore determined by trial and error. Comparison of experimental and calculated intensity and RD curves, Figures 1 and 2, shows that the agreement is satisfactory.

If the symmetry of our model is lowered to C_{3v}, two more adjustable parameters have to be included in the refinements, e.g., a second, symmetry-independent W–C bond distance and a second, symmetry-independent angle θ_2. Such a model would obviously be equally compatible with our data. *We conclude, therefore, that the coordination geometry of hexamethyltungsten is trigonal-prismatic D_{3h} or slightly deformed to C_{3v} symmetry.* WMe$_6$ is, to the best of our knowledge, the first electrically neutral molecule with monodentate ligands that has been found to violate the valence shell electron pair repulsion tenet that the coordination geometry in a molecule of type ML$_6$ where the metal is surrounded by six bonding electron pairs (and no nonbonding electrons) is octahedral.

W(NMe$_2$)$_6$,[5] W(OMe)$_6$,[6] and WF$_6$[7] all have octahedral coordination geometries in the gas phase with W–N = 2.035 (5) Å, W–O = 1.902 (3) Å, and W–F = 1.832 (3) Å. All these bonds are more polar than the W–C bond in WMe$_6$, and all the ligands have at least some π-donor capability. Like the other compounds mentioned above, W(CO)$_6$ is octahedral in the gas phase.[8] W(CO)$_6$, of course, is a d^6 rather than a d^0 complex, and the six d electrons occupy t$_{2g}$ orbitals which have the right symmetry for donation into ligand π^* orbitals. The six W–C bonds are therefore shorter, 2.059 (3) Å,[8] and stronger than in the hexamethyl analogue: the mean bond disruption enthalpies are 43.0 and 38.5 kcal mol^{-1}, respectively.[9]

Acknowledgment. We are grateful to the Norwegian Research Council for Science and the Humanities (NAVF) and the VISTA Program for general support and to the NAVF for a scholarship to A.H.

Note Added in Proof. Professor T. A. Albright has informed us that geometry optimization of WMe$_6$ at the ab initio level with a standard effective core potential and a double-ζ basis for the 5s, 5p, 5d, 6s, and 6p orbitals for W and 3-21 and STO-3G bases for C and H yields a *global* minumum of D_{3h} symmetry, W–C = 2.161 Å, C–H = 1.095 Å (mean value), ∠CWH = 111.1° (mean value), and θ = 51.0°. The energy of the prismatic configuration is 73 kcal mol^{-1} below the energy of the octahedral configuration at the Hartree–Fock level and 83 kcal mol^{-1} lower at the MP2 level.

Registry No. WMe$_6$, 36133-73-0.

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Fischer Route to Pyrido[3,2-*g*]indoles. A Novel Receptor for Urea Derivatives

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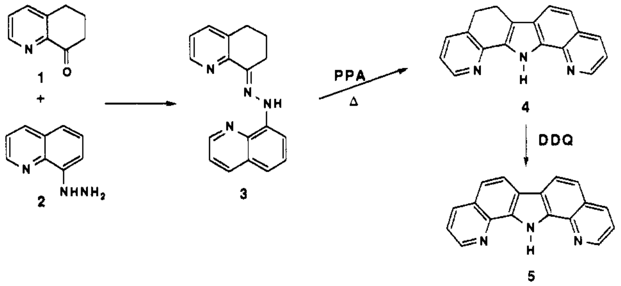
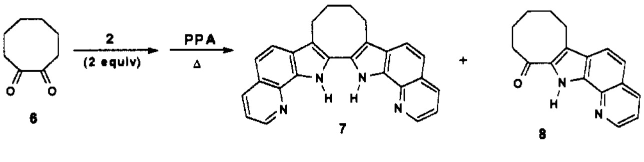
Received July 19, 1989

Recently we have demonstrated the utility of the Fischer indole synthesis in the conversion of phenylhydrazones of α-keto-2,3-cycloalkenopyridines to 3,3′-polymethylene-bridged derivatives of 2-(2′-pyridyl)indole.[1] This same procedure applied to the appropriate diketones also leads to bis-annelated derivatives of 2,6-di(2′-indolyl)pyridine or 3,3′-bridged 2,2′-biindoles.[1,2] These systems have been shown to undergo facile cyclopalladation to provide a metallocycle involving the indole nitrogen. In hopes of extending the utility of these molecules as hosts for other species, we have elaborated our synthetic approach to include pyrido-fused indole derivatives.



The prerequisite hydrazine is 8-quinolinylhydrazine (**2**), which can be prepared by stannous chloride reduction of the diazo derivative of 8-aminoquinoline.[3] This hydrazine condenses readily with 5,6,7,8-tetrahydro-8-quinolone (**1**)[4] to provide the corresponding hydrazone **3**. When **3** is heated to 100 °C in polyphosphoric acid (PPA), Fischer cyclization occurs to provide the pyrido[3,2-*g*]indole **4** in 96% yield. If this material is in turn treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), a 99% yield of the symmetrical, fully aromatized dipyridocarbazole **5** can be obtained.

In earlier work involving the phenylhydrazones of cyclic 1,2-diketones, it was found that the desired 2,2′-biindoles were contaminated by significant amounts of monoketones, indicating that only one Fischer cyclization had occurred.[1,2] For the bis(hydrazone) derived from the reaction of 1,2-cyclooctanedione with **2**, a similar problem was encountered affording a mixture of **7** and **8**. Recrystallization from ethanol provided pure **7** (68%).



