

palladium on the tin-bound carbon atom.^{1c}

The possibility of synthesizing ketones by using Pd(Ph-BIAN) catalysts was demonstrated by the coupling of benzoyl chloride with Sn(CH₃)₄ and reaction of benzyl bromide with Sn(CH₃)₄ under 1 bar of CO pressure. These reactions are highly selective, since in both cases the ketone was formed as the only product in good chemical yield (88–98%). In a separate experiment it was shown that [Pd(Ph-BIAN)Br(CH₂Ph)] in THF or CDCl₃ reacts rapidly with CO at atmospheric pressure and room temperature to yield the Pd-acyl complex [Pd(Ph-BIAN)Br(C(O)-CH₂Ph)] quantitatively,¹⁷ which explains the high efficiency and selectivity of the carbonylative coupling.

We conclude that the new palladium complexes of type 1 and 2, containing the cis-fixed bidentate nitrogen ligand Ph-BIAN, are active catalysts in a variety of selective carbon-carbon bond-forming reactions which can be carried out under mild reaction conditions using small amounts of catalyst (generally 1 mol %).

(17) NMR (in CDCl₃): 3.40 ppm, Pd(CH₂Ph); 4.14 ppm, Pd(C(O)-CH₂Ph). IR (CH₂Cl₂): 1715 cm⁻¹, Pd(C(O)CH₂Ph).

Further studies, involving the scope and limitations of the Pd(Ph-BIAN)-catalyzed carbon-carbon bond-forming reactions as well as mechanistic investigations and comparison with other ligands (e.g. other (cis-fixed) bidentate nitrogen ligands and phosphines), are currently in progress.

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Registry No. 1 (E = CO₂CH₃), 141062-94-4; (*p*-Tol)I, 624-31-7; PhI, 591-50-4; PhCH(Me)Br, 585-71-7; Me₂C=C=CHBr, 6214-32-0; PhCH=CHBr, 103-64-0; PhCH₂MgCl, 6921-34-2; (allyl)-MgCl, 2622-05-1; (*p*-Tol)MgBr, 4294-57-9; (*p*-Tol)ZnCl, 90252-89-4; (*p*-Tol)CH₂Ph, 620-83-7; (PhCH₂)₂, 103-29-7; PhCH₂Ph, 101-81-5; PhCH(Me)CH₂CH=CH₂, 10340-49-5; (PhCH(Me))₂, 5789-35-5; Me₂C=C=CH(*p*-Tol), 141062-93-3; (*p*-Tol)₂, 613-33-2; PhCH=CH(*p*-Tol), 4714-21-0; PhCH₂Br, 100-39-0; PhC(O)Cl, 98-88-4; SnMe₄, 594-27-4; (*p*-Tol)SnBu₃, 31614-66-1; PhCH₂CH₃, 100-41-4; PhCH₂C(O)CH₃, 103-79-7; PhC(O)CH₃, 98-86-2.

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Retro-Alkyne Cyclotrimerization in Thermal Gas-Phase Metal Ion-Arene Reactions

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Summary: The thermal energy reactions of Ta⁺, Nb⁺, and NbL⁺ (L = O, N) with arenes in the gas phase result in cleavage of the aromatic rings with formation of metallocyclopentadiene ion complexes via a retro-alkyne cyclotrimerization mechanism. The ring cleavage reactions are proposed to involve bent arene intermediates, analogous to recently observed Ta- and Nb-benzene complexes generated in solution by alkyne cyclotrimerization. The d⁰ system NbO₂⁺ reacts with pyridine exclusively via C-H bond activation involving a σ -metathesis transition state.

The interaction of arenes with transition-metal systems has clear implications for the metal-catalyzed [2 + 2 + 2] cycloaddition reactions of alkynes and nitriles and for the activation of C-H bonds in aromatic systems.^{1,2} In accord with this interest, the reactions of benzene and its halogen-substituted analogues with gas-phase atomic metal ions have been the subject of numerous recent investigations.³⁻⁶ Some of the most reactive gas-phase metal ions

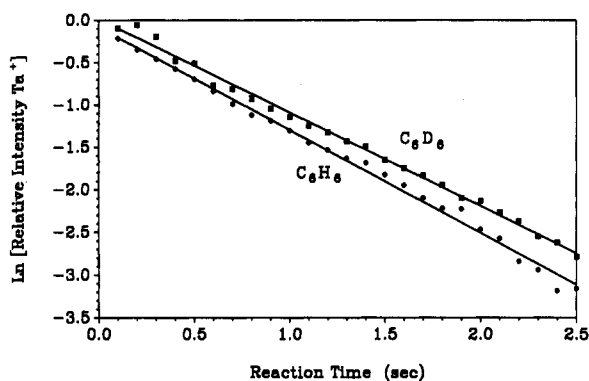


Figure 1. Plot of the decay of ln(Ta⁺) as a function of time in the reaction of thermalized Ta⁺ with (i) C₆H₆ and (ii) C₆D₆. The ratio of the slopes yields a kinetic isotope effect of $k_H/k_D = 1.1 \pm 0.1$.

