tathesis can be limiting, due to the requisite double loss of aromaticity upon cyclization, as the only product obtained was the α-methoxy amide **17** in 85% yield. Since it has been reported[9b] that hydrolysis of chromium complexed ketenimines produces acyl(amino)carbene complexes in contrast to free ketenimines which provide amides, this is further support for the demetalation of intermediate ketene complexes by the second equivalent of isonitrile.[9b,16]

In conclusion, we have demonstrated a new thermal benzannulation reaction of chromium carbene complexes that promises to have application to the synthesis of ortho alkoxy aromatic amine derivatives. The reaction is chemo- and regioselective and provides products uniquely regiocomplementary to those obtained from photochemical benzannulation reactions of aminocarbene complexes. Current experiments are exploring a range of interests including additional regioselectivity issues and applications to synthetic targets.

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Supplementary Material Available: Sample experimental procedure and spectral and analytical data for compounds **3a**, **3b**, **7**, **9**, **11**, **13**, **15**, and **17** (3 pages). Ordering information is given on any current masthead page.

High Valent Transition Metal Chemistry. Synthesis and Characterization of an Intermediate-Spin Iron(IV) Complex of a Strong π-Acid Ligand

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Iron(IV) through iron(VIII) compounds have rarely or never been encountered,[2] partly because most existing ligands are sensitive to oxidative degradation.[3] Iterative identification and replacement of oxidatively sensitive ligand groups is a viable approach for building oxidation-resistant ligand systems.[3b] The so-constructed tetraanion[3b] [η^4-**1**]$^{4-}$ (Scheme I) and related macrocycles[3a] stabilize both highly oxidizing[3a] and high valent middle and later transition metal (MLTM) complexes with hard anionic axial donors, e.g., O^{2-} and Cl^-.[4] Relatively unstable iron(IV) complexes of the general formulation $[Fe(L\text{-}L)_2X_2]^{2+}$ (L-L = diphosphine, diarsine; X = Cl, Br) containing characteristically weak π-acid phosphine and arsine ligands are known.[5]

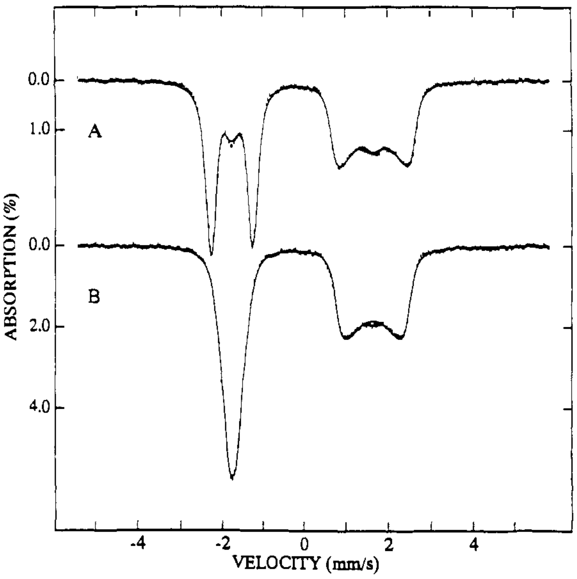
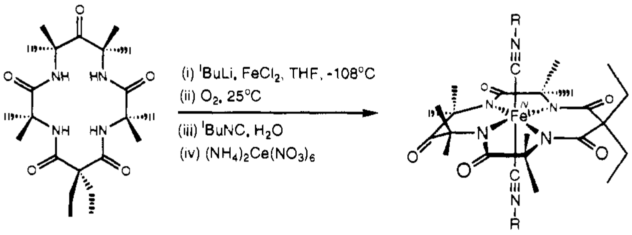


