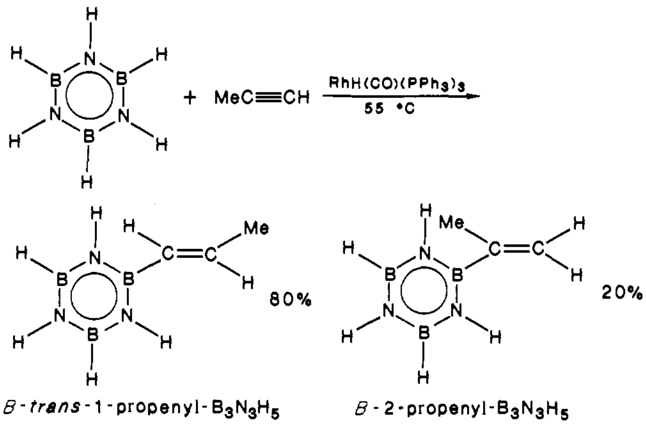
of each isomer were obtained by preparative GLC.



(2)

Alkenylborazines are of particular importance since it may be possible to convert these compounds to polymeric boron–nitrogen materials analogous to, for example, polystyrene. Such polymers may then be useful for the formation of boron nitride ceramics,[16-21] in the same way that organosilicon polymers have been found to be precursors to silicon carbide.[19,22,23] Several alkenyl-substituted derivatives of borazine have previously been reported;[24-26] however, it has been necessary in most cases to block the remaining ring nitrogen and boron positions with alkyl groups. This results in steric repulsion to polymerization[17] and lowers the BN/C ratios in these polymers. The synthetic method reported herein yields the parent compounds in high yields in a one-step reaction. Furthermore, we have observed that when reactions are carried out under more forcing conditions di-*B*-alkenyl products can be obtained.

Reactions 1 and 2 are the first reported transition-metal-catalyzed reactions of borazine; however, based on our previous work with boranes, it is now expected that transition-metal catalysts will be able to induce a wide variety of borazine reactions. In fact, all available experimental evidence indicates that the B–H bonds in borazine are considerably weaker than those in, for example, pentaborane(9): the B–H bond lengths are longer, 1.258 (14) Å[27] versus 1.181 (3) and 1.186 (2) Å in pentaborane(9);[28] the IR B–H stretching frequencies are lower, 2527, 2520, and 2514 cm^{-1} versus 2610 and 2598 cm^{-1};[29,30] and the B–H NMR coupling constants are smaller, 133 Hz versus 175 and 165 Hz.[31] These data all suggest that borazine should oxidatively add (a key step in most catalytic reactions) to transition metals much more readily than pentaborane(9).

Thus, while the mechanisms of reactions 1 and 2 are still unproven, the results of our studies are consistent with a reaction sequence similar to that which we have proposed for reactions with polyhedral boranes.[1-4] This could involve oxidative addition of the borazine at the metal center, displacement of a coordinated ligand by acetylene, and alkyne-insertion and reductive-elimination steps. Such a sequence is also in agreement with the mechanisms which have been proposed for the RhH(CO)(PPh$_3$)$_3$-catalyzed hydrosilylation of alkynes.[32]

We are now investigating the use of transition-metal catalysts to promote a number of transformations involving borazines, and, indeed, we have recently demonstrated[33] the high yield metal-catalyzed dehydrocoupling of borazine to yield the B–N coupled dimer $[B_3N_3H_5]_2$. This result and related reactions will be reported in future publications.

Preliminary results[34] have now also demonstrated that these *B*-alkenylborazines will readily undergo thermally induced polymerizations under mild conditions (<125 °C) and that upon heating to higher temperatures (~600 °C) these polymers are converted to ceramic materials. These studies will be reported in future publications.

Acknowledgment. We thank the National Science Foundation and the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research for the support of this research and Johnson Matthey Inc. for the generous loan of rhodium metal. We also thank Dr. Andrew McGhie for help in obtaining TGA results and Dr. Robert Paine for useful discussions and suggestions.

