Organometallics **1982,** *1,* 13-20

1 H), 1.94 (m, 1 H), 2.23 (m, 1 H), 2.50 (dd, 1 H, J = 1.9, 15.3 Hz), 2.78 (dd, 1 H, J = 4.7, 15.3 Hz), 7.09 (AB m, 2 H), 7.30 (dd, 1 H, J = 6.7, 1.5 Hz), 7.45 (dd, 1 H, J = 6.7, 1.5 Hz), 7.75 (br s, 1 H, N-*H*). IR ($CDCl_3$): 3469, 2920, 2860, 1464, 1380, 1349, 1329, 1310, 1297, 1238, 1177, 1156, 938, 876, 774, 665. MS: Calcd for $C_{18}H_{21}N$: 251.1674. Found: 251.1674, 253 (0.8), 252 (13.6), 251 (100), 250 (5.3), 236 (3.9), 195 (12.5), 194 (78.6), 182 (4.8), 181 (5.5), 180 (9.0), 167 (5.3), 44 (4.2), 40 (4.2).

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Registry No. 2a, 78672-93-2; **2b,** 78672-94-3; **3a,** 78672-95-4; **5a,** 78672-96-5; **6,** 41977-03-1; **6** acid chloride, 51372-02-2; **6** oxoindole, 78672-97-6; **7,** 42916-91-6; **7** 3-oxoindole, 78672-98-7; **8,** 78672-99-8; **9a,** 78685-49-1; **9b,** 78673-00-4; **10,** 78673-01-5; **11,** 78673-02-6; **13,** 78673-03-7; **14,** 78673-04-8; **15,** 78673-05-9; *N*-(trimethylsilyl)indole, 17983-42-5; silver tetrafluoroborate, 14104-20-2; palladium chloride, 7647-10-1.

Structures of Dineopentylbis(triethylphosphine)platinum(II) and Bis(triethylphosphine)-3,3-dimethylplatinacyclobutane: Reactant and Product in a Thermal Cyclometalation Reaction

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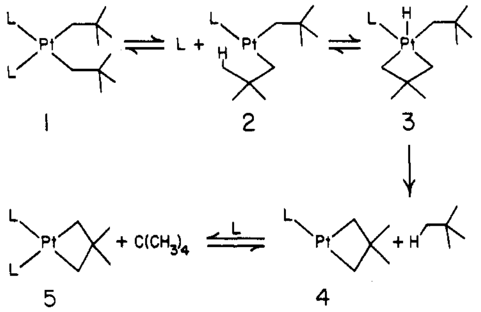
Thermal decomposition of dineopentylbis(triethylphosphine)platinum(II), 1, $Pt(CH_2C(CH_3)_3)_2(P(C_2H_5)_3)_2$, yields neopentane and bis(triethylphosphine)-3,3-dimethylplatinacyclobutane, 5, $\overline{Pt(CH_2C(CH_3)_2CH_2})$-$(P(C_2H_5)_3)_2$. Compound 1 crystallizes with four molecules in space group C^6_{2h}—$C2/c$ of the monoclinic system in a cell at −158 °C of dimensions a = 8.776 (2) Å, b = 17.761 (3) Å, c = 17.669 (3) Å, and β = 109.62 (1)°. The structure has been refined to an R index on F^2 of 0.035 for 6877 observations and 115 variables. Compound 1 has crystallographically imposed C_2 symmetry. Compound 5 crystallizes with four molecules in space group C^9_{2v}—$Pn2_1a$ of the orthorhombic system in a cell at −158 °C of dimensions a = 15.947 (3) Å, b = 14.301 (2) Å, and c = 9.383 (2) Å. The structure has been refined to a R index on F^2 of 0.032 for 3255 observations and 181 variables. Some average metrical parameters for 1 and 5 respectively are as follows: Pt–P, 2.322 (1), 2.285 (2) Å; Pt–C, 2.118 (2), 2.083 (3) Å; P–C, 1.839 (2), 1.827 (2) Å; C–C (ethyl), 1.525 (3), 1.521 (4) Å; P–Pt–P, 94.09 (3), 103.01 (9)°; C–Pt–C, 85.5 (1), 67.3 (3)°. In 1 the neopentyl group is of normal geometry with a C–C(terminal) distance of 1.529 (3) Å; in 5 the C–C distances of the metallacycle average 1.535 (6) Å and the β-C atom is 0.38 Å out of the plane through PPPtCC. A comparison of structures of 1 and 5 indicates that 1 is significantly sterically congested and suggests that relief of this congestion may be an important component of the thermodynamic driving force for the conversion of 1 to 5.

Introduction

The cleavage of carbon–hydrogen bonds of saturated hydrocarbons occurs readily over supported or bulk transition metals.[2-5] Only a few examples of analogous reactions involving soluble transition metals have been reported,[6-10] and rigorous proof that metal colloids are not involved in these reactions has been difficult to construct. By contrast, homogeneous *intramolecular* reactions which cleave unactivated carbon–hydrogen bonds ("unactivated" in the sense of having neither adjacent unsaturation nor heteroatoms) are well-known.[6,11-17]

Scheme I. Conversion of Dineopentylbis(triethylphosphine)platinum(II) to Bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (L = PEt_3)



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[1] (a) Northwestern University. (b) Massachusetts Institute of Technology.

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One group of these reactions, cyclometalation reactions involving platinum(II), is now relatively well characterized mechanistically.[16,17] The best defined of these reactions is the conversion of dineopentylbis(triethylphosphine)platinum(II) (**1**) to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (**5**) and neopentane.[16] The mechanism of this process involves three steps (Scheme I): creation of a vacant coordination site on platinum by dissociation of phosphine (**1** → **2**), oxidative addition of a methyl C–H bond from a neopentyl group to platinum(II) (**2** → **3**), and reductive elimination of neopentane from the resulting adduct (**3** → **4**). We have proposed the conversion of **3** to **4** to be rate limiting, on the basis of the high Arrhenius preexponential factor for the reaction ($\log A = 20 \pm 2$) and the significant kinetic isotope effect ($k_H/k_D \simeq 3$).[16]

Why does the cleavage of unactivated C–H bonds by addition to soluble organoplatinum species occur readily only when the cleavage reaction is intramolecular? The mechanism outlined in Scheme I provides a foundation on which to construct an analysis of the factors that facilitate intramolecular C–H activation by metals, and we hope ultimately to answer this question. As one step in this analysis, we must be able to rationalize the *direction* of the reaction: why does it proceed in the sense of **1** → **5** + neopentane, rather than the reverse? We submit that the answer to this question is not obvious. Simple considerations of bond strengths give no clue, since to a first approximation the sums of the bond energies of reactant and products are the same.[18] The platinacyclobutane ring seems to have no large stability or instability associated with it, since in related reactions five- and six-membered platinacycles form in competition with it.[17] The conversion of **1** to **5** is accompanied by changes of unknown magnitude in the bond angles, bond lengths, and electronic structure of the P_2PtC_2 moiety: these changes might involve significant changes in energy. The starting material is undoubtedly sterically congested, and expulsion of a neopentane moiety should help to relieve this congestion. The reaction produces two particles from one and is entropically favored on that basis.[19,20] Which one (or several) of these factors determines ΔG for the reaction?

