kene)$^+$ complexes which are formed by both initial loss of $H_2$ and initial loss of $CH_4$ (Scheme IV).

Another feature of the reaction of Co$^+$ with alkanes noted in I is that transfer of secondary $\beta$-hydrogens in reaction intermediates is more likely than primary $\beta$-hydrogen transfers.[12] For example, in the reaction with n-pentane, intermediate **7** which results from initial insertion into an internal C–C bond can either transfer a secondary $\beta$-hydrogen and eliminate ethane or transfer a primary $\beta$-hydrogen and lose propane (Scheme V). The product distributions listed in Scheme V show that in reactions with Ni$^+$ as well as Co$^+$ a secondary $\beta$-hydrogen transfer is greatly favored. However, reactions of Fe$^+$ with *n*-pentane and other alkanes deviate somewhat from this pattern. This may be due to the higher internal energy of **7** caused by the greater exothermicity of the initial insertion of Fe$^+$ into the C–C bond.

The M(alkene)$^+$ products may retain part of the exothermicity of the initial insertion reaction as internal excitation. Because the insertion process is most exothermic for Fe$^+$, one expects the Fe(alkene)$^+$ product to have more energy to further react than the corresponding products of Co$^+$ and Ni$^+$. Consistent with this observation are the higher proportions of M(alkadiene)$^+$ products of reactions of Fe$^+$ with alkanes relative to reaction of Co$^+$ and Ni$^+$.

**Periodic Trends in Metal Ion Reactivity.** The group 8 metal ions Fe$^+$, Co$^+$, and Ni$^+$ exhibit very similar reactivity with alkanes. Subtle differences are rationalized as being mainly due to differences in reaction thermochemistry. We have also examined the reactions of Mn$^+$ and Cr$^+$ with alkanes.[30] In comparison to the group 8 metals, these species are quite unreactive, and processes such as dehydrogenation and carbon–carbon bond cleavage are not observed. In part, this is due to weaker metal–hydrogen and metal–carbon bond dissociation energies for these elements. The possible relationship of these results to the electronic structures of the organometallic fragments is discussed elsewhere.[11] To compare with Co$^+$, we have also briefly examined the reaction of Rh$^+$[31] (which in analogy with Co$^+$ has a $^3$F ground state derived from the d$^8$ configuration). Unlike Co$^+$, Rh$^+$ does not readily cleave carbon–carbon bonds and instead is observed mainly to dehydrogenate hydrocarbons. With these limited results, it is obviously difficult to offer many generalizations concerning periodic trends in reactivity and thermochemical properties. Studies of a wider range of atomic metal ions and clusters are currently in progress. In addition, we are developing sources of metal atoms which will permit related chemistry of the neutral species to be explored.

**Acknowledgment.** We wish to thank Dr. Raymond Houriet for his contributions to this paper and to Mr. Arthur Voter and Dr. Arthur S. Gaylord for their help in providing computer programs used in fitting the data. This research was supported in part by the U.S. Department of Energy. Graduate fellowship support from Bell Laboratories (L.F.H.) is gratefully acknowledged.

**Registry No.** Fe$^+$, 14067-02-8; Co$^+$, 16610-75-6; Ni$^+$, 14903-34-5; propane, 74-98-6; butane, 106-97-8; 2-methylpropane, 75-28-5; pentane, 109-66-0; 2-methylbutane, 78-78-4; 2,2-dimethylpropane, 463-82-]; hexane, 110-54-3; 2,2-dimethylbutane, 75-83-2; 2,3-dimethylbutane, 79-29-8; heptane, 142-82-5; 2,2,3,3-tetramethylbutane, 594-82-1.

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(30) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L., unpublished data.

(31) Beauchamp, J. L., unpublished data.

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# Conformational Variability in Tricarbonyl(hexaethylborazine)chromium(0)

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Evidence is adduced from variable-temperature $^{13}$C NMR studies for the presence of two conformers in $CD_2Cl_2$ solutions of the title compound. Line-shape analyses are consistent with the assignment of $C_s$ symmetry to both conformers. In one of these, two terminal methyl groups on N–Et are proximal to the metal atom, while in the other only one such group is proximal. Interconversion of the conformers requires a barrier of $\Delta G^{\ddagger} = 10.4$ kcal mol$^{-1}$. The conformational variability in this system parallels similar findings for hexaethylbenzene transition metal $\pi$ complexes.

