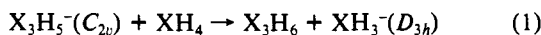


to out-of-plane rotation modes. While the cost in bending energy is considerable, planarization to **1f** results in enhanced π conjugation. However, the extent of this conjugation is underestimated by the rigid rotation barrier via **1g** (8.3 kcal/mol). This value is only a little higher than the relaxed barrier (**1a** \rightarrow **1e**, 4.4 kcal/mol) and is much lower than the rotational barrier in the allyl anion (ca. 21 kcal/mol).

An entirely different conclusion regarding the magnitude of the conjugation energy in planar Si_3H_5^- is reached by comparison of the stabilization energies of C_3H_5^- (**2**) vs Si_3H_5^- (**1f**) based on the appropriate planar XH_3^- (D_{3h}) species (eq 1).



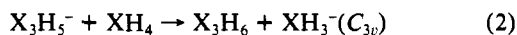
34.1 kcal/mol for Si_3H_5^- (**1f**)

30.1 kcal/mol for C_3H_5^- (**2**)

The larger stabilization energy of **1f** than **2** (eq 1) shows that charge delocalization in the second row can be as effective as that in the first. However, p - π conjugation in the second row must compete with the strong preference of lone pairs or single electrons (including those comprising double bonds) to occupy orbitals having a high degree of s -character. This preference results, for example, in the nonplanar Si_3H_5^- structures (e.g., **1a**, **1b**) found here (Figure 1).

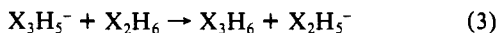
When eq 1 is reevaluated by employing data for the most stable nonplanar structures of SiH_3^- (C_{3v}) and Si_3H_5^- (**1a**) (as well as C_{3v} CH_3^-), the energy comparison with **2** (eq 2) is remarkable: the stabilization energy for Si_3H_5^- (**1a**) is almost as large as that for allyl anion (**2**)! Even if the fully nonconjugated minimum **1d** were substituted for **1a**, the $\text{X} = \text{C}$ vs Si comparison in eq 2 would give nearly the same energies!

However, when the lowest energy X_2H_5^- (and X_2H_6) species are used as the references (instead of XH_3^- and XH_4), **2** is clearly favored over **1a** (eq 3). The disilaethyl anion, Si_2H_5^- , is stabilized by its SiH_3 substituent, whereas C_2H_5^- is slightly destabilized by the methyl group.¹⁰ This difference is brought out in eq 4. The Si_2H_3 grouping, even in the nonconjugated **1d**, functions similarly to a SiH_3 substituent in stabilizing a SiH_2^- anion. The Si_3H_5^- rotational potential energy surface is relatively flat, because all of the conformations (**1a**-**e**) benefit to nearly equal extents from different combinations of conjugation, hyperconjugation, and electron delocalization.



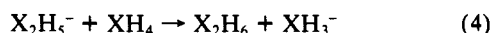
26.9 kcal/mol for $\text{X} = \text{Si}$ (**1a**)

27.8 kcal/mol for $\text{X} = \text{C}$ (**2**)



13.6 kcal/mol for $\text{X} = \text{Si}$ (**1a**)

31.0 kcal/mol for $\text{X} = \text{C}$ (**2**)



13.3 kcal/mol for $\text{X} = \text{Si}$

-3.2 kcal/mol for $\text{X} = \text{C}$

The trisilaallyl radical (**3**) was found⁶ to have a minimum similar to **1a**: all silicons are nonplanar. The stabilization energy of **3** with respect to Si_2H_5^* (6.0 kcal/mol; cf. eq 3) is about half the value for **1a** (13.6 kcal/mol). The rotation barrier of **3** (with imposed planarity of the rotating SiH_2 group) also is lower (5.0 kcal/mol) than the corresponding value (8.3 kcal/mol), **1f** \rightarrow **1g**.