The only factor for which it is possible to obtain a useful theoretical estimate is the change in entropy. We assume that ΔS is dominated by the change in translational entropy (that is, making two particles from one). At the temperature (157 °C) and concentration used (0.1 M reactants and products), $\Delta S_{\text{translation}} \simeq$ 14–16 kcal mol^{-1}.[21] The equilibrium constant from this contribution alone is sufficiently large that the concentration of **1** at equilibrium would be undetectable by direct observation (eq 1 and 2).

$$K(157\ ^\circ\text{C},\ T\Delta S_{\text{translation}}) = [\mathbf{5}][\text{C}_5\text{H}_{12}]/[\mathbf{1}] = 6 \times 10^7\ \text{M} \tag{1}$$

$$[\mathbf{1}]_{\text{equilibrium}} \simeq 10^{-10}\ \text{M} \tag{2}$$

Thus it is clear that entropic considerations by themselves are sufficient to rationalize both the conversion of **1** to **5** and the apparent absence of the reverse reaction or of reaction of **5** with other hydrocarbons under conditions in which it decomposes (to dimethylcyclopropane).[22,23] The fact the $T\Delta S_{\text{translation}}$ is sufficient to account for the presently available experimental observations does not mean, however, that this entropic term is necessarily the dominant contributor to ΔG for the reaction. We ultimately need to know both the magnitude of ΔG and its contributing components to undertand this C–H bond-breaking reaction. We have available experimental approaches to the ring strain in the platinacyclobutane ring.[17] To evaluate steric effects and local electronic effects, we require accurate structural data for reactant and product. This paper provides these data.[24]

Experimental Section

The platinum compounds were prepared as described previously.[16] Crystals of the dineopentyl complex **1** were readily obtained by recrystallization from pentane. Crystals of the metallacycle **5** were very difficult to grow. Ultimately the following procedure led to suitable crystals. About 100 mg of **5** was dissolved in the minimum amount of methanol necessary to effect solution at 0 °C. The solution was filtered through a 0.5-μm Millipore filter. The filtrate was kept at 0 °C, and argon was very slowly bubbled through water at room temperature and then passed over the top of the methanol solution. After 48 h the crystals which had slowly formed were collected by decanting away the methanol solution. The crystals were not washed but were immediately sealed under argon.

Photographic examination at room temperature of a crystal of **1** indicated that the material belongs to the monoclinic system, space group $C2/c$ or Cc. The absences observed at −158 °C on a Picker diffractometer are consistent with the room-temperature results. On the other hand, a crystal of **5** displays the systematic absences of space group $C222_1$ of the orthorhombic system at room

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(17) Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948–949. The estimated difference in ring strain between structurally similar platinacyclobutanes and platinacyclopentanes is less than 5 kcal mol^{-1}. An estimate from calorimetric (differential scanning calorimetry) examination of $PtCl_2(C_3H_6)(pyr)_2$ and related metallacycles suggests strain of ~12 kcal mol^{-1}. (Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149–194.) These estimates are not necessarily incompatible, since the Pt(II) and Pt(IV) complexes have different degrees of crowding.

(18) One C–H bond and one C–Pt bond are broken in the reaction, and one new C–H bond and one C–Pt bond are formed. There is presently no way of estimating differences in the energies of the old and new bonds.

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(21) Qualitative arguments outlined by Page and Jencks suggest $T\Delta S^\circ \simeq 10.5$ kcal/mol at 300 K either considering translational terms alone or estimating all of the terms.[20] Correction to concentrations of 0.1 M should add $R \ln (0.1) \simeq 1.3$ kcal/mol to their estimate. Additional corrections arising from peculiarities of the structures of **1** and **5** cannot be made with useful accuracy.

(22) Thermal decomposition of cyclohexane solutions of **5** in the presence of mercury(0) was performed in sealed tubes at 178 °C by using previously described procedures.[16] The appearance of 1,1-dimethylcyclopropane (monitored by GLC) was first order in **5** through 1 half-life: $k^{\text{obsd}} = 1.2 \times 10^{-5}\ \text{s}^{-1}$. Examination of reaction mixtures from thermal decompositions of **5** in cyclohexane, isooctane, or 2,2,4,4-tetramethylpentane and in the presence of mercury(0) by $^{31}P\{^1H\}$ NMR spectroscopy and GLC indicated no products were formed by oxidative addition of C–H bonds of the solvent to the platinum complexes in solution.

(23) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916. These authors have presented convincing evidence that addition of CH_4 to $Pt(PPh_3)_2$ is an endergonic reaction. Even if the adduct of a hydrocarbon solvent to platinum were not stable, however, it might still be detected through its decomposition products (for example, cyclopentene from cyclopentane).[7]

(24) A preliminary account of this work was presented at the Second International Symposium on Homogeneous Catalysis, Dusseldorf, Sept 1980.

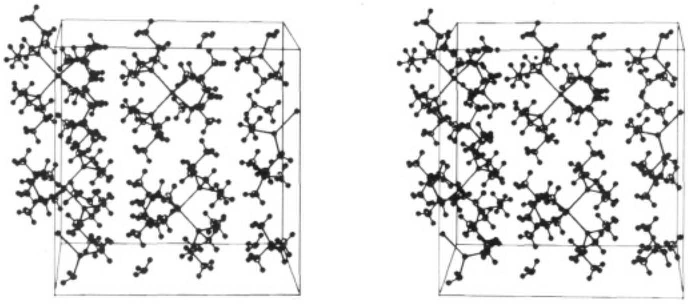

Figure 1. The unit cell of $Pt(CH_2C(CH_3)_3)_2(P(C_2H_5)_3)_2$ (1). All atoms in the cell are shown. Additional atoms have been added to complete some of the molecules. Here and in successive figures the 50% probability ellipsoids are shown, except for hydrogen atoms which have been drawn artificially small.