Recent structural studies of hexaethylbenzene (HEB) transition metal $\pi$ complexes of the type (HEB)·$ML_3$ (**1**)[2] have provided evidence of a marked preference for the four conformational types shown in Figure 1 (top and bottom rows). Examples of three types are known:[2] **1a** ((HEB)-Cr(CO)$_3$, (HEB)Mo(CO)$_3$), **1e** ((HEB)Cr(CO)$_2$PEt$_3$), and **1h** ((HEB)Cr(CO)$_2$PEt$_3$, (HEB)Cr(CO)$_2$PPh$_3$)). Although no representative of the missing type **1c** has yet been reported, a formal analogy may be drawn between **1c** and **2c** (Figure 1, middle row), the conformation found in the crystal of tricarbonyl(hexaethylborazine)chromium(0) (**2**).[3] In this compound, which also has the distinction of being the only borazine transition metal complex with a known

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(1) (a) University of Dundee. (b) On leave from South Dakota State University, 1980. (c) Princeton University.

(2) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073. Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Iverson, D. J.; Mislow, K. *Organometallics* **1982**, *1*, 448.

(3) Huttner, G.; Krieg, B. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 512; *Chem. Ber.* **1972**, *105*, 3437.

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Table I. $^{13}C$ NMR Data for Tricarbonyl(hexaethylborazine)chromium(0) (2)[a]

| sub-spectrum | assignt | measd chem shifts[c] |  | chem shifts[b] |  |
|---|---|---|---|---|---|
|  |  | at +25 °C | at −80 °C | major conformer | minor conformer |
|  | CO | 227.81 | 226.76, 227.72 | 226.76, 227.72 (2×) | 226.76 (2×), 227.72 |
| A | $NCH_2$ | 43.89 | 40.55, 41.14, 46.15, 47.20 | 40.55 (2×), 46.15 | 41.14, 47.20 (2×) |
| B | $NCCH_3$ | 20.29 | 17.76, 20.65, 21.17 | 17.76, 21.17 (2×) | 17.76 (2×), 20.65 |
| C | $BCCH_3$ | 9.85 | 8.24, 9.93 | 8.24, 9.93 (2×) | 8.24 (2×), 9.93 |
|  | $BCH_2$ | 5.53 | 4.76 |  |  |

[a] See text and Figure 2. [b] Chemical shifts (ppm) used in the simulation of the coalescing subspectra. Chemical shifts marked (2×) refer to symmetry equivalent carbons in $C_s$ structures 2c and 2e (Figure 1, middle row, carbonyls eclipse boron atoms). [c] In ppm in $CD_2Cl_2$, downfield from $Me_4Si$.

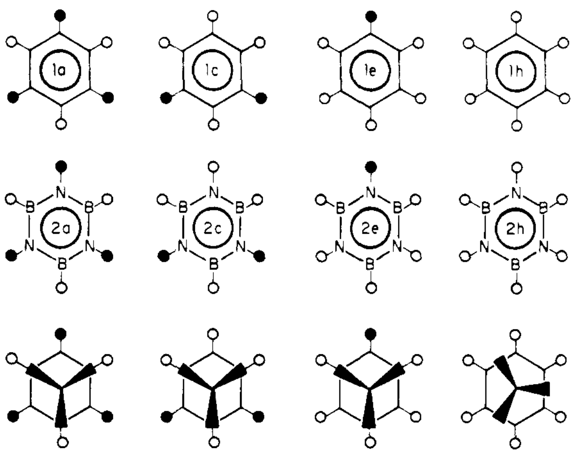

**Figure 1.** Selected conformations for transition-metal complexes of the type (hexaethylbenzene)·$ML_3$ (1, top row) and (hexaethylborazine)·$ML_3$ (2, middle row). The metal atom (M) is the point of reference and should be viewed as residing over the ring and above the plane of the paper. The filled circles represent terminal methyl groups projecting toward the complexed (proximal) side of the ring, i.e., toward the observer. The open circles represent methyl groups projecting toward the uncomplexed (distal) side, i.e., away from the observer. The descriptors follow a previously used notation.[2] Bottom row: torsional arrangement of ligands (L, wedges) for **1a–e** (eclipsed) and **1h** (staggered).