Figure 1. Mössbauer spectra of the polycrystalline Fe(η^4-**1**)(CN^{t}Bu)$_2$ recorded at 4.2 K (A) and 18 K (B) in a 6.0-T applied field. The spectra were fitted to the $S = 1$ spin Hamiltonian $H = D[(\mathbf{S}_z^2 - {}^2/_3) + E(\mathbf{S}_x^2 - \mathbf{S}_y^2)] + \beta\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{H} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I} + (eQV_{ZZ}/12)[3\mathbf{I}_z^2 - 15/4 + \eta(\mathbf{I}_x^2 - \mathbf{I}_y^2)] - g_n\beta_n\mathbf{H}\cdot\mathbf{I}$ using $D = 17.5$ cm^{-1}, $E = 0$, $g_x = g_y = 2.22$, $g_z = 1.99$, $A_x = A_y = -22.8$ MHz, $A_z = -6.2$ MHz, $\Delta E_Q = +3.38$ mm s^{-1}, $\eta = 0$, and 0.25 mm s^{-1} line width.

Scheme I



H$_4$[**1**]

Fe(η^4-**1**)(CN^{t}Bu)$_2$

In contrast, strong π-acid ligands, e.g., CO or CNR, are found only in lower valent iron complexes. Here we report on Fe(η^4-**1**)(CN^{t}Bu)$_2$, an Fe(IV) isocyanide complex that is stable, strongly oxidizing, and of intermediate spin ($S = 1$).

Synthesis of Fe(η^4-**1**)(CN^{t}Bu)$_2$ (Scheme I): *tert*-butyl isocyanide (Aldrich, 0.15 mL, 1.3 mmol) was added to a filtered solution of Li$_2$[FeCl(η^4-**1**)] (469 mg, ca. 0.9 mmol)[4b] in water (35 mL), and the solution was stirred (25 min). $(NH_4)_2Ce(NO_3)_6$ (Aldrich, 527 mg, 0.96 mmol) was added, and the precipitate was collected, washed with distilled water (20 mL), and dried. Black crystals were grown in the presence of excess *tert*-butyl isocyanide from benzene/hexane by vapor diffusion and collected early in the crystallization process at low yield to ensure high purity (118 mg, ca. 23% yield).[6] Cyclic voltammetry of Fe(η^4-**1**)(CN^{t}Bu)$_2$ shows a reversible Fe$^{IV/III}$ couple at $E_f = +450$ mV vs Fc$^+$/Fc (ca. 1.16 V vs NHE, CH_2Cl_2, 0.1 M $[Bu_4N][ClO_4]$). Therefore, Fe(η^4-**1**)(CN^{t}Bu)$_2$ is a stable, strong electron-transfer oxidant, a rare entity in high valent MLTM chemistry.

The zero-field Mössbauer spectrum of polycrystalline Fe(η^4-**1**)(CN^{t}Bu)$_2$ consists of a doublet with $\Delta E_Q = 3.38$ mm s^{-1} and $\delta_{Fe} = -0.04$ mm s^{-1} (relative to Fe metal at 298 K); ΔE_Q is independent of temperature for $T < 298$ K, implying an isolated orbital ground singlet. The absence of magnetic hyperfine interactions in zero field indicates a complex with integer or zero electronic spin. This absence, together with the distinctly low value of δ_{Fe}, supports an iron(IV) formulation. High field spectra

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[6] Anal. Calcd for $C_{32}H_{52}N_6O_5Fe$: C, 58.53; H, 7.98; N, 12.80. Found: C, 58.51; H, 7.91; N, 12.72. IR: ν(Nujol) 2226 cm^{-1} $\nu_{asym}[M(C{\equiv}NR)_2]$. UV/vis: λ_{max} (CH_2Cl_2) 865 nm, $\epsilon = 7800$ L mol^{-1} cm^{-1}.