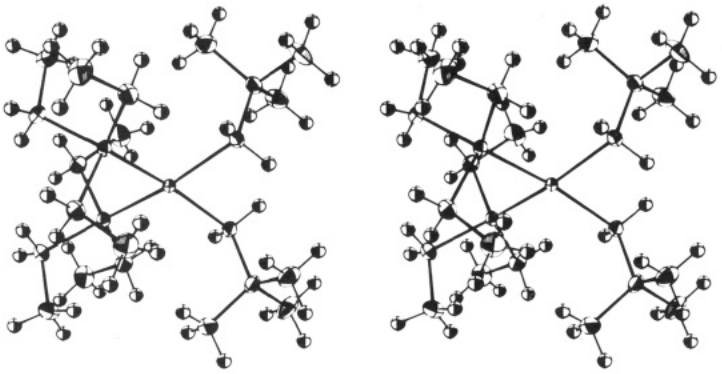

Figure 2. A stereoview of an individual molecule of $Pt(CH_2C(CH_3)_3)_2(P(C_2H_5)_3)_2$.

temperature but those of *Pnma* or $Pn2_1a$ at −158 °C. The phase transition is a smooth, nondestructive one.

Data collection proceeded by methods standard[25] at Northwestern. Table I presents crystallographic details on the two compounds. In each instance the crystal used was of excellent quality, leading to more extensive data sets than usual.

The structure of compound 1 was solved by Patterson methods and refined by our standard least-squares procedures.[25] That the compound crystallizes in space group $C2/c$, and hence has a crystallographically imposed twofold axis, was apparent from the course of the refinement and from the fact that Friedel pairs show an R index for averaging of 1.0%. After anisotropic refinement of the nonhydrogen atoms, the positions of the hydrogen atoms of the six independent methyl groups and three independent methylene groups were apparent. These positions were idealized (C–H = 0.95 Å) and were held fixed in the final cycle of anisotropic refinement of F_o^2. This final cycle also included an isotropic extinction parameter. The refinement converged to the R indices indicated in Table I.

Compound 5 was also solved by Patterson methods. It became apparent that the compound crystallizes in the noncentrosymmetric, polar space group $Pn2_1a$ rather than the centrosymmetric group *Pnma*. The correct enantiomer was established from the R indices of refinements of the two possibilities and by comparison of those 147 Friedel pairs of reflections whose intensities were greater than 400 e^2 and differed by more than 5%. The positions of the hydrogen atoms of the eight methyl and four methylene groups were apparent in a difference Fourier map obtained after the first cycle of anisotropic refinement of the nonhydrogen atoms. These positions were idealized and held fixed in the final cycle of anisotropic refinement on F^2. It is interesting that this final cycle also necessitated an isotropic extinction correction, despite the fact that the crystal had undergone a phase transition between room temperature and −158 °C. This refinement converged to the R indices given in Table I. In each instance analysis of R indices as a function of Miller indices, $|F_o|$, and setting angles revealed no unexpected trends. The principal peak in each of the final difference Fourier maps is associated with the Pt position and is 1.5 (2) and 1.2 (2) e/Å^3, respectively, for 1 and 5. Particularly for 1, where the data set extends to 0.86 Å^{-1}, there are indications that the residual density results from bonding effects; further analysis of the data is underway.

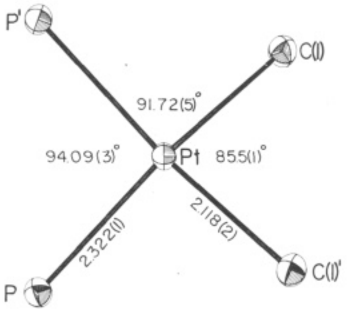

Figure 3. The inner coordination sphere of $Pt(CH_2C(CH_3)_3)_2(P(C_2H_5)_3)_2$.

Table II lists the final parameters for 1 and Table III the final parameters for 5. Tables IV[26] and V[26] list values of $10|F_o|$ and $10|F_c|$ for the two structures. A negative entry indicates that F_o^2 was observed to be less than zero. Tables VI[26] and VII[26] present the root-mean-square amplitudes of vibration of 1 and 5, respectively. Because the structure determinations were carried out on crystals maintained at −158 °C, these amplitudes are small and unexceptional.

Description of the Structures and Discussion

The crystal structure of 1, $Pt(CH_2C(CH_3)_3)_2(P(C_2H_5)_3)_2$, consists of the packing of four molecules in the unit cell, as shown in Figure 1. The shortest intermolecular interaction is calculated to be 2.32 Å between two H(2)C(10) atoms. A stereoview of an individual molecule is shown in Figure 2, and Figure 3 shows the inner coordination sphere along with some important bond distances and angles. Other metrical parameters are given in Table VIII. Similarly, the crystal structure of 5 is shown in Figure 4.

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[26] Supplementary material.