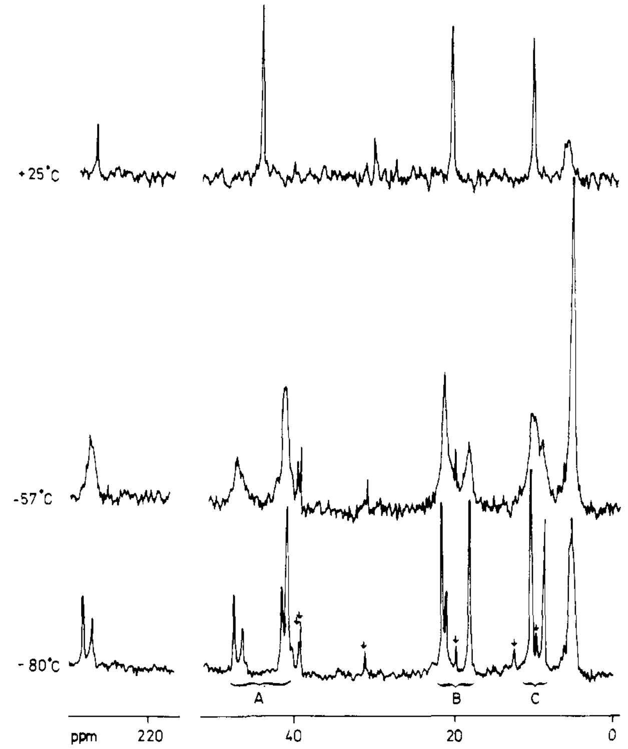

**Figure 2.** 90.56-MHz $^{13}C\{^1H\}$ NMR spectrum of 2 in $CD_2Cl_2$. Arrows indicate peaks which are not involved in the coalescence process and which are attributed to impurities.

X-ray structure, the molecule adopts a conformation in which the terminal methyl groups of the three ethyls attached to boron atoms are distal to the metal atom, while of the three ethyls attached to the nitrogen atoms, only two have terminal methyl groups which are proximal; the third is distal to the metal. The carbonyl groups eclipse the boron atoms. The contrast between this conformation (**2c**) and that of hexaethylborazine, in which the terminal methyl groups alternately project above and below the ring plane[4] (as they do in the isosteric HEB[2]), has been ascribed to the slight puckering of the borazine ring in the complex.[3]

It occurred to us that, liberated from the constraint of lattice forces, 2 might exhibit some of the conformational variability previously demonstrated for HEB. The present variable-temperature NMR study of 2 was undertaken in search of evidence for conformers other than **2c**.

## Results

At ambient temperature the 90.56-MHz $^{13}C\{^1H\}$ NMR spectrum of 2 in $CD_2Cl_2$ consisted of five resonances at $\delta$ 5.53 (m), 9.85 (s), 20.29 (s) 43.89 (s), and 227.81 (s). Single frequency off-resonance decoupling experiments indicated that the absorptions at 5.53 and 43.89 ppm can be assigned to methylene carbon resonances, those at 9.85 and 20.29 ppm can be assigned to methyl carbon resonances, and that at 227.81 ppm to carbonyl carbon resonances. Cooling the solution to −30 °C caused an increase in intensity of the resonance at 5.53 ppm which also lost its multiplicity and became a sharp singlet. Such behavior is consistent with that of a carbon bonded to boron.[5] At lower temperatures quadrupolar relaxation due to the $^{11}B$ nuclei is very efficient and effectively causes $^{11}B$–$^{13}C$ decoupling. At higher temperatures such relaxation becomes inefficient and indications of $^{11}B$–$^{13}C$ couplings appear in the spectrum. We accordingly assign the absorption at 5.53 ppm to the methylene carbons of the ethyl groups attached to the boron atoms, and the absorption at 43.89 ppm to those attached to the nitrogen atoms. At no temperature was any indication of $^{14}N$–$^{13}C$ coupling observed.

As the temperature was lowered a coalescence phenomenon was observed which involved all the resonances, although that assigned to the boron methylene carbons merely grew a downfield shoulder. The decoalescence was essentially complete at −80 °C, at which temperature the carbonyl resonance had become two signals of unequal intensity (approximately in the ratio 1.5:1), the nitrogen methylene carbon resonance had become four signals (subspectrum A in Figure 2), the methyl carbon resonance at 20.29 ppm had become three signals (subspectrum B), and the methyl carbon resonance at 9.85 ppm had become

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[4] Viswamitra, M. A.; Vaidya, S. N. *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1965**, *121*, 472.

[5] Wrackmeyer, B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1978**, *12*, 229.

two signals (subspectrum C). Our results are summarized in Table I.

