accord with the fact that the dissociation threshold of the $C_6H_5^+$ generation locates at about 12.3 eV from the neutral C_6H_5Cl, as it was examined by Durant et al.[8] Even higher threshold for the $C_6H_5^+$ generation is expected in the complex because of stabilization of the neutral complex by the vdW interaction. From the observed power dependence, thus, the $C_6H_5NH_3^+$ generation cannot be explained by the formation of $C_6H_5^+$ as a precursor of $C_6H_5NH_3^+$. Therefore, we conclude that $C_6H_5NH_3^+$ is produced by the substitution reaction within the complex ion. Detailed energetics of the present system including the complexes C_6H_5X-ND_3 are now in progress by using two-color photoionization mass spectroscopy.

In conclusion we have found that the "bimolecular" S_N reaction within the (1:1) vdW complex ion $C_6H_5Cl^+$-NH_3 yields the product $C_6H_5NH_3^+$ with a quite high efficiency. The present result demonstrates that the chemical reactivity of mutually stable reagents bound weakly in neutral vdW complexes is altered dramatically upon the ionization which triggers vigorous chemical reactions.

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Reductive Coupling of Nitriles via Formal [2 + 2] Cycloadditions to the Titanium-Carbon Double Bond

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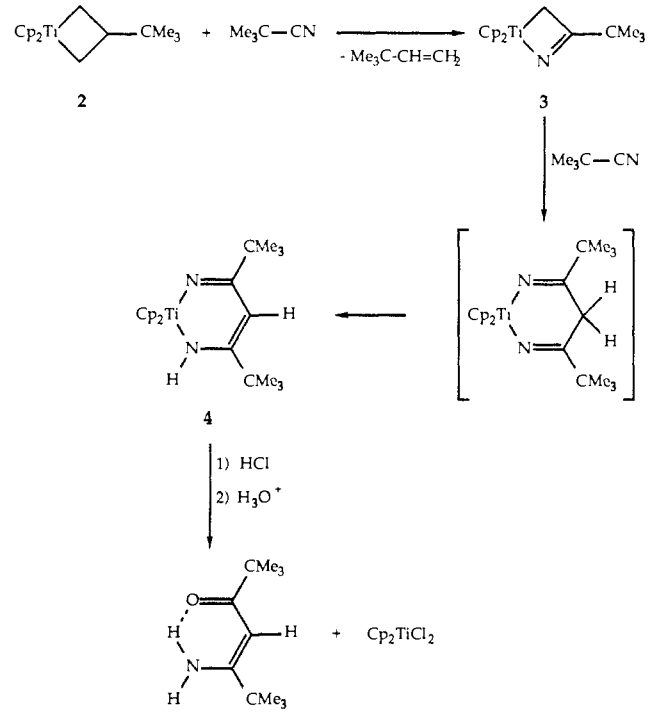
As part of a broader investigation of the synthesis and reactivity of metallacyclobutenes and related complexes,[1] we have begun an exploration of the reactivity of nitriles with sources of the reactive methylidene complex of bis(cyclopentadienyl)titanium.[2] We have prepared stable metallacyclic complexes resulting from simple formal [2 + 2] cycloaddition and have begun a systematic study of their reactivity and of their utility in synthetic organic transformations. Initial results of these studies are reported here.

Titanacyclobutanes serve as convenient precursors,[12] via metathetic loss of alkene, of either the free methylidene complex, $Cp_2Ti{=}CH_2$ (**1**), or its alkene complex. We have found that treatment of the metallacyclobutane **2** with pivalonitrile provides

Scheme I



an azametallacyclobutene, the product of formal [2 + 2] cycloaddition of methylidene complex **1** and the nitrile. Thus, treatment of a C_6D_6 solution of titanacyclobutane **2** with 1 equiv of pivalonitrile at 50 °C for 48 h, following the reaction progress by ^1H NMR, led to formation of metallacycle **3** (Scheme I).[13] Under these conditions, the reaction was quite sluggish, however, and various byproducts were also obtained. Isolation of the pure azametallacyclobutene from this mixture, which contains ca. 50% of **3**, has not yet proved possible. Use of 2 equiv of pivalonitrile accelerated the reaction, and the product was formed in essentially quantitative yield after 1.5 h at 60 °C. The azametallacyclobutene appears to be indefinitely stable under these conditions; no decomposition was observed even after prolonged heating (several days) at 60 °C, though very slow conversion to a follow-up product, **4** (vide infra), occurred (conversion to **4** was essentially complete after ca. 1 month at 60 °C).