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Facile Insertion of Nitriles into Paramagnetic Chromium(III) Alkyls. Crystal Structure of a μ_2-Ketimino Complex

Darrin S. Richeson, John F. Mitchell, and
Klaus H. Theopold*

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853

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The importance of paramagnetic compounds in catalytic and stoichiometric organometallic reactions is rapidly gaining acceptance.[1] We are exploring the reactivity of a novel class of electron deficient alkyl complexes of chromium(III). An earlier publication dealt with compounds containing the cyclopentadienyl ligand.[2] Here we report on the insertion of nitriles[3] into the chromium–carbon bond of the analogous pentamethylcyclopentadienyl complexes.

Treatment of chromium(III) alkyls of the type $RCrCl_2(THF)_3$ (R = Me, Et, Ph)[4] with Cp*Li (Cp* = η^5-Me_5C_5) afforded a series of purple crystalline complexes (**1**–**3**) in good yield.[5] On the basis

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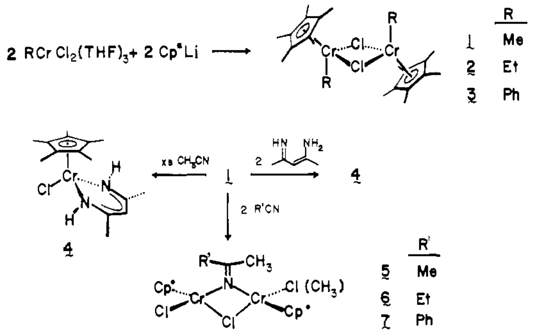
(5) Satisfactory elemental analyses have been obtained for all compounds reported herein.

0002-7863/87/1509-5868$01.50/0

Scheme I



of similarities in color, magnetic properties, and reactivity to the structurally characterized Cp analogue $[CpCr(Me)Cl]_2$, we assign to them the structure shown in Scheme I.

Addition of an excess of acetonitrile to an Et_2O solution of **1** at room temperature resulted in a slow color change from dark purple to brown. Evaporation of the solvent and extraction of the residue with pentane left behind a brown solid. Recrystallization of this material from ether afforded brick red crystals of β-diketimino complex **4** in 39% yield.[6] The IR spectrum of **4** exhibited a broad N–H stretching band at 3261 cm^{-1} and C=N absorptions at 1573 and 1538 cm^{-1}, consistent with partial double bond character. The proposed structure of **4** was confirmed by an independent synthesis from **1** and the β-diketimine derived from acetylacetone[7] (Scheme I). Analogues of **4** were also isolated from reactions of **1** with propionitrile[8] and **2** with acetonitrile and propionitrile.

In the formation of **4** two molecules of nitrile are incorporated, and two new C–C bonds are made in the coordination sphere of each chromium center. A similar reaction involving a scandium alkyl has recently been reported by Bercaw et al.[3c] These workers have also proposed a mechanism for this transformation consisting of—in sequence—coordination of nitrile, insertion into the metal alkyl followed by a 1,3-hydrogen shift,[9] attack of the so formed enamine on a second coordinated nitrile, and finally another 1,3-hydrogen shift to yield the β-diketimino group.

When **1** was treated with 2 equiv of nitrile, a series of blue crystalline materials (**5–7**, Scheme I) was produced. These compounds did not exhibit N–H stretching frequencies in the IR spectrum. Their magnetic properties indicated antiferromagnetic coupling between two Cr(III) nuclei. We were unable, however, to reconcile the elemental analyses with any reasonable structures, and their identity became clear only as a result of the determination of the structure of benzonitrile adduct **7** (see Figure 1).[10]