At ambient temperature the 115.55-MHz $^{11}B\{^1H\}$ spectrum of the compound dissolved in $CD_2Cl_2$ consisted of a single broad absorption (half-height line width 2.61 ppm) with a maximum intensity at 28 ppm downfield from boron trifluoride diethyl etherate. At −80 °C the $^{11}B\{^1H\}$ spectrum consisted of an even broader but now asymmetric absorption with a maximum at 29 ppm.

## Discussion

It is reasonable to assume that steric constraints which limit the conformational types in **1** (eclipsing cannot take place over carbons bearing proximal methyl groups)[2] impose a similar limit on **2**. Furthermore, because the three nitrogen atoms in the borazine ring and the three carbonyl carbons fix an octahedral coordination set, an arrangement in which the boron atoms are eclipsed is expected to be far more stable than one in which the carbonyls eclipse the nitrogen atoms; for the parent compound (tricarbonyl(borazine)chromium(0)), this stabilization energy is estimated[6] to be ≥18.3 kcal mol$^{-1}$. In contrast to **1**, where the (arene)chromium rotation barrier is unlikely to exceed ca. 5 kcal mol$^{-1}$,[2] in **2** such rotation is likely to be frozen on the NMR time scale at ambient temperature.

Accordingly, an analysis of the variable-temperature behavior of **2** requires consideration of only four conformations, shown in the middle row of Figure 1, in which the carbonyls eclipse the boron atoms and in which there is a high barrier to tripodal rotation about the borazine–chromium bond. In the absence of accidental isochrony, the two structures with $C_{3v}$ symmetry (**2a** and **2h**) are expected to display one signal, and the two structures with $C_s$ symmetry (**2c** and **2e**) are expected to display two signals, for each of the five nonequivalent carbon atoms (CO, $NCH_2$, $NCCH_3$, $BCCH_3$, and $BCH_2$). The appearance at the slow-exchange limit (−80 °C) of four signals in subspectrum A and three in subspectrum B therefore provides conclusive evidence of conformational heterogeneity. By the same token, the data in Table I require accidental isochrony among the $^{13}C$ signals in subspectra B and C, as well as among those in the carbonyl and $BCH_2$ region.

We consider it likely that one of the conformations present in solution is that observed in the crystal (**2c**). The observance of four $^{13}C$ resonances in the $NCH_2$ region is therefore compatible with a mixture of **2c** and **2e** or of **2c**, **2a**, and **2h**. If we admit to the possibility of additional accidental isochrony, mixtures containing **2c**, **2e**, and one or both of the other two conformers need also be considered. In the absence of compelling reasons to the contrary, however, and on the grounds of parsimony (Ockham's razor), we opt for the first of these possibilities, a mixture of **2c** and **2e**. This assumption is in harmony with the line-shape analysis (see below).

Since the four signals in subspectrum A collapse to a singlet at ambient temperature, any acceptable exchange scheme must satisfactorily account not only for the topomerization of the NEt groups in **2c** and **2e** but also for exchange between the two conformations. For steric reasons, rotation of the BEt groups is prevented by the presence of the eclipsing carbonyl groups, which remain locked into position over the boron atoms on the time scale of NEt rotation. An appropriate six-site exchange scheme involving **2c** and **2e** and leading to NEt group topomerization as well as to conformational interconversion is shown in Figure 3. Rotation of a single ethyl group or simultaneous rotation of three ethyl groups leads to conformational interconversion, while simultaneous rotation of two ethyl groups leads to ethyl topomerization within a single conformation. The set of 15 rate constants can therefore be separated into three subsets: a subset of six associated with a single ethyl rotation ($k_I$); a subset of six associated with simultaneous rotation of two ethyl groups ($k_{II}$); a subset of three associated with simultaneous rotation of three ethyl groups ($k_{III}$).

