denoted for convenience "graphitene", consists of two sheets of seven hexagonal rings, six arranged symmetrically about one, linked by six pairs of carbon atoms connecting pairs of pentagonal rings. The remaining six hexagonal rings are found between the pairs of pentagons. This structure has a marginally lower Hückel stabilization energy of 0.5418 β per carbon atom but is possibly destabilized by the extra strain of connected pentagonal rings. Vibrational analysis of C_{60} molecules will resolve the structure.

Due to the high symmetry of footballene, ab initio molecular orbital calculations can be used to calculate more accurately the properties of the molecule. More importantly, a synthetic route to footballene is eagerly awaited.

Acknowledgment. I thank my colleagues at Berkeley, especially Professor W. Maier, who suggested the "graphitene" C_{60} structure.

Novel Photochemical Alkyl Migrations of Dialkylboryl Acetylacetonate Complexes

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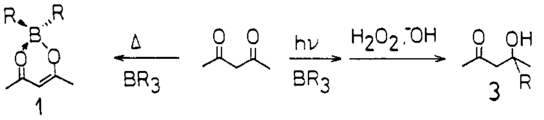
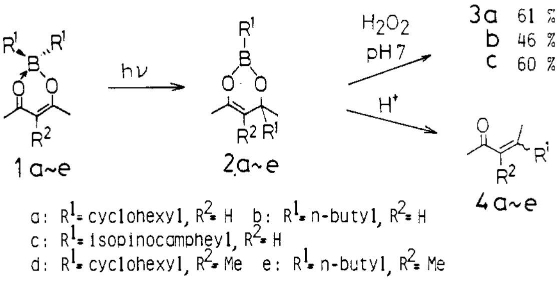
Although much attention has been focused on the ground-state chemistry of organoboranes, relatively little is known about their excited states.[1,2] Hawthorne and Reintjes reported that thermal reactions of trialkylboranes with acetylacetone yield dialkylboryl acetylacetonate complexes **1**.[3,4] Several years later, Nozaki and co-workers reported a sharp contrast between photochemical and thermal reactions of trialkylboranes with acetylacetone (eq 1).[5]



(1)

In their study, photochemically induced conjugate addition[2a] of trialkylboranes to the enolized acetylacetone was speculated to be responsible for the aldol formation. The participation of **1** in the photochemical reactions was not considered. From our interest in the borane complexes **1**, particularly in their unique absorption spectra (**1a**, λ_{max} 348 nm in C_6H_{12}),[6] we have been led to study the photochemical reactions of **1**. We now report a new photoalkylation reaction where an alkyl group migrates from boron to the acetylacetone carbonyl carbon of **1** (eq 2).



(2)

The borane complexes **1** are thermally stable and in fact heating a toluene solution of **1a** at 150 °C for 10 h in a sealed tube results in complete recovery of **1a**. However, when a benzene solution of **1a** was irradiated with a 500-W xenon lamp through a UV filter (>330 nm), the yellow color due to **1a** rapidly disappeared. Evaporation of the solvent and measurement of the ^1H NMR spectrum ($CDCl_3$) of the residual transparent oil showed a narrow quartet (1 H) at 4.48, a narrow doublet (3 H) at 1.76, a singlet (3 H) at 1.20 ppm, and a multiplet due to cyclohexyl protons, suggesting the existence of an olefinic enol proton, a vinyl methyl group, and a methyl group on a saturated tertiary carbon, respectively. An IR spectrum of the oil showed an enol borate absorption (C=C stretching) at 1695 cm^{-1}.[7] These data and the following chemical reactions establish the structure of this oil as **2**. Oxidative hydrolysis with a solution of pH 7 phosphate buffer, MeOH, THF, and aqueous 30% H_2O_2 (5:8:10:1 v/v) gave an aldol **3a** in 61% yield. Acidic hydrolysis gave the corresponding α,β-unsaturated carbonyl compound **4a** in 60% yield.[8]

The reaction proceeded in moderate quantum yield ($\Phi = 0.08$) and was not quenched by oxygen (2×10^{-3} M) or piperylene (2.0 M), suggesting that the singlet is the reactive excited state. Product analysis of the volatile components obtained after distillation from the reaction mixtures of benzene-d_6 or decalin solutions revealed the formation of cyclohexane and cyclohexene[9] in a 6:1 ratio amounting to ca. 10% of the total yield. Bicyclohexyl and phenylcyclohexane, which are typical products from cyclohexyl radicals, were also detected by GC analysis as minor products (<1%).[10]

In order to clarify whether the reaction proceeds intramolecularly or intermolecularly, crossover experiments were performed using **1a** and **1e** (or **1b** and **1d**). Photolysis of an equimolar mixture of **1a** and **1e** in benzene followed by GC analysis of the hydrolyzed mixture of α,β-unsaturated carbonyl compounds showed that the alkyl migration is essentially intramolecular (95%) with 5% of the crossed products **4b,d**: similar results were obtained for **1b,d**. The participation of radical species, indicated by the formation of the hydrocarbons and the production of small amounts of crossed products, suggests a radical pair mechanism (eq 3).