Table I. Crystallographic Details for 1 and 5

compd	$\mathrm{Pt(CH_2C(CH_3)_3)_2(P(C_2H_5)_3)_2}$ (1)	$\mathrm{\overline{Pt(CH_2C(CH_3)_2C}H_2)(P(C_2H_5)_3)_2}$ (5)
formula	$\mathrm{C_{22}H_{52}P_2Pt}$	$\mathrm{C_{17}H_{40}P_2Pt}$
f w, amu	573.70	501.55
space group	C_{2h}^6-C2/c	$C_{2v}^9-Pn2_1a$
a, Å	8.776 (2)	15.947 (3)
b, Å	17.761 (3)	14.301 (2)
c, Å	17.669 (3)	9.383 (2)
β, deg	109.62 (1)	
vol, Å^3	2594	2140
Z	4	4
ρ_{obsd}(25 °C), g/cm^3	1.39 (3)	1.43 (3)
ρ_{calcd}(−158 °C), g/cm^3	1.468	1.556
linear abs coeff, cm^{-1}	55.9	67.6
bounding cryst faces	{001} (0.170),[a] {010} (0.276), {110} (0.340, 0.388)	{100} (0.302), {010} (0.390), {111} (0.318, 0.333, 0.260, 0.302)
cryst vol, mm^3	0.0167	0.0211
radiation	Mo Kα (λ(Mo Kα_1) = 0.7093 Å from graphite monochromator	same
data collection temp	−158 °C[b]	same
transmission factors	0.251 to 0.429, 0.370 average	0.187 to 0.265, 0.239 average
detector aperture	4.5 wide by 5.5 mm high, 32 cm from crystal	same
takeoff angle, deg	2.6	3.0
scan speed	2° in 2θ/min	same
2θ limits	$4° \leqslant 2\theta \leqslant 75°$	$3° \leqslant 2\theta \leqslant 60°$
bkgnd counts	10 s at each end of scan with rescan option[c]	same
scan range	1.1° below Kα_1 to 0.9° above Kα_2	0.9° below Kα_1 to 0.9° above Kα_2
data collected	$\pm h,k,l$ (and $\pm h,-k,-l$, $2\theta < 30°$)	h,k,l (and $h,-k,l$, $2\theta < 32°$)
P	0.03	0.03
unique data	6877	3255
final no. of variables	115	181
R (on F^2)[d]	0.035	0.032
R_{w} (on F^2)[d]	0.053	0.053
error in observn of unit wt, electrons	0.923	0.961
R (on F),[d] $F_o^2 > 3\sigma(F_o^2)$	0.024	0.023

[a] Following the form, in parentheses are the distances in millimeters between the members of the form. [b] The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. [c] Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568-570. [d] $R(\text{on } F^2) = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$; $R_{\mathrm{w}}(\text{on } F^2) = \Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4$; $R(\text{on } F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.

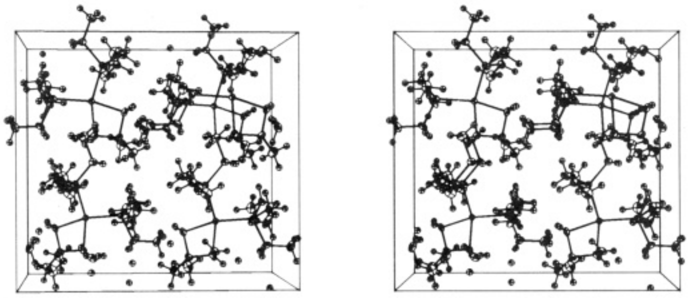

Figure 4. The unit cell of $\mathrm{\overline{Pt(CH_2C(CH_3)_2C}H_2)(P(C_2H_5)_3)_2}$ (5).

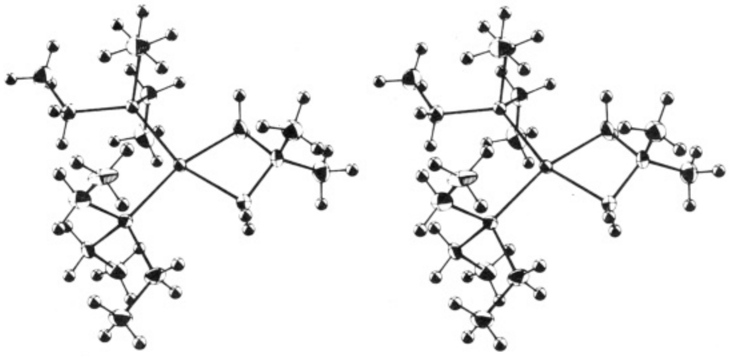

Figure 5. A stereoview of an individual molecule of $\mathrm{\overline{Pt(CH_2C(CH_3)_2C}H_2)(P(C_2H_5)_3)_2}$.

Table II. Positional and Thermal Parameters for the Atoms of $Pt(CH_2C(CH_3)_2(P(C_2H_5)_3)_2$ (1)

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
PT	0	0.0140690(52)	1/4	31.05(11)	6.04(2)	8.32(3)	0	3.84(4)	0
P	0.046210(58)	0.103144(26)	0.351423(29)	43.74(56)	7.78(11)	10.13(13)	0.67(20)	6.10(22)	-0.57(10)
C(1)	-0.09137(23)	-0.07351(10)	0.16556(11)	52.4(22)	8.71(43)	11.64(53)	-1.82(79)	4.76(88)	-0.36(39)
C(2)	-0.26702(25)	-0.10112(11)	0.14995(12)	60.9(25)	10.38(48)	13.88(59)	-6.94(86)	3.52(97)	0.85(43)
C(3)	-0.39164(28)	-0.03765(15)	0.12796(18)	49.8(26)	17.32(66)	35.3(11)	-3.1(11)	4.8(18)	5.57(73)
C(4)	-0.28419(29)	-0.14175(14)	0.22314(14)	75.6(30)	20.38(73)	17.49(71)	-14.0(12)	8.1(12)	3.19(57)
C(5)	-0.30956(33)	-0.15711(15)	0.08022(15)	111.1(38)	20.03(74)	16.99(74)	-24.3(14)	4.0(13)	-4.01(59)
C(6)	0.15014(24)	0.19892(11)	0.35329(12)	55.7(24)	10.16(47)	14.88(59)	-3.67(84)	5.66(96)	-2.10(43)
C(7)	0.33927(27)	0.17933(13)	0.37167(14)	56.5(26)	17.99(66)	19.28(73)	-6.3(10)	2.6(11)	-0.91(55)
C(8)	-0.15074(25)	0.13969(12)	0.34977(13)	57.7(24)	12.31(52)	17.82(66)	4.07(88)	12.5(10)	-1.13(47)
C(9)	-0.26518(30)	0.07795(15)	0.35753(17)	73.6(31)	20.31(75)	32.7(10)	-2.7(12)	29.0(15)	-1.76(70)
C(10)	0.13372(27)	0.07337(12)	0.45715(12)	74.8(27)	13.48(53)	10.33(53)	3.83(96)	8.28(98)	-0.01(43)
C(11)	0.14451(33)	0.13232(14)	0.52145(14)	121.0(39)	18.58(78)	12.77(64)	-0.9(13)	11.9(13)	-3.40(53)