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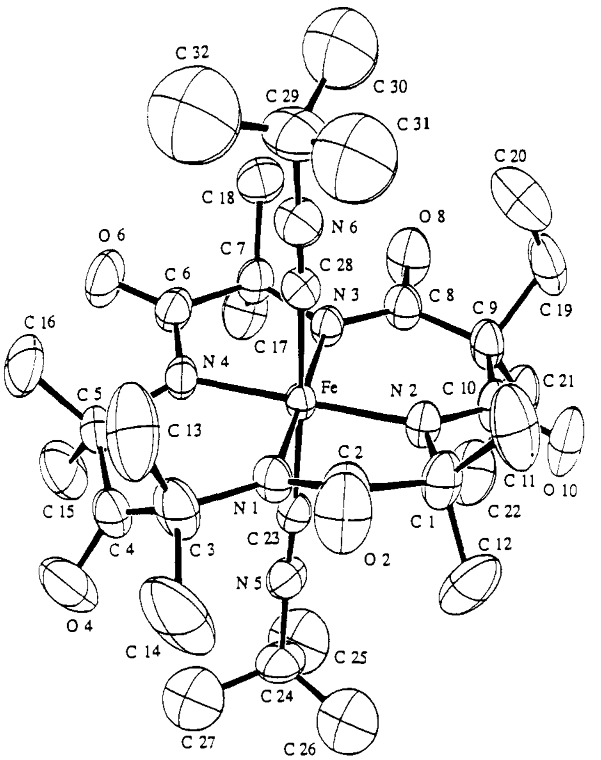

Figure 2. Molecular structure of Fe(η^4-**1**)(CN^{t}Bu)$_2$; ORTEP drawing with all non-hydrogen atoms drawn to encompass 50% of electron density. Key bond distances (Å) are Fe–C23, 1.973 (3); Fe–C28, 1.965 (3); Fe–N1, 1.927 (2); Fe–N2, 1.905 (2); Fe–N3, 1.895 (2); Fe–N4, 1.914 (2); C23–N5, 1.138 (4); C28–N6, 1.143 (4). Selected bond angles (deg): C29–N6–C28, 178.2 (3); C24–N5–C23, 176.2 (3).

(Figure 1) exhibit magnetic hyperfine interactions, indicating an integer electronic spin. Attempts to explain these data with high spin ($S = 2$) iron(IV) were unsuccessful because the fits require A values 3–4 times smaller than expected for a high spin configuration.[7] However, the data fit well to an $S = 1$ spin Hamiltonian resulting from a tetragonally or rhombically distorted t_{2g}^4 configuration (see caption of Figure 1). The Mössbauer spectra show that the magnetic hyperfine field is essentially axial. Using the model of Oosterhuis and Lang,[8] the tetragonal splitting of the t_{2g} set is $\Delta \approx 5\xi = 2000$ cm^{-1}, where $\xi = 400$ cm^{-1} is the spin–orbit coupling constant. Within this model, an axial hyperfine field can be produced even for a rhombic ligand field. Independent of the assumed symmetry, our data place the first excited state in the t_{2g} set at least 1500 cm^{-1} above the ground state.

The geometry around the iron atom of Fe(η^4-**1**)(CN^{t}Bu)$_2$ is an axially distorted octahedron (Figure 2).[9] The RMS deviation from the plane of Fe and the four N donor atoms is 0.03 Å. The average Fe–C distance is 1.969 Å, while the average Fe–N distance is 1.910 Å. The average C–N length in the isocyanides is 1.14 Å, and the CNC isocyanide angles are nearly 180°. Iron–isocyanide complexes have been structurally characterized for Fe(0), Fe(I), and Fe(II).[10] Comparison with the literature data shows that a C–N triple bond formulation is appropriate, indicating that the π-acid character of the isocyanides is not highly expressed.[11] This agrees with the observance of a nonzero spin d^4 iron center, ruling out an electronic structure in which strong π-interactions between two dπ metal orbitals and empty π^* isocyanide orbitals bring about spin pairing. The existence of Fe(η^4-**1**)(CN^{t}Bu)$_2$ demonstrates that the coordination chemistry of high valent iron can be expanded.

Acknowledgment. We gratefully acknowledge the NSF (Grant CHE-8714720, T.J.C.) and the NIH (Grants GM22701, E.M., and U41 RR04154, Pittsburgh Supercomputing Center).