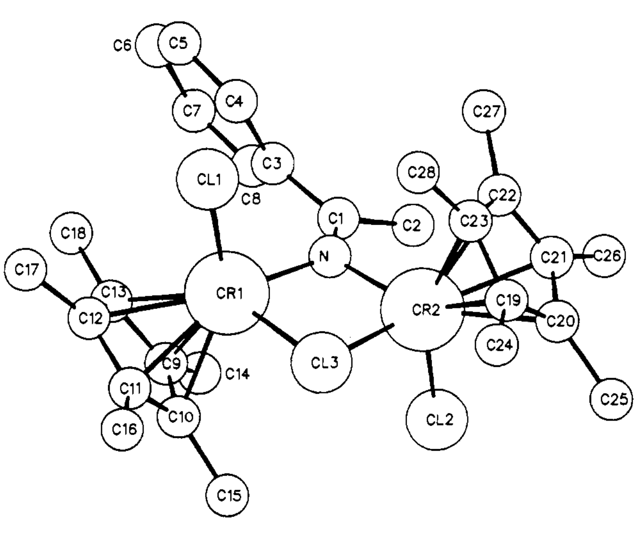
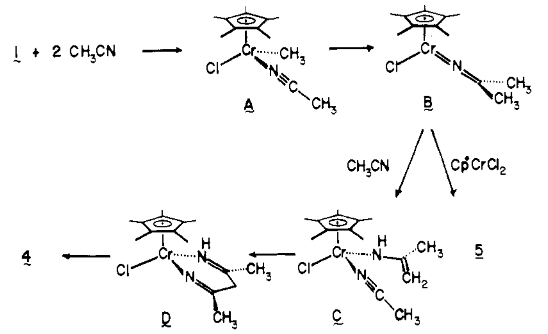


Figure 1. The molecular structure of **7**. Selected bond distances are as follows: Cr1–Cr2, 3.180 (2); Cr1–N, 2.058 (6); Cr2–N, 2.037 (8); N–C1, 1.279 (12) Å. Interatomic angles are as follows: Cr1–N–Cr2, 101.9 (3); Cr1–N–C1, 131.7 (7); Cr2–N–C1, 125.9 (6).

Scheme II



The molecule is a dinuclear complex and results from insertion of one molecule of benzonitrile into the chromium–methyl bond of mononuclear Cp*Cr(Me)Cl and subsequent trapping of the so generated fragment by a Cp^*CrCl_2 unit. The two chromium atoms are bridged by a chloride ligand and the nitrogen of a ketimino group.[11] The N–C1 distance of 1.29 (1) Å is consistent with a double bond between those atoms. The organic fragment is twisted out of the electronically preferred coplanarity with the Cr_2N plane, presumably by a steric interaction of the phenyl group with the bulky Cp* ligand. The Cr–Cr distance is too long for any bonding interaction, consistent with the magnetic behavior.

The formation of **7** from **1** requires not only the insertion of the nitrile but also the substitution of the second methyl group of **1** with a chloride ligand. This may come about by a parallel ligand redistribution between reaction intermediates. Indeed, the blue materials isolated from these reactions were shown to be mixtures of molecules containing either chloride or methyl as indicated in Scheme I. Treatment with HCl gas yielded nonstoichiometric amounts of CH_4 and blue crystals of **5–7**, which now analyzed correctly.

Complexes **5–7** do not react with more nitrile to yield **4** or its analogues. Thus they are not intermediates in the formation of the mononuclear β-diketimino complexes. A mechanism which accounts for our observations is depicted in Scheme II (letters designate proposed intermediates). Cleavage of the chromium dimer by nitrile and its insertion into the chromium alkyl bond lead to imino intermediate B. In excess nitrile B (or its tautomer) is trapped, forming pseudooctahedral C, which goes on to final product **4**. Low concentrations of nitrile on the other hand lead to irreversible trapping of B with an unsaturated chromium fragment.

We find that electron deficient Cr(III) alkyls undergo facile insertions of nitriles and other unsaturated molecules into the metal–carbon bond. We are continuing our exploration of the reactivity of these paramagnetic organometallics.