ATOM	X	Y	Z	$B, Å^2$	ATOM	X	Y	Z	$B, Å^2$
H1C(1)	-0.085	-0.057	0.116	2.3	H3C(4)	-0.262	-0.108	0.267	3.3
H2C(1)	-0.022	-0.116	0.184	2.3	H1C(5)	-0.415	-0.177	0.071	3.6
H1C(6)	0.143	0.223	0.393	2.5	H2C(5)	-0.307	-0.132	0.033	3.6
H2C(6)	0.115	0.214	0.302	2.5	H3C(5)	-0.233	-0.197	0.093	3.6
H1C(8)	-0.200	0.165	0.300	2.7	H1C(7)	0.386	0.161	0.425	3.1
H2C(8)	-0.134	0.174	0.393	2.7	H2C(7)	0.356	0.144	0.335	3.1
H1C(10	0.240	0.056	0.465	2.6	H3C(7)	0.388	0.226	0.367	3.1
H2C(10	0.070	0.033	0.465	2.6	H1C(9)	-0.372	0.098	0.344	3.6
H1C(3)	-0.367	-0.002	0.171	3.7	H2C(9)	-0.264	0.038	0.322	3.6
H2C(3)	-0.389	-0.013	0.080	3.7	H3C(9)	-0.231	0.060	0.411	3.6
H3C(3)	-0.496	-0.058	0.119	3.7	H1C(11	0.172	0.109	0.572	3.4
H1C(4)	-0.391	-0.160	0.210	3.3	H2C(11	0.225	0.168	0.522	3.4
H2C(4)	-0.213	-0.182	0.238	3.3	H3C(11	0.043	0.157	0.510	3.4

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

Here the shortest intermolecular interaction is calculated to be 2.36 Å between atoms H(2)C(6) and H(3)Me(2). A stereoview of the molecule is shown in Figure 5, and Figure 6 displays the inner coordination sphere along with pertinent distances and angles. Additional distances and angles are in Table IX while Table X presents results on least-squares planes.

Although the number of known structures involving the *cis*-PtP_2 geometry is extensive, none of these also involves neopentyl groups as additional ligands. Thus direct comparison of the structure of 1 with others in the literature is not possible. The structures of known platinacyclobutanes have been summarized.[17,27] The only structure of accuracy comparable with that of 5 is $\overline{Pt(C(CN)_2CH_2C}(CN)_2)(P(C_6H_5)_3)_2$,[27] and the two structures are similar. In 5 the Pt–C and Pt–P distances are significantly shorter than in the cyano-substituted derivative (averages of 2.083 (6) vs. 2.138 (6) Å and 2.285 (3) vs. 2.303 (2) Å, respectively). The twist between the PPtP and CPtC planes is 18.0° in the cyano derivative vs. 1.8° in 5. These comparisons suggest that 5 is less congested than its cyano analogue. Yet, the Pt–C–C–C rings are remarkably similar. Both show approximately the same deviation from planarity, the dihedral angles between the C(3)–Pt–C(1) and C(1)–C(2)–C(3) planes being 24.4 and 22.4°, respectively, for the cyano complex and for 5. But in keeping with our objective to compare the structures of the present reactant 1 and product 5, the discussion here will concentrate on the differences in these two structures.

Several features of the structures of 1 and 5 suggest strain in the former and at least partial release of this strain in the latter. First, the twist between the PPtP and CPtC planes of 1 (18.7°) disappears in 5 (1.8°). Although calculations by Tatsumi and Hoffmann[28] and the observation of similar twists in bis(phosphine)(olefin)metal complexes[29] both suggest that the energy intrinsic to the distortion from ideal planar geometry is small, it is one indication of strain in 1 that might be released in going to 5. Second, the Pt–P and Pt–C bond lengths shorten in going from 1 to 5 (by 0.037 (2) and 0.035 (4) Å, respectively). Although the details of the interactions responsible for this shortening are not known, the qualitative observation of shortening is also compatible with release of steric strain in going from 1 to 5. Estimates of differences in metal–carbon bond energies in other organometallic compounds containing neopentyl and smaller alkyl groups indicate that the strain energy arising from steric crowding around a neopentyl group may be large (>5 kcal mol^{-1}).[30] The skewing of the $C(CH_3)_3$ groups of the neopentyl moieties out of the P_2PtC_2(quasi) plane in 1, the substantial (9°) increase in the PPtP angle on going from 1 to 5, and the kinetic observation that decomposition of

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(27) Yarrow, D. J.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Organomet. Chem.* **1974**, *70*, 133–145.

(28) Tatsumi, K.; Hoffmann, R. unpublished. Extended Hückel calculations suggest that the energy required to twist the PPtP and CPtC planes of $Pt(CH_3)_2(P(CH_3)_3)_2$ by 30° is less than 5 kcal mol^{-1}. An examination of $\overline{Pt(CH_2C(CH_3)_2CH_2})(P(CH_3)_3)_2$ suggests that no special stability is associated with the platinacyclobutane ring. Thus, these calculations also may indicate, qualitatively, that 1 is strained but do not suggest a large magnitude for this strain.

(29) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33–61.

(30) Steric crowding about transition-metal alkyls has been reported to contribute to both the decrease in bond energies and the lengthening of M–C bonds: the mean M–C bond energy in $[M(CH_2C(CH_3)_3)_4]$ (M = Ti, Zr, or Hf) is 19–20 kcal mol^{-1} less than that of sterically less demanding alkyl substituents (Lappert, M. F.; Patil, D. S.; Padley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, *830*–831), and the Zr–C (sp^3) bond lengths in $[Zr(\eta\text{-}C_5H_5)_2(CH_2C(CH_3)_3)_2$ are 0.037 Å longer than for an analogous dimethyl complex (Jefferey, J.; Lappert, M. F.; Luong-Thi, N. T.; Atwood, J. L., Hunter, W. E. *Ibid.* **1978**, 1081–1083). Halpern and co-workers have observed differences in cobalt-*n*-propyl and cobalt-neopentyl bond energies of ~7 kcal/mol in certain cobalt(III) organometallics (Halpern, J., private communication).