Attempted isolation of **3** from the 2:1 reaction mixture via evaporation of solvent and excess pivalonitrile in vacuo led cleanly to formation of a new metallacyclic product, **4**. Apparently, the increase in concentration of pivalonitrile as the more volatile benzene is removed accelerates this insertion over the very slow insertion seen at the lower concentration of the NMR experiment. The presumed initial insertion product was not observed but underwent a tautomerization to afford the conjugated product, **4** (Scheme I). This structure is in full accord with all spectral data.[14]

Compound **4** is stable thermally in both solution (no observable decomposition in C_6D_6 after 1 month at 110 °C) and in the solid state (mp 133-135.5 °C under nitrogen, without apparent decomposition). The solid is also quite air stable, surviving intact in air for at least several hours, though benzene solutions are more air sensitive. Compound **4** proved not only sufficiently robust but also sufficiently volatile in the solid inlet probe of the mass spectrometer to provide a clean parent ion (*m/e* 358), intensity 18% of that of the 100% peak. The absence of higher mass ions,

(1) Initially reported at 3rd Chemical Congress of North America and the 195th ACS National Meeting, Toronto, Canada, June 5, 1988.

(2) Previous reports of the reactivity of nitriles with organotransition-metal complexes have suggested insertion,[3-5] cycloaddition,[6-9] and cyclooligomerization[10,11] as primary reaction modes. Discreet cycloadducts have not been directly observed but rather inferred as intermediates.

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(13) ^1H NMR spectrum of **3** reported in Table I: ^1H coupled ^{13}C NMR (C_6D_6) δ 28.5 (q, J = 125 Hz, CH_3), 40.2 (s, C-CH_3), 41.3 (t, J = 123 Hz, CH_2), 112.4 (d, J = 173 Hz, Cp), 165.0 (s, —C=N).

(14) ^1H NMR (C_6D_6) δ 1.02 (s, 9 H, *t*-Bu), 1.21 (s, 9 H, *t*-Bu), 4.86 (d, 1 H, J = 1.46 Hz, —CH=), 5.70 (s, 10 H, Cp), 5.9 (br, 1 H, NH); ^{13}C NMR (C_6D_6) δ 29.51 (CH_3), 29.89 (CH_3), 37.10 (C—CH_3), 37.64 (C—CH_3), 87.70 (—CH=), 110.99 (Cp), 175.02 (—C=N or =C—N), 175.73 (=C—N or —C=N); IR (C_6H_6) ν = 3371, 3314 cm^{-1} (N—H).

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Table I. Spectral Data and Yields of Azatitanacyclobutenes and Diazatitanacyclohexadienes[a]

RCN R =	azatitanacyclobutenes[b]				diazatitanacyclohexadienes[c]			
	Cp	CH_2	R	yield	Cp	CH	R	yield
Me	*d*	*d*	*d*	*d*	5.71	4.49	1.64, 1.73	93%
t-Bu	5.67	3.01	1.05	48%[f]	5.70	4.86	1.02, 1.21	*e*
C_6H_5	5.73	3.79	7.2-7.4 (m), 7.6-7.8 (m)	51%[g]	5.70	5.60	7.10-7.45 (m), 7.65-7.85 (m)	90%
p-Me-C_6H_4	*d*	*d*	*d*	*d*	5.75	5.67	2.14, 2.17; 7.86, 7.12 (AB); 7.45, 6.95 (AB)	93%
p-MeO-C_6H_4	*d*	*d*	*d*	*d*	5.78	5.70	3.30, 3.34; 7.84, 6.88 (AB); 7.41, 6.85 (AB)	93%
p-CF_3-C_6H_4	5.68	3.52	7.53	49%[g]	5.69	5.34	7.66, 7.48 (AB); 7.44, 7.16 (AB)	97%
C_6F_5	5.77	3.31		51%[g]	5.74	4.80		96%