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[6] **4**: ^{1}H NMR (C_6D_6) 53.5 (br, 15 H), 3.6 (1 H), −16.4 (br, 6 H) ppm; IR (KBr) 3261 (s), 3037 (w), 2937 (s), 2912 (s), 2870 (s), 1573 (s), 1537 (s), 1432 (s), 1377 (s), 1107 (m), 1023 (m), 497 (s) cm^{-1}; MS, 319 321 (M^+); μ_{eff} (299 K) = 4.00μ_B. Anal. Calcd for $C_{15}H_{24}ClCrN_2$: C, 56.33; H, 7.56; N, 8.76; Cl, 11.09. Found: C, 56.12; H, 7.60; N, 8.53; Cl, 10.96.

[7] McGeachin, S. G. *Can. J. Chem.* **1968**, *46*, 1903.

[8] The product of the reaction of **1** with propionitrile exhibited nine resonances in the ^{1}H NMR spectrum (ranging from 55.2 to −16.4 ppm). Assuming that the NH protons are too broad to be observed, this number of signals and the integrated intensities are consistent with the formation of the two possible isomers in a 3:2 ratio.

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[10] Dark blue crystals from Et_2O/pentane: monoclinic $P2_1/n$; a = 12.675 (4) Å, b = 9.244 (2) Å, c = 29.377 (7) Å, β = 103.92 (2)°; Z = 4; R = 0.087, R_w = 0.10.

[11] For other structurally characterized ketimino complexes, see: (a) Bright, D.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1967**, 245. (b) Erker, G.; Froemberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1984**, *96*, 72. (c) Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Dalton Trans.* **1986**, 377. (d) Werner, H.; Knaup, W.; Dziallas, M. *Angew. Chem.* **1987**, 277.

Corporation, Dow Chemical Co., Rohm and Haas Co., Smith Kline and French Laboratories, and Cornell University.

Supplementary Material Available: Tables of X-ray structure determination of **7** (7 pages). Ordering information is given on any current masthead page.

Ultrahigh Resolution in Proton NMR Spectra at 500 MHz: Two-Bond Intrinsic Chlorine and Silicon Isotope Effects

Frank A. L. Anet* and Max Kopelevich†

Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

Received May 6, 1987

"Heavy-atom" isotope effects on NMR ^{1}H chemical shifts have been reported in a few cases[1-3] but only for second-row elements. We now show that ^{37}Cl/^{35}Cl isotope effects on the ^{1}H chemical shifts in chlorinated methanes are about +0.2 ppb (ca. 0.1 Hz at 500 MHz) and that the ^{29}Si/^{28}Si isotope effect on the ^{1}H chemical shift in tetramethylsilane (TMS) is +0.06 ± 0.01 ppb. It is likely that previously unreported splittings arising from heavy-atom isotope effects will be observable in the ^{1}H NMR spectra of other organic compounds, given the excellent resolution of modern high field NMR spectrometers.

The ^{1}H spectra of methyl chloride (CH_3Cl), dichloromethane-d_1 ($CHDCl_2$, deuterium decoupled), and chloroform ($CHCl_3$) are shown in Figure 1 together with a line shape for the internal TMS reference line.[4] Since the natural abundances for ^{35}Cl and ^{37}Cl and 75.5 and 24.5%, respectively, the statistical intensity distributions in the multiplets for CH_3Cl, $CHDCl_2\{D\}$, and $CHCl_3$ are as shown in Table I. The observed multiplets, especially after some resolution enhancement, show intensities that are close to these values (Table I)[5] and require that these isotope effects be positive.[2] The sign of the chlorine isotope shift for ^{1}H in $CHCl_3$ is the same as for ^{19}F in $CFCl_3$.[6] The ^{37}Cl/^{35}Cl isotope effects in the chlorinated methanes decrease monotonically as the number of chlorine atoms is increased, and they are additive in $CHCl_3$ and $CHDCl_2$ (Table I). The ^{29}Si/^{28}Si two-bond isotope effect on the ^{1}H chemical shift in TMS is of the same order of magnitude as the above two-bond chlorine isotope effects when the different mass changes are taken into account. Measurement of this very small isotope effect (30 mHz at 500 MHz) is helped by the nonoverlapped spectrum [$^2J(^{29}\text{Si}-^1\text{H})$ = 6.65 Hz].[3] None of the molecules studied here give any indication of significant molecular alignment caused by the high magnetic field.[7]