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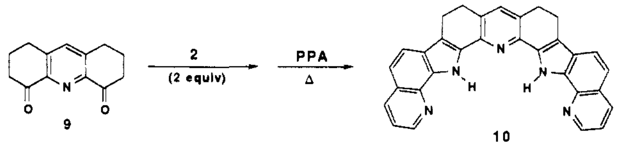
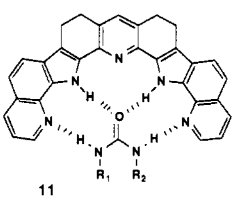
The 3,3′-tetramethylene bridge of **7** causes an estimated twist of about 65° about the 2,2′-bond so that the two pyridoindole subunits do not really form a cavity as indicated in the structure drawing. Each of these subunits can undergo a cyclometallation reaction with palladium 2,4-pentanedionate, resulting in the formation of a binuclear complex.[5]

When the pyridyl diketone **9** is treated with 2 equiv of **2**, a bis(hydrazone) is formed, which after treatment with PPA provided the cavity-shaped molecule **10** in 77% yield. This system is interesting in that the interior of the cavity contains five nitrogens arranged in a 1,4-relation to one another. The three pyridine ring nitrogens are electron-pair donors while the pyrrole ring NH's are potential electron-pair acceptors in a hydrogen-bonding fashion. Inspection of a molecular model indicates that this system should be a good host for urea derivatives. A variety of related donor-acceptor-type hosts have recently been described.[6]

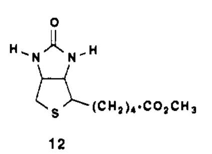


We find that **10** not only solubilizes urea in chloroform but also forms complexes with a variety of substituted ureas. When incremental amounts of the guest were added to a 0.005 M solution of **10** in 1:1 CD_2Cl_2–$CDCl_3$ at 18 °C, the chemical shift of the NH of **10** moved downfield over a 2 ppm range. The NMR titration data were analyzed by using a linear least-squares fitting procedure similar to that described by Wilcox and Cowart,[7] and the calculated association constants are given with structure **11**. We were unable to measure urea and some of its simpler derivatives due to their insolubility in our solvent system.



11

	$K_a{}^b$
$R_1 = R_2 = CH_3$	0.5
R_1 = n-Bu, R_2 = H	80
$R_1, R_2 = CH_2CH_2$	3530
Methyl Biotin (12)	3000
Butyrolactam	13



12

The K_a values are consistent with the binding model depicted in structure **11**. The weakest binder is dimethylurea, whose most favorable binding conformation is hindered by its two *N*-methyl groups. This steric problem is somewhat alleviated for *n*-butylurea, which binds 160× better while bridging the two nitrogens as in imidazolidone provides an excellent host-guest fit. To test the generality of this binding, we employed methyl biotin (**12**) as the guest and again observed strong binding. Butyrolactam is a simple amide analogue of imidazolidone. Although it is only capable of forming three H bonds, it still associates reasonably well.

These results are significant in that the receptor contains a relatively rigid, well-defined cavity, allowing predictions to be made regarding binding interactions with a suitable guest. Systems with greater conformational mobility do not enjoy this advantage.[9] Other receptors for urea-type molecules have been reported but they bind primarily through the NH's such that the carbonyl group is pointed *away* from the binding site.[10] The receptor **10**, however, binds urea with its carbonyl group pointed *inward*, permitting the potential incorporation of a wide variety of substituted derivatives. It is particularly interesting that a cavity-shaped receptor allows greater latitude as a host than cyclic species which have more stringent size requirements.

Future efforts will be aimed at defining the scope of the binding interaction by structural variations in both the host and the guest. Predictive computations will also be employed in this regard.

Acknowledgment. Financial support from the Robert A. Welch Foundation and the National Science Foundation (CHE-8607935) is gratefully acknowledged. The NMR spectrometer was also partially funded by the NSF (CHE-866352). We also thank Prof. Craig Wilcox and Prof. Paul Street for helpful discussions.

Registry No. 1, 56826-69-8; **2**, 14148-42-6; **3**, 126664-10-6; **4**, 126664-11-7; **5**, 126664-12-8; **7**, 126664-13-9; **8**, 126664-14-0; **9**, 63371-62-0; **10**, 126664-15-1; **11** ($R_1 = R_2$ = Me), 126664-18-4; **11** (R_1 = Bu; R_2 = H), 126664-19-5; **11** (R_1, R_2 = CH_2CH_2), 126664-20-8; **11**·**12**, 126783-78-6; **11**·butyrolactam, 126664-21-9; **12**, 608-16-2; VH-157, 126664-16-2; VH-189, 126664-17-3; VH-226, 126664-22-0; MeNHCONHMe, 96-31-1; $BuNHCONH_2$, 592-31-4; $Pd(acac\text{-}F_6)_2$, 64916-48-9; 1,2-cyclooctanedione, 3008-37-5; 8-aminoquinoline, 578-66-5; imidazolidin-2-one, 120-93-4; butyrolactam, 616-45-5.

Supplementary Material Available: Experimental details for the preparation of several compounds including **2–5**, **7**, and **10** and the measurement of association constants (5 pages). Ordering information is given on any current masthead page.

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Inverse-Electron-Demand Diels–Alder Reactions of Fischer Carbene Complexes: A New and Efficient Dihydrobenzene Synthesis via a Retrocycloaddition of Chromium Hexacarbonyl[†]

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Received December 11, 1989

Over the last six years, it has been clearly established that α,β-unsaturated Fischer carbene complexes[1] are potent dienophiles in their Diels–Alder reactions with 1,3-dienes.[2] We report here the first examples of an inverse-electron-demand Diels–Alder reaction of Fischer carbene complexes involving the reactions of

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[†] Dedicated to Professor Wolfgang Kirmse on the occasion of his 60th birthday.

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