Table III. Positional and Thermal Parameters for the Atoms of $\overline{Pt(CH_2C(CH_3)_2CH_2})(P(C_2H_5)_3)_2$ (5)

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
PT	0.2360360(96)	-1/4	0.016951(16)	9.78(6)	14.30(8)	36.60(18)	-0.29(21)	-0.63(8)	-0.66(92)
P(1)	0.195272(96)	-0.09890(11)	-0.01958(17)	10.85(55)	15.48(65)	50.8(16)	-0.22(46)	-2.58(78)	1.5(13)
P(2)	0.379143(76)	-0.24012(24)	0.01579(13)	10.67(36)	16.4(11)	44.2(12)	1.74(66)	0.37(51)	2.0(16)
C(1)	0.22635(39)	-0.39364(44)	0.04747(71)	15.5(23)	18.9(27)	65.8(72)	-2.7(21)	-4.2(36)	5.3(36)
C(2)	0.13275(38)	-0.39933(48)	0.01032(66)	17.2(23)	16.4(29)	58.3(77)	-5.3(20)	-3.4(31)	-1.2(40)
C(3)	0.11197(36)	-0.29531(45)	0.03063(71)	11.5(21)	25.4(30)	77.8(79)	-4.7(19)	2.1(32)	-3.0(41)
ME(1)	0.12193(57)	-0.42885(69)	-0.14488(74)	26.0(33)	38.2(52)	52.3(74)	-3.3(33)	-2.8(37)	3.1(49)
ME(2)	0.08223(53)	-0.46418(63)	0.10527(85)	24.5(39)	31.6(44)	65.0(93)	-6.6(34)	4.1(46)	1.5(54)
C(4)	0.13727(53)	-0.06575(57)	-0.18694(81)	18.2(31)	22.6(41)	58.0(87)	2.6(28)	-8.5(40)	8.3(49)
C(5)	0.18116(45)	-0.12672(56)	-0.31537(69)	33.5(31)	39.0(40)	47.4(68)	-3.5(28)	-3.8(34)	3.2(43)
C(6)	0.27012(37)	-0.00128(44)	-0.02245(69)	19.1(24)	16.6(25)	90.4(77)	-0.7(20)	-0.5(35)	6.1(38)
C(7)	0.23600(46)	0.09819(53)	-0.02322(80)	26.1(28)	21.9(31)	129.(10)	5.3(25)	7.9(45)	1.2(47)
C(8)	0.11797(43)	-0.06284(53)	0.11182(74)	16.8(26)	22.3(33)	64.2(81)	1.5(24)	5.9(36)	-6.5(44)
C(9)	0.15073(45)	-0.06619(57)	0.26425(67)	30.2(31)	49.2(42)	66.3(68)	-7.8(31)	7.1(35)	-16.4(44)
C(10)	0.43019(40)	-0.35440(44)	0.03088(68)	24.0(24)	18.9(26)	78.7(72)	9.1(20)	-3.3(33)	-3.0(38)
C(11)	0.52615(41)	-0.35730(56)	0.02137(70)	18.7(24)	37.7(38)	83.5(75)	8.4(24)	-1.1(34)	9.2(47)
C(12)	0.42869(37)	-0.19109(48)	-0.14190(64)	18.0(24)	37.8(35)	53.6(64)	6.0(23)	6.5(29)	7.1(38)
C(13)	0.40676(34)	-0.24218(82)	-0.27755(53)	27.0(23)	50.2(43)	53.0(55)	21.8(43)	10.5(26)	19.7(70)
C(14)	0.42735(32)	-0.17323(41)	0.16011(62)	13.2(19)	19.0(27)	66.0(64)	-4.2(18)	-3.1(26)	-1.9(33)
C(15)	0.39739(39)	-0.20368(52)	0.30733(61)	24.0(25)	46.4(38)	38.1(58)	-0.3(25)	-5.3(29)	-4.2(39)

ATOM	X	Y	Z	B,A^2	ATOM	X	Y	Z	B,A^2
H1C(1)	0.263	-0.428	-0.011	2.8	H2ME(2	0.066	-0.524	0.053	4.2
H2C(1)	0.238	-0.411	0.147	2.8	H3ME(2	0.112	-0.487	0.188	4.2
H1C(3)	0.087	-0.280	0.120	2.9	H1C(5)	0.190	-0.191	-0.301	3.6
H2C(3)	0.078	-0.268	-0.044	2.9	H2C(5)	0.148	-0.118	-0.400	3.6
H1C(4)	0.084	-0.116	-0.182	3.1	H3C(5)	0.234	-0.096	-0.329	3.6
H2C(4)	0.126	-0.021	-0.209	3.1	H1C(7)	0.278	0.142	-0.045	3.9
H1C(6)	0.307	-0.008	0.059	3.1	H2C(7)	0.192	0.102	-0.093	3.9
H2C(6)	0.305	-0.009	-0.106	3.1	H3C(7)	0.213	0.112	0.068	3.9
H1C(8)	0.097	0.003	0.091	3.0	H1C(9)	0.106	-0.061	0.333	3.7
H2C(8)	0.065	-0.100	0.104	3.0	H2C(9)	0.179	-0.123	0.278	3.7
H1C(10	0.415	-0.382	0.120	3.0	H3C(9)	0.188	-0.015	0.280	3.7
H2C(10	0.409	-0.395	-0.043	3.0	H1C(11	0.546	-0.420	0.008	3.5
H1C(12	0.412	-0.128	-0.155	3.0	H2C(11	0.544	-0.321	-0.059	3.5
H2C(12	0.488	-0.194	-0.132	3.0	H3C(11	0.550	-0.332	0.105	3.5
H1C(14	0.487	-0.181	0.155	2.4	H1C(13	0.347	-0.246	-0.286	3.7
H2C(14	0.415	-0.108	0.148	2.4	H2C(13	0.430	-0.212	-0.357	3.7
H1ME(1	0.068	-0.414	-0.180	3.4	H3C(13	0.428	-0.305	-0.272	3.7
H2ME(1	0.163	-0.395	-0.204	3.4	H1C(15	0.412	-0.158	0.376	3.3
H3ME(1	0.133	-0.493	-0.158	3.4	H2C(15	0.339	-0.212	0.306	3.3
H1ME(2	0.030	-0.439	0.137	4.2	H3C(15	0.424	-0.261	0.333	3.3