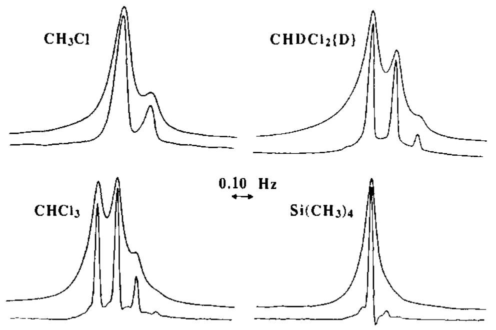

Figure 1. 500-MHz ^{1}H NMR spectra of CH_3Cl, $CHDCl_2$ (deuterium decoupled), and $CHCl_3$, showing ^{37}Cl/^{35}Cl isotope effects, and of $Si(CH_3)_4$ as a line shape and resolution reference (the ^{29}Si satellites lie outside the region shown). The upper trace in each spectrum has been obtained without any processing of the FID except for zero filling, and the lower trace represents the application of Lorentzian–Gaussian resolution enhancement, which is not the same for all the spectra.

Table I. Chlorine Isotope Effects on ^{1}H Chemical Shifts

compound	Δ^a (ppb)	fractional intensities calcd	fractional intensities obsd^b
$CH_3{}^{35}Cl$		0.755	0.78
$CH_3{}^{37}Cl$	0.25 ± 0.03	0.245	0.22
$CHD^{35}Cl_2$		0.570	0.56
$CHD^{35}Cl^{37}Cl$	0.21 ± 0.03	0.370	0.38
$CHD^{37}Cl_2$	0.42 ± 0.05	0.060	0.06
$CH^{35}Cl_3$		0.431	0.42
$CH^{35}Cl_2{}^{37}Cl$	0.17 ± 0.03	0.419	0.44
$CH^{35}Cl^{37}Cl_2$	0.35 ± 0.05	0.136	0.13
$CH^{37}Cl_3$	0.52 ± 0.08	0.015	0.01_5

[a] δ (molecule with no ^{37}Cl) − δ (molecule with one or more ^{37}Cl). [b] From peak heights of resolution enhanced spectra, normalized to 1 for each compound, error ca. ±0.01.

We would like to make a few comments on the procedures required to obtain ultrahigh resolution spectra, especially for protons.[8] Careful sample preparation, temperature control of the probe, and magnetic field shimming are essential.[8,9] Furthermore, so-called "radiation damping" effects,[10,11] which are not

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[†] Graduate Fellow of the Division of Organic Chemistry, ACS, sponsored by the Proctor & Gamble Company, 1986–1987.

(1) "Heavy" refers to atoms of higher atomic number than hydrogen.

(2) For recent reviews, see: (a) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 105–234. (b) Jameson, C. L. In *Specialist Periodical Reports*; The Royal Society of Chemistry: London, 1986; NMR Spectroscopy, Vol. 15, pp 1–27. (c) Hawkes, C. E. In *Specialist Periodical Reports*; The Royal Society of Chemistry: London, 1986; NMR Spectroscopy, Vol. 15, pp 28–80. A positive isotope effect corresponds to a greater shielding for the heavier isotope.