[a] ^1H NMR spectral data obtained in C_6D_6 and reported in ppm downfield from tetramethylsilane. Yields determined by ^1H NMR of reaction mixtures. [b] Prepared from **2** and 1.0 equiv of RCN. [c] Prepared from **2** and 2.0 equiv of RCN. [d] 1:1 complex not observed under reaction conditions. [e] 2:1 complex formed sluggishly in solution (see text); isolated yield >90%. [f] 1:1 complex is formed in >95% yield in presence of 2 equiv of ^{t}BuCN. [g] Remainder is unreacted **2** (27-50%), which slowly decomposes upon prolonged reaction, and 2:1 complex (16-19%).

coupled with spectral and reactivity studies, strongly suggests the mononuclearity of **4**.

Final confirmation of the molecular structure of compound **4** was obtained through acidolysis. Treatment of **4** with excess dry HCl gas, followed by aqueous workup and ether extraction, afforded a white crystalline solid whose ^1H NMR, ^{13}C NMR, IR, and mass spectra and melting point were identical with those of an authentic sample[15] of the expected β-ketoenamine (Scheme I).[28]

Intrigued by this unusual reductive coupling of nitriles and realizing the potential importance of both the intermediate azametallacyclobutene **3** and diazametallacyclohexadiene **4** and of the β-ketoenamine acidolysis products, we have carried out initial exploration of the generality of this reaction sequence. We find that the course of the reaction is critically dependent on the nature of the nitrile employed. Electron rich nitriles led immediately to 2:1 complexes, while electron deficient or sterically hindered nitriles gave comparatively stable 1:1 complexes, with slower conversion to the 2:1 complexes. The results of these studies are summarized in Table I.

From a synthetic standpoint, the β-ketoenamine acidolysis products are well-recognized[16,17] and versatile intermediates for heterocyclic and related syntheses.[18-27] Though a variety of routes to such compounds are known, this unusual reductive coupling of nitriles should serve as a convenient complement, given especially the ease of synthesis of nitriles through simple nucleophilic displacement reactions. We will report our studies of these materials and of intramolecular variants in due course. The metallacyclic products also bear promise for synthetic applications, and we are exploring their follow-up reaction chemistry before removal of the metal. Finally, the electronic effects on 1:1 versus 2:1 complex formation and the surprisingly rapid tautomerization are also being explored.

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(15) Prepared by the general procedure of Baraldi et al. (Baraldi, P. G.; Simoni, D; Manfredini, S. *Synthesis* **1983**, 902-903): ^1H NMR (C_6D_6) δ 0.91 (s, 9 H, *t*-Bu), 1.24 (s, 9 H, *t*-Bu), 4.8 (br s, 1 H, N*H*), 10.7 (br s, 1H, N*H*); ^{13}C NMR (C_6D_6) δ 28.26 (C—*C*H_3), 28.70 (C—*C*H_3), 35.85 (*C*-CH_3), 42.30 (*C*-CH_3), 86.23 (—CO—*C*H=CH—), 173.07 (—CO—CH=*C*H—), 204.60 (—*C*O—CH=CH—); IR ν = 3407 (m, br, N-H), 3346 (m, br, N—H), 2968 (s, C—H), 2928 (m, C—H), 2870 (mw, C=H), 1719 (w), 1634 (m), 1596 (s), 1524 (s) cm^{-1}; MS, *m/e* = 183 (9.1), 126 (100); mp 127-129 °C.

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The Gas-Phase Displacement Reaction of Chloride Ion with Methyl Chloride as a Function of Kinetic Energy

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Nucleophilic displacement reactions are among the most extensively studied chemical processes in solution[1] and in the gas phase,[2] both by theory[3] and by experiment.[4] The symmetric thermoneutral reactions, for example,

$$^{37}Cl^- + CH_3{}^{35}Cl \rightarrow {}^{35}Cl^- + CH_3{}^{37}Cl \quad (1)$$

are of central importance in characterizing the potential energy surfaces for these displacement processes, since their reactivity reflects the intrinsic S_N2 barrier in the absence of a thermodynamic driving force. Nevertheless, such thermoneutral substitution reactions have not previously been observed in the gas phase.[5,6]

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