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(1) Notable examples of photoreactions of organoboranes: (a) Glogowsky, M. E.; Zumbulyadis, N.; Williams, J. L. R. *J. Organomet. Chem.* **1982**, *231*, 97; and a series of their papers. (b) Hancock, K. G.; Uriarte, A. K. *J. Am. Chem. Soc.* **1970**, *92*, 6374. (c) Hancock, K. G.; Dickinson, D. A. *J. Chem. Soc., Chem. Commun.* **1972**, 962. (d) Hancock, K. G.; Dickinson, D. A. *J. Am. Chem. Soc.* **1972**, *94*, 4396. (e) Hancock, K. G.; Dickinson, D. A. *Ibid.* **1973**, *95*, 280. (f) Hancock, K. G.; Kramer, J. D. *Ibid.* **1973**, *95*, 3425. (g) Hancock, K. G.; Uriarte, A. K.; Dickinson, D. A. *Ibid.* **1973**, *95*, 6980. (h) Trubini, L. J.; Poter, R. F. *Inorg. Chem.* **1975**, *14*, 1252. (i) Calhoun, G. C.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 1925 and references cited therein. (j) Pachaly, B.; West, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 454. (k) Pachaly, B.; West, R. *J. Am. Chem. Soc.* **1985**, *107*, 2987.

(2) Reactions of organoboranes with excited states of organic molecules: (a) Brown, H. C.; Kabalka, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 714. (b) Miyamoto, N.; Isiyama, S.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1971**, 4597. (c) Davies, A. G.; Griller, D.; Roberts, B. P.; Scaiano, J. C. *J. Chem. Soc., Chem. Commun.* **1971**, 196. (d) Scaiano, J. C.; Ingold, K. U. *Ibid.* **1975**, 878. (e) Lane, C. F.; Brown, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 1025. (f) Yamamoto, Y.; Brown, H. C. *J. Chem. Soc., Chem. Commun.* **1973**, 801. (g) Brown, H. C.; De Lue, N. R. *Tetrahedron Lett.* **1977**, 3007.

(3) (a) Hawthorne, M. F.; Reintjes, M. *J. Am. Chem. Soc.* **1964**, *86*, 5016. (b) Hawthorne, M. F.; Reintjes, M. *J. Org. Chem.* **1965**, *30*, 3851.

(4) Other derivatives of this type of compound: (a) Roth, H. J.; Miller, B. *Arch. Pharm. (Weinheim, Ger.)* **1964**, *297*, 617. (b) Umland, F.; Schleyerbach, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 432. (c) Balaban, A. T.; Rentea, C. N.; Mocanu-Paraschiv, M.; Romas, E. *Rev. Roum. Chim.* **1965**, *10*, 849. (d) Balaban, A. T.; Rentea, C. N.; Bacescu-Roman, M. *Ibid.* **1965**, *10*, 865. (e) Toporcer, L. H.; Dessy, R. E.; Green, S. I. E. *Inorg. Chem.* **1965**, *4*, 1649. (f) Köster, R.; Rotermund, G. W. *Liebigs Ann. Chem.* **1965**, *689*, 40. (g) Umland, F.; Hohaus, E.; Brodte, K. *Chem. Ber.* **1973**, *106*, 2427.

(5) Utimoto, K.; Tanaka, T.; Nozaki, H. *Tetrahedron Lett.* **1972**, 1167. The absence of alkane in the reaction mixture in Nozaki's study might suggest the occurrence of conjugate additions of trialkylboranes for the aldol formation. However, since the complex formation of acetylacetone with trialkylboranes proceeds even at room temperature in a suitable concentration region and can be easily recognized by yellow color development, the borane complex **1** is at least one of the key intermediates of the photochemical reactions of acetylacetone with trialkylboranes.

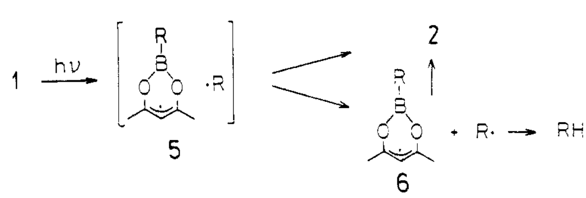
(6) The unusual spectrum is probably to be attributed to the red-shifted π–π* absorption by the intramolecular coordination of the borane group to the carbonyl group. The fact that the absorption maximum is slightly red-shifted in nonpolar solvents (**1a**, λ_{max} 348 nm in C_6H_{12}, 345 nm in CH_2Cl_2, 344 nm in CH_3CN) may suggest that the excited state has a smaller CT contribution than the ground state. Experiments on this unusual absorption including the substituent effect are in progress.