react directly with benzene to generate benzyne complexes,⁴ and subsequent reactions for some metals produce coordinated polyphenylenes.²⁻⁵ We report here on the unusual thermal reactions of Nb⁺ and Ta⁺ with benzene and pyridine, including ring cleavage by a retro-alkyne

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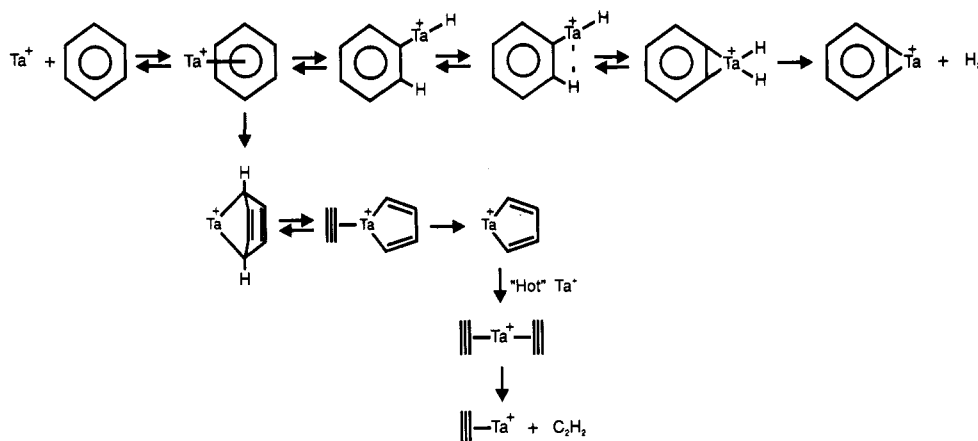
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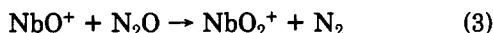
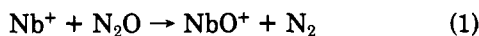
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Scheme I



cyclotrimerization mechanism and the generation of coordinated polycyclic aromatic hydrocarbons by fragment coupling at the metal center.

Atomic metal cations were generated in a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR)^{7,8} by laser desorption/ionization of pure rods of Nb or Ta.⁹ After desorption, the ions in the trap underwent a 0.5-s thermalization period, during which time they were translationally and electronically cooled by roughly 15 collisions with the reactant benzene or pyridine (1×10^{-6} Torr). The remaining unreacted metal cations were then isolated using swept RF ejection pulses. Thermalization is confirmed by the linearity of the kinetic plots (see Figure 1); plots for nonthermal reactions show significant initial curvature. The NbL^+ complexes were synthesized by reactions 1–3.¹⁰



The primary products in the gas-phase reactions of Ta^+ , Nb^+ , and NbL^+ ($\text{L} = \text{O}, 2\text{O}, \text{N}$) with benzene and pyridine are shown in Table I. Products include formation of the benzyne and pyridyne complexes, elimination of acetylene and HCN, and formation of the acetylene complex. Production of TaC_2H_2^+ from benzene only occurs if the Ta^+ reactant ions are not thermalized, suggesting the reaction is endothermic. The primary products are unusual because all other metal ions reported to date react with benzene by slow adduct formation or by C–H bond activation to form metal–benzyne complexes.^{3–5}

Thermochemical values implied by these reactions are also shown in the tables.¹¹ Cleavage of a benzene or

Table I. Primary Reaction Products

M^+	d^n	products ^a	implied $D^{\circ,b}$ kcal mol ⁻¹
M^+-Benzene Primary Reaction Products			
Ta^+	d^4	TaC_6H_4^+	>77
		TaC_4H_4^+	>152
Nb^+	d^4	$\text{TaC}_2\text{H}_2^{+c}$	
		NbC_6H_4^+	>77
M^+-Pyridine Primary Reaction Products^d			
Ta^+	d^4	TaC_4H_4^+	>116
Nb^+	d^4	NbC_4H_4^+	>116
NbO^+	d^2	$\text{NbOC}_4\text{H}_4^{+e}$	>116
NbN^+	d^2	$\text{NbNC}_4\text{H}_4^{+e}$	>116
NbO^{2+}	d^0	$\text{NbO}_2\text{C}_5\text{H}_3\text{N}^+$	

^a Products accounting for $\geq 90\%$ of reaction yield.

^b Thermochemical data used to derive these values were obtained from ref 11. ^c Product formed from reaction of nonthermalized Ta^+ reactant ions. ^d Coordinated C_2H_2 is a minor ($\leq 7\%$) product of thermal pyridine–metal ion reactions. ^e Small ($\leq 10\%$) amounts of dehydrogenation and/or adduct formation are also observed.