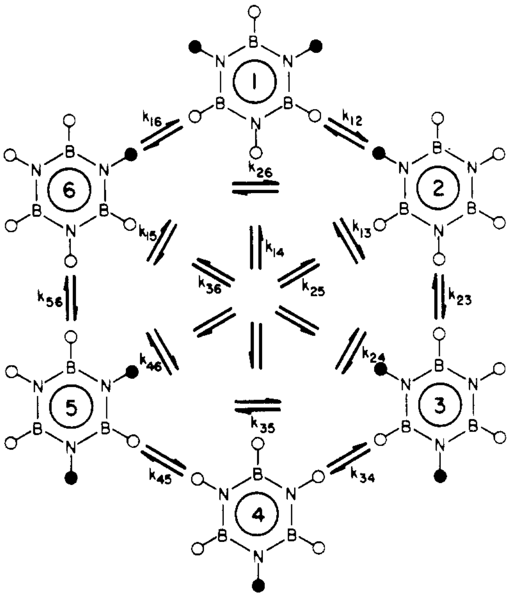

**Figure 3.** Pictorial representation of the exchange scheme used to simulate the coalescences involving the $NCH_2$, $NCCH_3$, $BCCH_3$, and CO $^{13}C$ resonances. There are three topomers each for the two conformations, **2c** and **2e**, which are indexed 1, 3, 5 and 2, 4, 6, respectively, and 15 rate constants which fall into three classes: $k_I$ (e.g., $k_{12}$), $k_{II}$ (e.g., $k_{13}$), $k_{III}$ (e.g., $k_{14}$).

**Table II. Calculated Rate Constants for Site Exchange in 2 from Line-Shape Analysis of VT $^{13}C\{^1H\}$ NMR Spectra**

| | first-order rate constants, s$^{-1}$ | | |
|---|---|---|---|
| temp, °C | $k_I$ | $k_{II}$ | $k_{III}$ |
| −48 | 360 | 180 | 10 |
| −57 | 100 | 80 | 5 |
| −63 | 80 | 60 | 5 |
| −71 | 35 | 28 | 1 |

The CO, $NCH_2$, $NCCH_3$, and $BCCH_3$ regions of the $^{13}C\{^1H\}$ NMR spectrum under conditions of slow exchange (i.e., at temperatures below −30 °C) were simulated using the chemical shifts in Table I, assuming frozen tripodal rotation, and employing a version of the DNMR3 program[7] modified to handle single-spin, *n*-site exchange. Satisfactory fits of simulated on observed spectra at four temperatures were obtained by using the rate constants in Table II and allowing only small changes with temperature in the relative intensities of lines. From these data, $\Delta G^{\ddagger}_{220}$ was calculated to be 10.4 ± 0.2 kcal mol$^{-1}$ for single (uncorrelated) ethyl group rotation and 10.6 ± 0.3 kcal mol$^{-1}$ for simultaneous (correlated) rotation of two ethyl groups.[8]

The conclusion that correlated and uncorrelated rotations have similar energy requirements is unprecedented for this type of compound. Empirical force field calculations[2] have shown that ethyl group rotation in HEB is completely uncorrelated,[9] and even bearing in mind the

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(6) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

(7) Kleier, D. A.; Binsch, G. *QCPE* **1970**, *11*, 165.

(8) The contribution by $k_{III}$ to the overall lineshape was small and the value of $\Delta G^{\ddagger}$ calculated from $k_{III}$ was considered too imprecise to be meaningful.

substantial differences between benzene and borazine $\pi$ complexes, a mechanistic rationale for correlated motion of two ethyl groups in **2** is far from obvious. A variety of other schemes were therefore tried in an attempt to find alternatives to the above conclusions. A site-exchange process involving borazine–metal bond dissociation was ruled out by the observations of separate resonances in an equimolar mixture of hexaethylborazine and **2** in $CD_2Cl_2$ at the fast exchange limit of **2**.[10] Random exchange, which requires that all rate constants should be equal for a given temperature, did not give satisfactory fit of simulated on experimental spectra over the observed temperature range even when large changes with temperature were allowed in the relative intensities of lines within a subspectrum. However, by allowing large changes in relative intensities, it was possible to obtain reasonably satisfactory fits of simulated on observed spectra (though noticeably poorer than those obtained by using the $k$'s in Table II) by fixing the sets of rate constants $k_{\mathrm{II}}$ and $k_{\mathrm{III}}$ equal to zero. In consequence, we cannot rigorously exclude the possibility that both topomerization and conformational interconversion can be achieved by successive single (uncorrelated) ethyl group rotations. For this mechanism, the calculated $\Delta G^{\ddagger}_{220}$ is 10.1 ± 0.2 kcal mol$^{-1}$.

Attempts at line-shape fitting by including conformers **2a** and **2h** in an exchange scheme, along with **2c** and **2e**, proved unsuccessful. This evidence, though of a negative kind, tends to support our initial assumption that **2c** and **2e** are the only significant components in the conformational mixture.