Table VIII. Bond Distances and Bond Angles in $Pt(CH_2C(CH_3)_3)_2(P(C_2H_5)_3)_2$ (1)

bond dist, Å			bond angle, deg			
Pt-P	2.322 (1)		P-Pt-P′ [a]	94.09 (3)	Pt-P-C(6)	123.09 (7)
Pt-C(1)	2.118 (2)		P-Pt-C(1)	166.15 (5)	Pt-P-C(8)	107.99 (7)
C(1)-C(2)	1.552 (3)		P-Pt-C(1)′	91.72 (5)	Pt-P-C(10)	119.49 (7)
C(2)-C(3)	1.527 (3)	1.529 (3) [b]	C(1)-Pt-C(1)′	85.5 (1)	P-C(6)-C(7)	113.7 (1)
C(2)-C(4)	1.532 (3)		Pt-C(1)-C(2)	118.4 (1)	P-C(8)-C(9)	112.9 (2)
C(2)-C(5)	1.529 (3)		C(1)-C(2)-C(3)	113.3 (2)	P-C(10)-C(11)	117.3 (2)
P-C(6)	1.837 (2)	1.839 (4)	C(1)-C(2)-C(4)	111.8 (2)	C(6)-P-C(8)	101.2 (1)
P-C(8)	1.837 (2)		C(1)-C(2)-C(5)	107.9 (2)	C(6)-P-C(10)	100.8 (1)
P-C(10)	1.843 (2)		C(3)-C(2)-C(4)	107.3 (2)	C(8)-P-C(10)	100.8 (1)
C(6)-C(7)	1.526 (3)	1.525 (3)	C(3)-C(2)-C(5)	108.3 (2)		
C(8)-C(9)	1.524 (3)		C(4)-C(2)-C(5)	107.9 (2)		
C(10)-C(11)	1.525 (3)					
interplanar angle (deg) Pt,P,P′/Pt,C(1),C(1)′	18.7					

[a] The primed atom is related to the corresponding unprimed atom by the crystallographically imposed twofold axis.
[b] Here and elsewhere the estimated standard deviation given in parentheses is the larger of that calculated for an individual observation on the assumption that the values averaged are from the same population or of that calculated from the inverse least-squares matrix.

complexes of the structure $Pt(CH_2C(CH_3)_3)_2(PR_3)_2$ takes place more rapidly with large phosphines than with small[31] are all compatible with significant steric strain in **1** and significant relief of this strain in going to **5**.

In summary, this work provides structures for the reactant and a product of a cyclometalation reaction involving cleavage of an unactivated C–H bond by oxidative addition to platinum(II). These structures indicate that

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(31) Treatment of (1,5-cyclooctadiene)$Pt(CH_2C(CH_3)_3)_2$ with $P(CH(CH_3)_2)_3$ at 50 °C results in rapid formation of the bis(triisopropylphosphine) analogue of **5**: DiCosimo, R., unpublished data.

Table IX. Bond Distances and Angles in $\overline{Pt(CH_2C(CH_3)_2CH_2})(P(C_2H_5)_3)_2$ (5)

bond dist, Å			bond angle, deg	
Pt-P(1)	2.282 (2)		P(1)-Pt-P(2)	103.01 (9)
Pt-P(2)	2.287 (1)		P(1)-Pt-C(1)	159.2 (2)
Pt-C(1)	2.080 (6)		P(2)-Pt-C(3)	165.1 (2)
Pt-C(3)	2.086 (6)		P(1)-Pt-C(3)	91.9 (2)
C(2)-C(1)	1.535 (9)		P(2)-Pt-C(1)	97.8 (2)
C(2)-C(3)	1.536 (9)		C(1)-Pt-C(3)	67.3 (3)
C(2)-Me(1)	1.526 (10)		Pt-C(1)-C(2)	95.4 (4)
C(2)-Me(2)	1.518 (10)		Pt-C(3)-C(2)	95.1 (4)
P(1)-C(4)	1.832 (8)	1.827 (8)	C(1)-C(2)-C(3)	97.5 (5)
P(1)-C(6)	1.837 (6)		C(1)-C(2)-Me(1)	110.0 (6)
P(1)-C(8)	1.818 (7)		C(1)-C(2)-Me(2)	114.5 (6)
P(2)-C(10)	1.831 (7)		C(3)-C(2)-Me(1)	111.2 (6)
P(2)-C(12)	1.818 (6)		C(3)-C(2)-Me(2)	113.9 (6)
P(2)-C(14)	1.828 (6)		Me(1)-C(2)-Me(2)	109.3 (6)
C(4)-C(5)	1.512 (10)	1.521 (9)	Pt-P(1)-C(4)	111.7 (3)
C(6)-C(7)	1.523 (10)		Pt-P(1)-C(6)	122.5 (2)
C(8)-C(9)	1.523 (9)		Pt-P(1)-C(8)	111.1 (2)
C(10)-C(11)	1.533 (9)		Pt-P(2)-C(10)	112.8 (3)
C(12)-C(13)	1.509 (10)		Pt-P(2)-C(12)	117.5 (2)
C(14)-C(15)	1.525 (8)		Pt-P(2)-C(14)	116.7 (2)
			P(1)-C(4)-C(5)	114.2 (6)
			P(1)-C(6)-C(7)	118.5 (4)
			P(1)-C(8)-C(9)	113.3 (5)
			P(2)-C(10)-C(11)	117.6 (5)
			P(2)-C(12)-C(13)	113.5 (5)
			P(2)-C(14)-C(15)	112.9 (4)
			C(4)-P(1)-C(6)	103.7 (3)
			C(4)-P(1)-C(8)	102.1 (4)
			C(6)-P(1)-C(8)	103.6 (3)
			C(10)-P(2)-C(12)	102.4 (3)
			C(10)-P(2)-C(14)	102.9 (3)
			C(12)-P(2)-C(14)	102.6 (3)

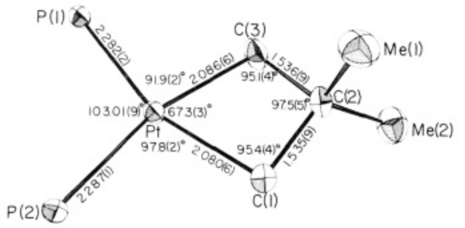

Figure 6. The inner coordination sphere of $\overline{Pt(CH_2C(CH_3)_2CH_2})(P(C_2H_5)_3)_2$.

