pylene (3 atm) gave mainly hexanal in 70% yield and only a low yield (10-15%) of 4-nonanone. The same alkylation in the presence of excess 1-hexene gave only hexanal in 94% yield. The high yields of aldehyde reflect the presence of complex **2** and suggest that while higher alkenes may serve as ligands for the carbonyl insertion process subsequent acyl transfer is inhibited. We have found, however, that a number of olefins which are Michael acceptors readily participate in this process forming the basis of a versatile method for the conjugate addition of acyl anion equivalents. These results will be reported shortly.

Acknowledgments. We thank the Research Corporation and the Washington State University Research Committee for support of this research.

References and Notes

(1) M. P. Cooke, Jr., *J. Am. Chem. Soc.*, **92**, 6080 (1970).

(2) (a) J. P. Collman, S. R. Winter, and D. R. Clark, *J. Am. Chem. Soc.*, **94**, 1788 (1972); (b) J. P. Collman and N. W. Hoffman, *ibid.*, **95**, 2689 (1973).

(3) J. P. Collman, S. R. Winter, and R. G. Komoto, *J. Am. Chem. Soc.*, **95**, 249 (1973).

(4) Similar results were obtained with commercial $Na_2Fe(CO)_4$ (Ventron Corporation).

(5) Such complexes have been isolated and characterized: W. O. Siegl and J. P. Collman, *J. Am. Chem. Soc.*, **94**, 2516 (1972).

(6) J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **94**, 5905 (1972).

(7) Related insertions involving acyl migrations have been observed in organonickel[8] and organocobalt[9] reactions. These cases invariably involve intramolecular acyl transfer to substituted olefins resulting mainly in the formation of cyclic ketones. An analogous cyclization of certain olefinic halides with $Na_2Fe(CO)_4$ has recently been reported.[10] Insertion was found to occur only in cases allowing six-membered ring formation thereby giving cyclohexanones in poor to moderate yields.

(8) G. P. Chiusoli, *Acc. Chem. Res.*, **6**, 422 (1973).

(9) R. F. Heck, *Adv. Organomet. Chem.*, **4**, 243 (1967).

(10) J. Y. Mekour, J. L. Roustan, C. Charrier, and J. Collin, *J. Organomet. Chem.*, **51**, C24 (1973).

(11) M. McPartlin and R. Mason, *J. Chem. Soc. A*, 2206 (1970).

(12) Deuterium content at C_1 was analyzed by mass spectroscopy after aqueous base catalyzed removal of any deuterium at C_2 or C_4 resulting from either exchange under the reaction conditions or from the use of labeled components.

(13) K. Maruya, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **46**, 993 (1973).

(14) This expectation assumes the absence of a large isotope effect for any process involving removal of a hydrogen atom from ethylene-d_2. In the absence of a large secondary isotope effect in the production of **3a** and **3b**, the data require that k_H/k_D exceed 20-25 in order to invalidate this assumption.

(15) The presence of a small amount of undeuterated ketone may be a result of incomplete α-methylene exchange,[12] unequal formation of **3a** and **3b** through a small secondary isotope effect or an isotope effect in the suggested $\beta \rightarrow \alpha$ rearrangement operating on the small amount (4%) of ethylene-d_1 contaminating our sample of ethylene-d_2, or a combination of any of these factors.

(16) A $\beta \rightarrow \alpha$ metallocarbonyl rearrangement has been implicated in reactions of $KHFe(CO)_4$ with unsaturated esters: H. Masada, M. Mizuno, Y. Watanabe, and Y. Takegami, *Bull. Chem. Soc. Jpn.*, **43**, 3824 (1970).

(17) Structures of this type have been proposed as intermediates in base promoted reductions of unsaturated carbonyl compounds with $Fe(CO)_5$ (R. Noyori, I Umeda, and T. Ishigami, *J. Org. Chem.*, **37**, 1547 (1972)) and as intermediates in the reduction of dienes by $HCo(CO)_4$ (R. W. Goetz and M. Orchin, *J. Am. Chem. Soc.*, **85**, 2782 (1963)). A related π-oxapentadienyltricarbonylmanganese complex has been isolated: W. D. Bannister, M. Green, and R. N. Haszeldine, *J. Chem. Soc. A*, 194 (1966).

Manning P. Cooke, Jr.,* Robert M. Parlman
Department of Chemistry, Washington State University
Pullman, Washington 99163

Received May 13, 1975

Bis(1-substituted-borabenzene)iron Complexes

Sir:

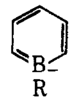
The borabenzene anion **2** like the long known cyclopentadienide **1** is an anionic 6π-electron aromatic ring. Herberich et al. found that **3** could be produced via ring expansion of cobaltocene with boron halides.[1] Recently **3** has been elegantly converted to other transition metal complexes.[2,3]

Following our synthesis of the free 1-phenylborabenzene anion **2a**,[4] we undertook to prepare transition metal complexes directly from the ligand. Specifically we now wish to report on the general synthesis of bis(1-substituted-borabenzene)iron complexes **4**.[5,6] These materials exhibit properties and show reactions which find a close parallel in the well-known chemistry of ferrocene.