## Experimental Section

A sample of tricarbonyl(hexaethylborazine)chromium(0) (**2**),[11] prepared by Dr. M. Scotti, was supplied to us through the courtesy of Professor H. Werner. The sample contained about 10% of tricarbonyl(hexa*methyl*borazine)chromium(0). The 90.56-MHz $^{13}C\{^1H\}$ and 115.55-MHz $^{11}B\{^1H\}$ NMR spectra were obtained by using a Bruker WH360 spectrometer operating in the Fourier transform mode. The temperature of the probe was measured by a thermocouple inserted in an NMR tube filled with toluene to the same depth as the solution in the sample tube. Temperatures were considered accurate to ± 2 °C. The single frequency off-resonance decoupling experiments were performed at 15.08 MHz and ambient temperature by using a Bruker WP60 NMR spectrometer.

The sample solution, approximately 70 mM in $CD_2Cl_2$, was filtered under $N_2$ through a Grade 3 glass sinter, degassed by several freeze–pump–thaw cycles and sealed under vacuum.

**Acknowledgment.** We thank Drs. I. Sadler and D. Reid of the SERC High Field NMR Facility at the University of Edinburgh for obtaining the 90.56-MHz $^{13}C$ and 115.55-MHz $^{11}B$ NMR spectra, Professor H. Werner (Würzburg) for supplying us with a sample of **2**, and Mr. J. H. Archer, Jr., for preliminary experiments. The work at Princeton was supported by the National Science Foundation (Grant CHE-8009670).

**Registry No.** **2**, 34829-57-7.

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(9) Similarly, the rotation of the neopentyl groups in 1,2-dineopentyl-3,4,5,6-tetramethylbenzene is a stepwise process (Iverson, D. J.; Mislow, K. *Organometallics* **1982**, *1*, 3).

(10) In the 15.08-MHz $^{13}C$ NMR spectrum, the methyl absorptions of hexaethylborazine and **2** are almost isochronous, but the $NCH_2$ absorptions are well separated at 40.3 ppm (hexaethylborazine) and 44.1 ppm (**2**).

(11) Scotti, M.; Werner, H. *Helv. Chim. Acta* **1974**, *57*, 1234.

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# Enthalpies of Formation of Bis($\eta^5$-cyclopentadienyl)diphenyltitanium and Bis($\eta^5$-cyclopentadienyl)diferrocenyltitanium

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The standard enthalpies of formation of the title crystalline complexes at 298.15 K were determined by reaction–solution calorimetry. The results gave $\Delta H_f^\circ$ [Ti($\eta^5$-$C_5H_5$)$_2$Ph$_2$(c)] = 294.4 ± 8.8 and $\Delta H_f^\circ$ [Ti($\eta^5$-$C_5H_5$)$_2$Fc$_2$(c)] = 520.4 ± 12.0 kJ mol$^{-1}$ (Ph = phenyl and Fc = ferrocenyl). The titanium–carbon mean bond disruption enthalpies ($\bar{D}$) and mean bond enthalpy terms ($\bar{E}$) were also derived.

## Introduction

Metal–ligand bond distances are commonly considered as measurements of metal–ligand bond strengths, which in turn are used to explain patterns of reactivity and stability of organometallic complexes. For example, Razuvaev et al.[1] explained some reactivity features of Ti($\eta^5$-$C_5H_5$)$_2$Ph$_2$ and Ti($\eta^5$-$C_5H_5$)$_2$Fc$_2$ (Ph = $C_6H_5$ and Fc = ($\eta^5$-$C_5H_5$)Fe($\eta^5$-$C_5H_4$)) by assuming that the Ti–Fc bond strength is greater than the Ti–Ph bond strength (Ti–C bond distances are 219 and 227 pm, respectively).[2,3] As this hypothesis can be analyzed if reliable thermochemical data are available, we decided to study the thermochemistry of both complexes, by use of a reaction–solution calorimeter.

## Experimental Section

The reaction and solution enthalpies were measured in the reaction–solution calorimeter previously described.[4] The ther-

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(1) Razuvaev, G. A.; Sharutin, V. V.; Domrachev, G. A.; Suvorova, O. N. *IX ICOM*, Dijon 1979.

(2) Zakharov, L. N.; Struchkov, Yu. T.; Sharutin, V. V.; Suvorova, O. N. *Cryst. Struct. Commun.* **1979**, *8*, 439.

(3) Kocman, V.; Rucklidge, J. C.; O'Brien, R. J.; Santo, W. *J. Chem. Soc., Chem. Commun.* **1971**, 1340.

(4) Calado, J. C. G.; Dias, A. R.; Martinho Simões, J. A.; Ribeiro da Silva, M. A. V. *Rev. Port. Quim.* **1979**, *21*, 129.