pyridine ring is clearly a high-energy process involving loss of aromaticity and C–C (and in pyridine, C–N) bond breaking. The Ta^+ –benzene reaction implies $D(\text{Ta}^+-\text{C}_4\text{H}_4) > 152$ kcal/mol, while the $\text{NbL}^+=\text{pyridine}$ reactions indicate $D(\text{NbL}^+-\text{C}_4\text{H}_4) > 116$ kcal/mol. The high ligand binding energies are a reflection of the product stability that drives the ring cleavage. Both of these values are only consistent with formulation of MC_4H_4^+ as a metallacyclopentadiene ion (structure I). Typical M–C σ bonds



for these metals are in the range of 55–65 kcal/mol.¹² Though the binding energy for TaC_4H_4^+ is greater than the sum expected for two M–C σ -bonds (~ 110 – 130 kcal/mol), in this case the metal has two extra electrons that can be donated to the π -system to form an aromatic complex of enhanced stability. A metallacyclopentatriene structure, similar to structure II, is not possible for the NbL^+ products because it requires an unreasonable oxidation state for the metal. Any other reasonable structure for MC_4H_4^+ would involve side-on olefin coordination to the metal. Typical Ta^+ –olefin and Nb^+ –olefin binding energies are in the range of 45–70 kcal/mol,¹³ well below

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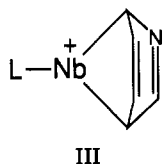
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the presently observed values. Pyridine, but not benzene, cleavage by Nb⁺ occurs simply because HCN elimination from pyridine requires 32 kcal/mol less energy than acetylene elimination from benzene, which also explains why nitrogen is not retained in the metal complex in any of the pyridine reactions.

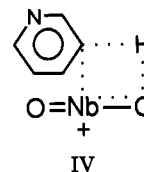
Scheme I presents a mechanism for the reactions of Ta⁺ with benzene, corresponding to the reverse of the cyclo-trimerization of alkynes.^{1,2} The reaction of Ta⁺ with C₆D₆ generates the analogous deuterated products with a very small to negligible kinetic isotope effect ($k_H/k_D = 1.1 \pm 0.1$; see Figure 1), consistent with the formation of a tantalacyclopentadiene intermediate that does not require a C–H bond-cleavage step. The formation of the acetylene complex from “hot” Ta⁺ involves subsequent decomposition of internally excited TaC₄H₄⁺ by a retro-Reppe mechanism.¹ An analogous mechanism is proposed for the pyridine reactions.

The mechanism shown in Scheme I involves a “bent” ring system. Recent structural characterizations of a few tantalum–benzene complexes have shown the benzene distorted into a “boat” configuration with a 26° out-of-plane bend.¹⁴ The two benzene carbon atoms bent toward the metal center have Ta–C distances close to that expected for σ -bonds. These complexes were synthesized by [2 + 2 + 2] cycloaddition reactions. Niobium cluster complexes have also been characterized which incorporate multiple boat benzene ligands, each with at least a 22.6° out-of-plane bend.¹⁵ The d⁴ Nb⁺ and Ta⁺ and the d² NbN⁺ and NbO⁺ systems all can form the Nb–C bonds (see structure III) necessary to initiate the ring-cleavage



process. This is consistent with the condensed-phase ob-

servation that boatlike benzene structures are only observed for lower oxidation state early transition metals with two or more d electrons. The d⁰ NbO₂⁺ cannot form the necessary Nb–C bonds; thus, pyridine ring cleavage is not observed. However, many d⁰ systems can activate C–H bonds through four-centered σ -metathesis transition states,¹⁶ as in structure IV. In accord with this, NbO₂⁺ slowly dehydrogenates pyridine.



The primary benzyne and metallacyclopentadiene products will undergo subsequent reactions with either benzene or pyridine. Reactions out to 90 s and at pressures up to 1×10^{-6} Torr have been investigated. Ta⁺ reacts with benzene as many as four times while Nb⁺ dehydrogenates up to three benzene molecules. Previous work on the reactions of halogenated benzene showed coupling of benzyne ligands to form metal ion–polyphenylene complexes.^{3,4} To probe for coupling of the unsaturated ligands on Ta⁺ we have performed collision-induced dissociation experiments on the TaC₁₀H₈⁺ product of reaction 4.



Observation of a small peak at the m/e value corresponding to naphthalene cation suggests the secondary formation of Ta(naphthalene)⁺, most likely by a Diels–Alder mechanism. Subsequent reactions of TaC₁₀H₈⁺ with benzene support the view of coupled hydrocarbon fragments that leave the metal center relatively unhindered. We are currently investigating the reactions of a variety of arenes with these metal cations to probe these interesting processes in more detail.

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Stereoselection Effects in the Catalytic Hydroamination/Cyclization of Aminoolefins at Chiral Organolanthanide Centers

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Summary: The chiral organolanthanide complexes Me₂Si(Me₄C₅)(C₅H₃R*)LnE(SiMe₃)₂ (R* = (–)-menthyl, (+)-neomenthyl; Ln = La, Sm; E = N, CH) serve as precatalysts for the enantioselective or diastereoselective hydroamination/cyclization of aminoolefins to chiral pyrrolidines and piperidines.

We recently reported^{1a} on the synthesis, structural

characterization, and efficacy (high enantiomeric excesses and turnover frequencies) as precatalysts for asymmetric olefin hydrogenation of the chiral organolanthanide complexes Me₂Si(Me₄C₅)(C₅H₃R*)SmCH(SiMe₃)₂ (1 and 3; R*

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