We conclude that the lowest energy structure of the trisilaallyl anion (**1a**) is governed by the inherent nonplanarity of tricoordinated silyl anions rather than by conjugation. When planarity is imposed (eq 1), the stabilization energy of **1f** (relative to planar SiH_3^-) is even larger than that of allyl anion. Hyperconjugation

provides substantial stabilization of the nonplanar Si_3H_5^- conformers, as well as $\text{SiH}_3\text{SiH}_2^-$.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Stiftung Volkswagenwerk, the Convex Computer Corporation, and the awards of fellowships by the Alexander von Humboldt Foundation to A.A.K.

Aminobenzannulation via Metathesis of Isonitriles Using Chromium Carbene Complexes

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The Dötz benzannulation reaction¹ based on alkyne cycloaddition to chromium carbene complexes is the most important reaction of Fischer carbene complexes.² Numerous advances have been achieved in application of the Dötz reaction to total synthesis projects³ and in further development of benzannulation reactions based on Fischer carbene complexes.⁴ However, a long-standing problem has been development of general annulation reactions which incorporate triple bonds other than carbon-carbon triple bonds for the synthesis of heterosubstituted benzene derivatives from chromium carbene complexes. Although reactions utilizing phosphalkynes successfully generate phospharenes,⁵ use of nitriles or isonitriles fails in a general sense to produce pyridine or aminobenzene derivatives.^{6,7} Typical reactions of carbene complexes with nitriles led to imino carbene complexes,⁸ while isonitriles provide, initially, metal complexed ketenimines,⁹ then

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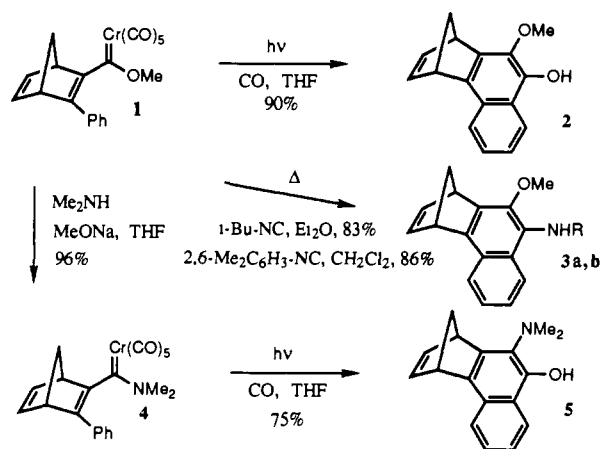
(7) For two examples of aminobenzene products formed from a chromium carbene complex plus isonitrile reaction via subsequent Diels-Alder and oxidation reactions, see: Aumann, R.; Heinen, H. *Chem. Ber.* 1986, 119, 3801.

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Scheme I



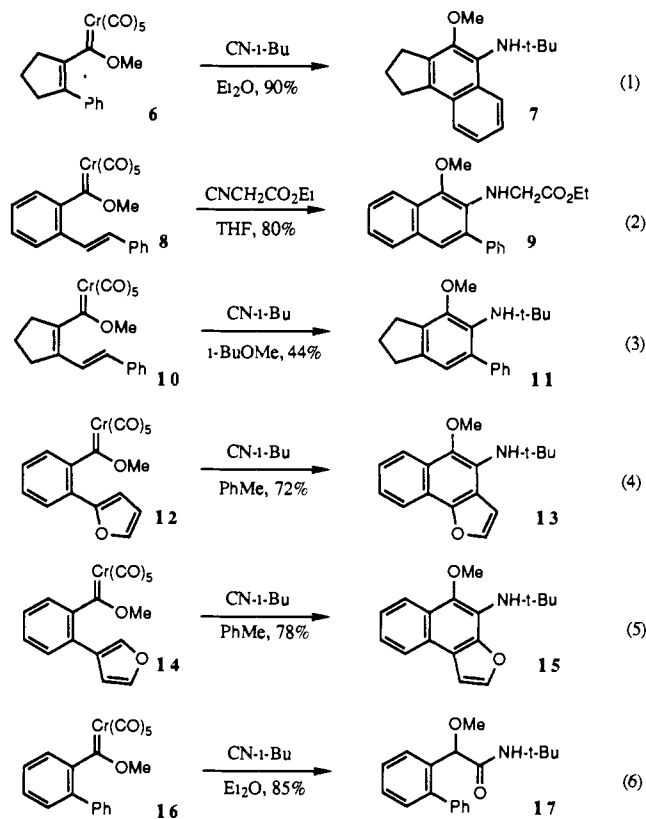
a range of products including aminocarbene complexes, 2,3-bis(imino)azetidines, 1,2-bis(imino)cyclobutane complexes, 1,2-bis(imino)indane complexes, δ -carbolinones, 2,3-dihydroazete complexes, imidazole complexes, indoles, nitrile complexes, and pyrroles depending on the reaction stoichiometry and the structures of the carbene complex and isonitrile.¹⁰ We report herein on successful, designed aminobenzannulation reactions of chromium dienylcarbene complexes with isonitriles that produce synthetically useful ortho alkoxy aromatic amine products.