(7) For C=C stretching vibrations of enol borates, see, for instance: (a) Fenzl, W.; Kosfeld, H.; Koster, R. *Liebigs Ann. Chem.* **1976**, 1370. (b) Koster, R.; Zimmermann, H.-J.; Fenzl, W. *Ibid.* **1976**, 1116.

(8) α,β-Unsaturated carbonyl compounds were obtained as a mixture of cis and trans isomers (1:8 for **4a**, 1:1.1 for **4b**).

(9) (a) Gordon, A. S.; Smith, S. R. *J. Chem. Phys.* **1961**, *34*, 331. (b) Livant, P.; Lawer, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 6044. (c) Bennett, J. E.; Gale, L. H.; Hayward, E. J.; Mile, B. *J. Chem. Soc., Farady Trans. 1* **1973**, *69*, 1655.

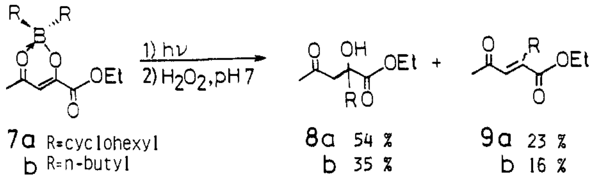
(10) (a) Hermans, P.; Van Eyk, J. *J. Polym. Sci.* **1946**, *1*, 407. (b) Walling, C.; Gibian, M. *J. Am. Chem. Soc.* **1965**, *87*, 3361. (c) Shelton, J. R.; Uzelmeier, C. W. *Ibid.* **1966**, *88*, 5222.



(3)

The singlet excited state of **1** gives the radical pair **5** in the solvent cage, which mainly rearranges intramolecularly to the noncrossed borane complex **2** and partly dissociates into free radicals. The free radicals, **6** and cyclohexyl, may recombine to yield crossed **2** or give typical free radical products, such as cyclohexane and cyclohexene.[11]

The reaction was successfully extended to ethyl acetopyruvate borane complexes **7a,b**. The alkyl group migrates regiospecifically on the α-carbon to the ester yielding **8** and **9** (eq 4). This result



(4)

may reflect a larger spin density on the α-carbon of the ester group in the radical pair **5**. The hypothesis is supported by an analogy with allyl radicals, which have a larger ESR coupling constant to the proton α to electron-withdrawing groups (carbomethoxy and cyano).[12]

Application of this reaction to the borane complex **1c** which has optically active isopinocampheyl as the migrating alkyl group is interesting. Photolysis and successive neutral hydrolysis of **1c**, however, resulted in an equimolar diastereomeric mixture of the aldols and no diastereoselectivity was observed.

Further study is currently in progress in our laboratory.

Acknowledgment. We thank Prof. P. de Mayo (University of Western Ontario, Canada) for useful discussions.

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(11) The CIDNP experiment is interesting in this context, though we have not yet succeeded in it. We thank Dr. S. K. Wong (the University of Western Ontario, Canada) for the CIDNP experiment.

(12) (a) Sustmann, R.; Trill, H.; Brandes, D. *Chem. Ber.* **1977**, *110*, 245. (b) Sustmann, R.; Trill, H.; Vahrenholt, F.; Brandes, D. *Ibid.* **1977**, *110*, 255.

Reversible Transformation of 10-P-3 ADPO[1] to an 8-P-3 ADPO·PtI$_2$ Adduct

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We have synthesized a phosphorus–platinum complex containing an 8-P-4 center which is formally derived from the 8-P-3 ADPO electromorph.[2] This provides the first evidence that the ADPnO (Pn = pnictogen: P, As, Sb) systems may exhibit electromorphism between 8-Pn-3 and 10-Pn-3[2-4] structures. Multinuclear NMR spectra (^{1}H, ^{13}C, and ^{15}N) indicate a dramatic electronic and geometric reorganization of the ring system between free and complexed ADPO. Ligand substitution affords the first reversible reorganization between normal and hypervalent bonding arrangements (vide infra).[5]