Table X. Best Weighted Least-Squares Planes in $\overline{Pt(CH_2C(CH_3)_2CH_2})(P(C_2H_5)_3)_2$ (5)

Coefficients $Ax + By + Cz = D$[a]

plane no.	*A*	*B*	*C*	*D*
1	0.075	−2.209	−9.271	0.413
2	−0.078	2.220	9.270	−0.416
3	0.311	1.954	9.294	−0.257
4	−3.432	−2.447	9.022	0.615
5	12.573	−8.720	0.766	5.161

Deviations (Å) from Planes

	1	2	3	4	5
Pt	0.0000 (1)	0	0		0.0000 (1)
P(1)	0.002 (2)	0			
P(2)	0.000 (1)	0			
C(1)	0.034 (7)		0	0	
C(2)	0.384			0	−0.002 (6)
C(3)	−0.036 (7)		0	0	
Me(1)	1.887				0.001 (10)
Me(2)	−0.357				0.001 (9)

Dihedral Angles (Deg) between Planes

1-2	179.96	3-4	22.38
1-3	178.27	3-5	89.26
1-4	157.59	4-5	89.25
1-5	89.01		
2-3	1.77		
2-4	22.44		
2-5	91.03		

[a] The plane is in crystal coordinates as defined by: Hamilton, W. C. *Acta Crystallogr.* **1961**, *14*, 185-189.

1 is a sterically congested molecule and that this congestion is relieved during its transformation to **5**. This information suggests that relief of steric congestion may provide one of the factors contributing to the greater facility of intramolecular cleavage of unactivated C–H bonds relative to analogous intermolecular cleavage reactions. It further suggests, by extension, that intermolecular oxidative addition of C–H bonds to platinum should proceed most readily by using complexes in which the PPtP angle is constrained to a value close to 90° (perhaps by chelation) and the species oxidatively adding is relatively small. The observation by Yoshida et al. that treatment of $PtCl_2[(t\text{-}Bu)_2PCH_2CH_2P(t\text{-}Bu)_2]$ with sodium/mercury alloy in tetrahydrofuran yields $PtH_2[(t\text{-}Bu)_2PCH_2CH_2P(t\text{-}Bu)_2]$ may provide an example of such a reaction.[32]

Although the structures of **1** and **5** qualitatively identify release of nonbonded steric strain as one possible contribution to ΔG for the reaction, they do not establish whether one principal interaction or the sum of many small interactions dominates this contribution: certainly, at first glance, no single interaction seems glaringly more obvious than others. Moreover, as discussed above, the relative importance of enthalpic and entropic terms in determining the free energy of reaction remains to be established. All of these analyses will require additional information, but

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[32] Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063–2073.

all will ultimately rest on the structural data given here.

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Supplementary Material Available: Tables IV and V, listings of $10|F_o|$ vs. $10|F_c|$ for **1** and **5**, respectively, and Tables VI and VII, root-mean-square amplitudes of vibration for **1** and **5**, respectively (37 pages). Ordering information is given on any current masthead page.

Deprotonation of 1,1-Diboronic Esters and Reactions of the Carbanions with Alkyl Halides and Carbonyl Compounds

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The efficient deprotonation of 1,1-diboronic esters has been accomplished with lithium 2,2,6,6-tetramethylpiperidide in the presence of tetramethylethylenediamine in tetrahydrofuran. Bis(1,3,2-dioxaborin-2-yl)methane, $(C_3H_6O_2B)_2CH_2$, is slightly more acidic than triphenylmethane and has been deprotonated to a diborylmethide salt, $(C_3H_6O_2B)_2CH^-Li^+$, which has been alkylated by alkyl halides, RX, to form 1,1-bis(1,3,2-dioxaborin-2-yl)alkanes, $(C_3H_6O_2B)_2CHR$, which in turn have been deprotonated and alkylated with a second alkyl halide to form fully substituted *gem*-diboronic esters, $(C_3H_6O_2B)_2CRR'$. The carbanionic intermediates have also been condensed with carbonyl compounds to form alkeneboronic esters, useful intermediates for synthesizing carbonyl compounds homologous to the original. The carbanions, $(C_3H_6O_2B)_2C^-R$, condense with carboxylic esters, $R'CO_2CH_3$, with elimination of boron to form ketones, RCH_2COR'. The synthesis of 1,1-diboronic esters, $(C_3H_6O_2B)_2CHR$, from methanediboronic ester anion and alkyl halide is possible only if the alkyl group, R, is primary, but an alternative route involving catalytic hydrogenation of alkene-1,1-diboronic esters, $(C_3H_6O_2B)_2C{=}CR_2'$, has been developed, and the deprotonation of these more hindered alkane-1,1-diboronic esters has been demonstrated.

Introduction

Lithium bis(dialkoxyboryl)methides, $Li^{+-}CH[B(OR)_2]_2$, are known to react with alkyl halides to form alkane-1,1-diboronic esters[1-4] and with aldehydes or ketones to form 1-alkene-1-boronic esters.[1,4-6] The latter reaction is the key step in an efficient conversion of carbonyl compounds to the homologous aldehydes.[7]

The synthetic utility of these reactions was formerly limited by the requirement that a boronic ester group be replaced in order to form the carbanion.[4]

$$R'C[B(OR)_2]_3 + R''Li \rightarrow Li^{+-}CR'[B(OR)_2]_2 + R''B(OR)_2$$

The method of synthesis of tris(dialkoxyboryl)methanes, $R'C[B(OR)_2]_3$, was successful where $R' = (RO)_2B$, H, C_6H_5, or CH_3, with decreasing yields in the sequence listed,[4,8] and would be impractical for more complex R′ groups. Attempts to alkylate lithium tris(dimethoxyboryl)methides, $Li^{+-}C[B(OR)_2]_3$, with alkyl halides, R′X, resulted in disproportionation and formation of a mixture of $R'_2C[B(OCH_3)_2]_2$ and $R'C[B(OCH_3)_2]_3$.[2] When the more hindered propanediol boronic ester group was used in the hope of avoiding the disproportionation, methyl iodide with $Li^{+-}C(CO_2C_3H_6)_3$ efficiently yielded $CH_3C(BO_2C_3H_6)_3$ but ethyl iodide was converted to ethylene, confirmed by conversion to ethylene dibromide.[9]

Several synthetic routes to alkane-1,1-diboronic esters [1,1-bis(dialkoxyboryl)alkanes], $R'CH[B(OR)_2]_2$, have been reported,[2-4,8,10-12] and it appeared that these would be useful synthetic intermediates if a base could be found which would attack the α-proton in preference to the boron atoms. The report of the deprotonation of 9-methyl-9-borabicyclo[3.3.1]nonane with lithium 2,2,6,6-tetramethylpiperidide by Rathke and Kow[13] prompted us to

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