We have recently reported new photochemical benzannulation reactions of alkoxy (1 to 2)¹¹ and amino (4 to 5)¹² chromium dienylcarbene complexes that employ photolytic conversion of carbene complexes to chromium complexed *dienylketenes* with subsequent electrocyclicization (Scheme I). Additionally, Aumann has established that isonitriles undergo metathesis with carbene complexes to produce pentacarbonylchromium complexed ketenimines⁹ which can subsequently react in a number of pathways (vide supra). Hence, a designed aminobenzannulation reaction can be envisaged through metathesis of a chromium *dienylcarbene* complex with a simple isonitrile to generate a chromium complexed *dienylketenimine* with subsequent electrocyclicization and tautomerism to an aminobenzene derivative.¹³ This benzannulation process would then provide a facile complement to photochemical benzannulation reactions of aminocarbene complexes¹² since the aminoaromatic products are regioisomeric (3 vs 5).

As an initial test substrate, bicyclic carbene 1 was treated with 2 equiv of *tert*-butyl isocyanide in ether under nitrogen in the dark at 0 °C and warmed to reflux for 8 h. Chromatographic purification provided an 83% yield of the aromatic amine 3a¹⁴ (Scheme I). Use of 2,6-dimethylphenyl isocyanide (3 equiv) was also quite efficient at effecting the benzannulation reaction to 3b¹⁴ (Scheme I).

Given these results, a number of substrates which are formally dienylcarbene complexes were examined for the new process and most were found to provide high yields of benzannulated products (eqs 1–6). Since the metathesis was unaffected by a range of ethereal solvents, solvent choice was based on the temperature necessary to effect thermal electrocyclicization of the intermediate dienylketenimine. A range of isonitriles can be used in the benzannulation reaction and selected examples are shown here with

the most notable being the very sterically hindered 2,6-dimethylphenyl isocyanide (Scheme I). All reactions required at least 2 equiv of isonitrile reactant, but some (eqs 4 and 5) required 3 equiv. In general, the product structure is strictly defined by the geometry of the starting material, but eqs 4 and 5 illustrate the regioselectivity possible and the facility of construction of isomeric products. The regioselectivity demonstrated by furan containing substrate 14 for reaction at C-2 over C-4 is due to frontier orbital control of the electrocyclicization.¹⁵



The mechanism for the benzannulation reaction can be formulated as initial metathesis of the isonitrile to form a pentacarbonylchromium complexed dienylketenimine, demetalation by the second equivalent of isonitrile,^{9b,16} electrocyclicization of the free dienylketenimine, and tautomerism of the resultant imine to form the final product. In contrast to the reports by Aumann,^{10,17} no products from incorporation of two or more equivalents of isonitrile were found even when sterically less hindered isonitriles such as benzyl and *n*-butyl isocyanide were used.¹⁸ Although we propose that the second equivalent of isonitrile serves to demetalate the intermediate ketenimine complex, the chromium pentacarbonyl fragment could serve to template and activate the electrocyclicization reaction with subsequent demetalation. In either case, high yields of the isocyanide (pentacarbonyl)chromium byproduct are recovered upon completion of the reaction.