(3) ^{13}C/^{12}C isotope effects give rise to *nonoverlapped sharp* ^{1}H lines whose frequencies can be accurately measured. One-bond and two-bond ^{13}C/^{12}C isotope effects on ^{1}H chemical shifts are typically 1–5 and 0.5–1.5 ppb, respectively.[2a] The few known analogous ^{15}N/^{14}N and ^{18}O/^{16}O isotope effects have similar magnitudes.[2a]

(4) The CH_3Cl sample contained about 5% of CH_3Cl in CD_2Cl_2. The $CHDCl_2$ was observed as the isotopic impurity in CD_2Cl_2. These solutions were filtered into high quality 5-mm NMR tubes (Wilmad 535), and oxygen was removed by bubbling argon into the solution for a short time. The $CHCl_3$ was in a sealed degassed Bruker "line shape" sample (10% $CHCl_3$ in acetone-d_6). All samples contained about 1% TMS. A Bruker AM500 equipped with an Oxford Instrument 11.7 T solenoid was used with the spectrometer locked on deuterium, except for the $CHDCl_2$ sample, where C_6F_6 was used as an ^{19}F lock. Shimming was done manually on the TMS free induction decay (FID), finishing with an acquisition time of about 20 s. Data acquisition times were between 30 and 60 s, and a spectral resolution of 2 mHz per point was achieved by using small spectral windows set to either TMS or to the chlorinated methane and by zero filling of the FID's. The TMS line shown in Figure 1 has a full line width at half height of 60 mHz before resolution enhancement.

(5) The protons in the chloromethanes are expected to have small coupling constants to chlorine, but strong quadrupole relaxation leads to almost complete decoupling. The T_2 in $CHCl_3$ has been reported to be 10 s, corresponding to a line width of 0.03 Hz; the two chlorine isotopes have broadening effects that differ by only 10% because of cancelling differences in gyromagnetic ratios and quadrupole moments (Abragam, A. *The Principles of Nuclear Magnetism*; Oxford: London, **1961**; p 332).

(6) Carey, P. R.; Kroto, H. W.; Turpin, M. A. *J. Chem. Soc., Chem. Commun.* **1969**, 188. Brey, W. S., Jr.; Ladner, K. H.; Block, R. E.; Tallon, W. A. *J. Magn. Reson.* **1972**, *8*, 406–409. The ^{37}Cl/^{35}Cl isotope effect in $CFCl_3$ is temperature dependent and about two orders of magnitude larger than that in $CHCl_3$.

(7) For a review of molecular alignment at high magnetic fields in isotropic solvents, see: (a) van Zijl, P. C. M.; Ruessink, B. H.; Bulthuis, J.; MacLean, C. *Acc. Chem. Res.* **1974**, *17*, 172–180. See, also: (b) Anet, F. A. L. *J. Am. Chem. Soc.* **1986**, *108*, 1354–1355. (c) Bastiaan, E. W.; Bulthuis, J.; MacLean, C. *Magn. Reson. Chem.* **1986**, *24*, 723–728.

(8) For "ultrahigh" resolution in 50-MHz ^{13}C NMR spectroscopy, see: (a) Allerhand, A.; Addleman, R. E.; Osman, D. *J. Am. Chem. Soc.* **1985**, *107*, 5809–5810. (b) Allerhand, A.; Dohrenwend, M. *J. Am. Chem. Soc.* **1985**, *107*, 6684–6688. (c) Allerhand, A.; Addleman, R. E.; Osman, D.; Dohrenwend, M. *J. Magn. Reson.* **1985**, *65*, 361–363. (d) Maple, S. R.; Allerhand, A. *J. Magn. Reson.* **1986**, *66*, 168–171. (e) Allerhand, A.; Bradley, C. H. *J. Magn. Reson.* **1986**, *67*, 173–176. (f) Maple, S. R.; Allerhand, A. *J. Am. Chem. Soc.* **1987**, *109*, 56–61. For ultrahigh resolution in ^{1}H spectroscopy, see ref 7b and references therein.

(9) Temperature homogeneity in the sample for ^{1}H appears to be less important than for ^{13}C.[8a] However, temperature stability is required for proper shimming.

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