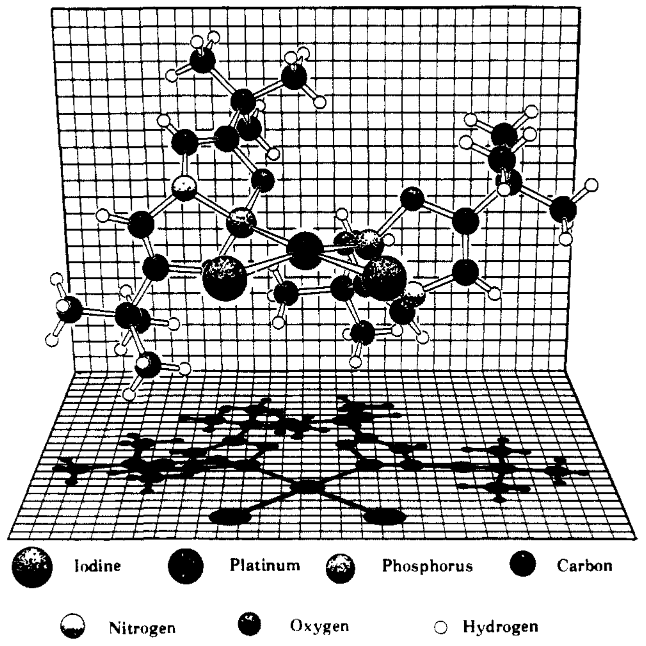
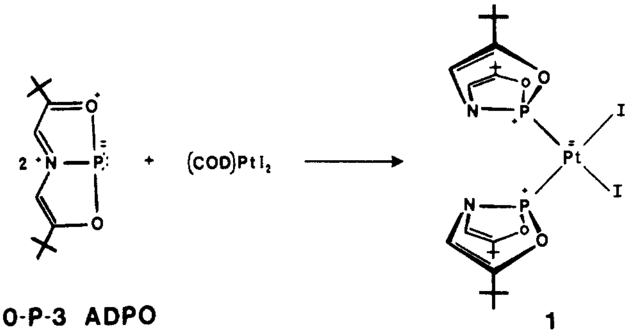


Figure 1. KANVAS[9] drawing of **1**.

The reaction of 2 equiv of ADPO with (1,5-cyclooctadiene)platinum(II) diiodide in toluene provides **1** in good yield (>85%).



10-P-3 ADPO

1

Complex **1** is a yellow crystalline solid melting at 245 °C with decomposition. The 2:1 nature of the complex is consistent with elemental analysis (CHN) and NMR spectra.[6]

The ^{195}Pt NMR (CD$_2$Cl$_2$) exhibits a triplet at -3487 ppm (J_{PtP} = 5622 Hz) upfield from K$_2$PtCl$_4$ (D$_2$O). The ^{31}P NMR of **1** shows a single resonance at 126.5 ppm with ^{195}Pt satellites. This ^{31}P resonances is upfield of the 10-P-3 ADPO resonance (189 ppm) and is suggestive of the 8-P-4 nature of the phosphorus environment. In addition the ^{13}C resonance for the carbons attached to oxygen are substantially upfield relative to 10-P-3 ADPO ($\Delta\delta$ = 13.9). The ring proton on the ADPO moiety also shows a significant upfield shift ($\Delta\delta$ = 1.5) relative to the free ligand. Finally the ^{15}N NMR shows a doublet at -276 ppm with platinum satellites ($^1J_{PN}$ = 44.8, $^2J_{PtN}$ = 108 Hz) clearly indicative of the pyramidal (8-N-3) nature of the nitrogen environment.[7] These NMR data indicate the ADPO ring system has a bent structure

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(1) The *N*-X-*L* system has previously been described (Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753). *N* valence electrons about a central atom X, with *L* ligands.

(2) Culley, S. A.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1984**, *106*, 1164.

(3) Culley, S. A.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1985**, *107*, 1089.

(4) Stewart, C. A.; Harlow, R. L.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1985**, *107*, 5543.

(5) A referee indicated another type of ligand reorganization process different from that reported here; see: Vierling, P.; Riess, J. G. *J. Am. Chem. Soc.* **1981**, *103*, 2466.

(6) We have obtained the following NMR data on **1** in CD$_2$Cl$_2$. ^{1}H NMR δ 1.20 (s, 18 H), 5.95 (d and dd, J_{PH} = 29.0, J_{PtH} = 16.7 Hz, 2 H); ^{13}C{^{1}H} NMR δ 26.7 (CH$_3$), 32.1 (*C*(CH$_3$)), 113.9 (CH), 156.0 (CO); ^{31}P{^{1}H} NMR δ 126.5 (d and dd, J_{PtP} = 5622 Hz); ^{15}N NMR δ -276 (d and dd, $J_{P^{15}N}$ = 44.8, $J_{Pt^{15}N}$ = 108 Hz); ^{195}Pt{^{1}H} NMR δ -3487 (t, J_{PPt} = 5622 Hz). ^{15}N resonance relative to NH$_4{}^{15}$NO$_3$ in D$_2$O and ^{195}Pt resonance relative to K$_2$PtCl$_4$ in D$_2$O. Satisfactory elemental analysis were obtained (CHN).

(7) "Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy", Levy, G. C.; Lichter, R. L., Eds.; Wiley: New York, 1979; pp 84, 100.

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