A structural requirement of the dienylcarbene substrates is *cis* α,β -unsaturation, but alkenyl, aryl, and furyl groups can all function as the alkene components. The biphenyl carbene complex 16, though, illustrates that the electrocyclicization step after me-

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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., O²⁻ and Cl⁻.⁴ Relatively unstable iron(IV) complexes of the general formulation [Fe(L-L)₂X₂]²⁺ (L-L = diphosphine, diarsine; X = Cl, Br) containing characteristically weak π -acid phosphine and arsine ligands are known.⁵

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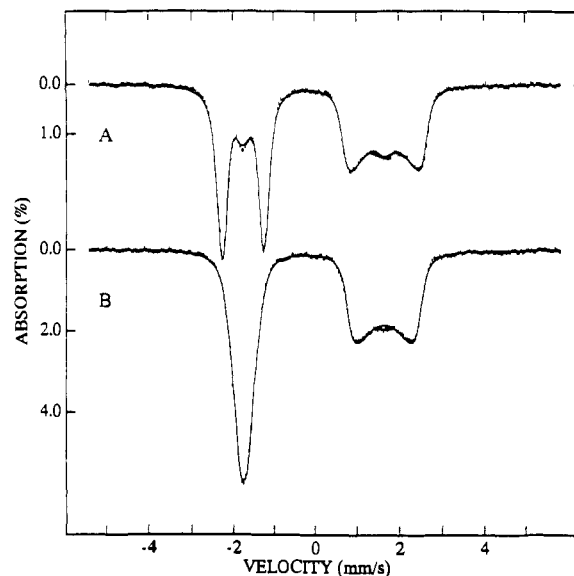
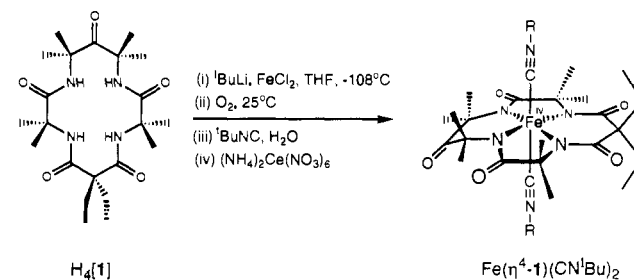


Figure 1. Mössbauer spectra of the polycrystalline Fe(η^4 -**1**)(CN^tBu)₂ recorded at 4.2 K (A) and 18 K (B) in a 6.0-T applied field. The spectra were fitted to the $S = 1$ spin Hamiltonian $H = D[(S_x^2 - 2/3) + E(S_x^2 - S_y^2)] + \beta S \cdot g \cdot H + S \cdot A \cdot I + (eQV_{zz}/12)[3I_z^2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

Scheme I



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^tBu)₂, an Fe(IV) isocyanide complex that is stable, strongly oxidizing, and of intermediate spin ($S = 1$).

Synthesis of Fe(η^4 -1**)(CN^tBu)₂ (Scheme I):** *tert*-butyl isocyanide (Aldrich, 0.15 mL, 1.3 mmol) was added to a filtered solution of Li₂[FeCl(η^4 -**1**)] (469 mg, ca. 0.9 mmol) in water (35 mL), and the solution was stirred (25 min). (NH₄)₂Ce(NO₃)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^tBu)₂ shows a reversible Fe^{IV/III} couple at $E_f = +450 \text{ mV}$ vs Fe³⁺/Fe²⁺ (ca. 1.16 V vs NHE, CH₂Cl₂, 0.1 M [Bu₄N][ClO₄]). Therefore, Fe(η^4 -**1**)(CN^tBu)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^tBu)₂ consists of a doublet with $\Delta E_Q = 3.38 \text{ mm s}^{-1}$ and $\delta_{Fe} = -0.04 \text{ mm s}^{-1}$ (relative to Fe metal at 298 K); ΔE_Q is independent of temperature for $T < 298 \text{ K}$, 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

(6) Anal. Calcd for C₃₂H₅₂N₆O₅Fe: C, 58.53; H, 7.98; N, 12.80. Found: C, 58.51; H, 7.91; N, 12.72. IR: $\nu(\text{Nujol})$ 2226 cm⁻¹ $\nu_{\text{asym}}[\text{M}(\text{C}\equiv\text{NR})_2]$. UV/vis: λ_{max} (CH₂Cl₂) 865 nm, $\epsilon = 7800 \text{ L mol}^{-1} \text{ cm}^{-1}$.