Supplementary Material Available: Tables of data collection information, atom coordinates, Gaussian amplitudes, and bond lengths and angles for Fe(η^4-**1**)(CN^{t}Bu)$_2$ (7 pages); listing of structure factor amplitudes for Fe(η^4-**1**)(CN^{t}Bu)$_2$ (20 pages). Ordering information is given on any current masthead page.

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(7) An $S = 2$ fit yields $A_x \approx A_y \approx -7.6$ MHz and $A_z \approx -2$ MHz. This should be compared with $A_x \approx A_y \approx A_z \approx -20$ MHz for the $S = 2$ high spin Fe(IV) complex with the same macrocycle, [Fe(η^4-**1**)Cl]$^-$; the latter compound yields an integer spin EPR signal at $g = 8$, which is characteristic for an $S = 2$ system, unpublished results. A values of ca. 20 MHz have also been reported for the $S = 2$ Fe(IV) sites of $M_{0.5}La_{1.5}Li_{0.5}Fe_{0.5}O_4$ (where M = Ca, Sr, Ba): Demazeau, G.; Fournes, L.; Soubeyroux, J.-L.; Takeda, Y.; Thomas, M.; Pouchard, M. *Rev. Chim. Miner.* **1983**, *20*, 155–172.

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(9) Crystal data: Single crystals of Fe(η^4-**1**)(CN^{t}Bu)$_2$ at 293 K are triclinic, space group $P\bar{1}$ with $a = 11.491$ (1) Å, $b = 10.481$ (2) Å, $c = 15.015$ (8) Å, $\alpha = 95.26$ (2)°, $\beta = 91.29$ (2)°, $\gamma = 81.58$ (1)°, $V = 1718.2$ Å^3, and $Z = 2$ [$d_{calcd} = 1.268$ g cm^{-3}, μ(Mo Kα) = 4.34 cm^{-1}]. A total of 7726 independent reflections ($2° < 2\theta < 55°$) were collected using $\omega/2\theta$ scans with graphite-monochromated Mo Kα radiation. The structural parameters have been refined to convergence, R_1 (unweighted, based on F) = 0.058 for 6679 observed reflections [$I > 3\sigma(I)$].

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(11) A detailed analysis will appear elsewhere.

Solid-State Photochemistry. Remarkable Effects of the Packing of Molecules in Crystals on the Diastereoselectivity of the Intramolecular 2 + 2 Photocycloaddition of a 4-(3'-Butenyl)-2,5-cyclohexadien-1-one

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The intramolecular 2 + 2 photocycloadditions of 4-(3'-alkenyl)-2,5-cyclohexadien-1-ones give tricyclo[5.2.1.0^{5,10}]dec-2-en-4-ones in excellent yields.[1] Enantioselective constructions of these synthetically useful tricycles are possible[1a] because of the availability of methods for asymmetric synthesis of 2,5-cyclohexadien-1-ones[2] and the demonstration that the intramolecular 2 + 2 photocycloaddition proceeds without racemization of the photosubstrate.[3] In this paper we describe a fundamentally different kind of asymmetric control involving photochemistry of a 4-(3'-butenyl)-2,5-cyclohexadien-1-one (e.g., **1b** → **2b** or **3b**) in the solid state.[4] We show that competing and nearly isoenergetic (in the solution state) unimolecular photocycloadditions[5] can be selectively partitioned in the solid state as a result of the

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(3) This result is in contrast to the type A photorearrangement of enantiomerically pure 4-carbomethoxy-3-methoxy-4-methyl-2,5-cyclohexadien-1-one, which has been shown to occur with partial racemization of the photosubstrate; see ref 1a.

(4) For the first report of a solid-state photorearrangement of a 2,5-cyclohexadien-1-one (santonin), see: Matsuura, T.; Sata, Y.; Ogura, K. *Tetrahedron Lett.* **1968**, 4627.

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