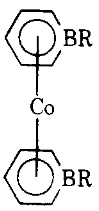
Diene **6a** is readily available from the exchange reaction of 1,1-dibutyl-1,4-dihydrostannabenzene (**5**) with phenylboron dibromide.[4] Treatment with *tert*-butyllithium produces **2a**[4] which yields air-stable red-orange crystals of bis(1-phenylborabenzene)iron (**4a**) on treatment with ferrous chloride in an overall yield of 31%: mp 156-157.5°; mass spectral *m/e*, 362 (M^+, $C_{22}H_{20}{}^{11}B_2{}^{56}Fe$); ^{1}H NMR ($CDCl_3$) τ 5.21 (d, J = 9.5 Hz, 4 H), 4.41-4.66 (m, 6 H), 2.61 (m, 6 H), 2.18 (m, 4 H); ^{11}B NMR ($CDCl_3$) δ −14.4; uv (C_2H_5OH) $\lambda_{max}{}^{nm}$ 234 (28000), 270 (15400), 362 (1500). Since the ^{1}H NMR spectrum of bis(1-phenyl-d_5-borabenzene)iron, available ultimately from the reaction of **5** with phenyl-d_5-boron dibromide, showed signals only at τ 5.21 and 4.41-4.66, the low field signals of **4a** were due to the uncomplexed phenyl protons. The borabenzene ring protons of **4a** are shifted upfield approximately 1.5 ppm relative to **2a**. This upfield shift on complexation is similar to that between ferrocene (τ 6.0) and sodium cyclopentadienide (τ 4.7). Similarly the reaction of methylboron dibromide with **5** gave **6b**: ^{1}H NMR ($CDCl_3$), τ 9.2 (s, 3 H) 6.9 (m, 2 H); 3.3 (dt, J = 13, 2 Hz, 2 H); 2.8 (brd, J = 13 Hz, 2 H); ^{11}B NMR ($CDCl_3$) δ −52.8. On deprotonation by *tert*-butyllithium in tetrahydrofuran-pentane, followed by reaction with ferrous chloride, **6b** afforded bis(1-methylborabenzene)iron **4b**. The yield from **5** is 34%: mp 44-45°; ^{1}H NMR ($CDCl_3$) τ 9.31 (s, 6 H), 5.70 (brd, J = 10 Hz, 4 H), 4.7 (m, 6 H); mass spectral *m/e*, 238 (M^+, $C_{12}H_{16}{}^{11}B_2{}^{56}Fe$); ^{11}B NMR ($CDCL_3$), δ −20.5, uv (C_2H_5OH) $\lambda_{max}{}^{nm}$ 214 (35000), 274 (2170), 312 (1320), 362 (660).

In a variation of this procedure, **5** is treated directly with boron tribromide at −78°, giving dibutyltin dibromide and 1-bromo-1,4-dihydroborabenzene (**6d**), which is easily separated by distillation: ^{1}H NMR ($CHCl_3$), τ 7.15 (m, 2 H),

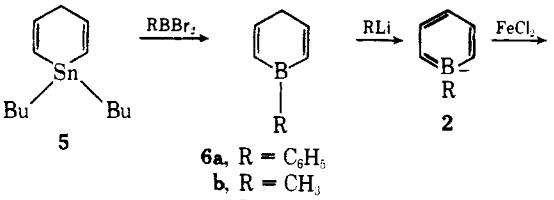
1



2



3



6a, R = C_6H_5
b, R = CH_3
c, R = $C(CH_3)_3$
d, R = Br

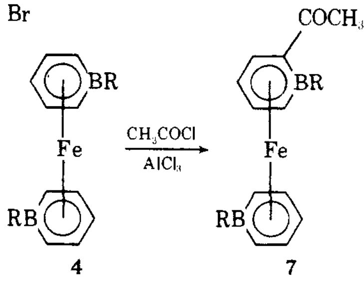


Table I. Ionization Potentials of Ferrocenes and Bis(1-substituted-borabenzenes)iron[a]

Compound	Ia	Iv
Ferrocene		6.88[11]
1,1′-Diacetylferrocene	7.05	7.41
4a	7.04	7.67
4b	7.22	7.73
4c	7.16	7.67

[a] Ia and Iv are ±0.05 eV. Calibration relative to HXe/ϕ.

3.5 (dt, J = 13, 2 Hz, 2 H); 2.9 (brd, J = 13 Hz, 2 H). Interesting, although the mass spectrum of **6d** has a strong peak for the molecular ion (m/e, 156 for $C_5H_6{}^{11}B^{79}Br$), the base peak occurs at m/e 76, which corresponds to a loss of HBr to the parent borabenzene ($C_5H_5B^+$).[7] Treating **6d** with excess *tert*-butyllithium followed by ferrous chloride produces bis(1-*tert*-butylborabenzene)iron (**4c**) in an overall yield of 28%: Mp, 144–145°; ^1H NMR ($CDCl_3$), τ 8.85 (s, 18 H), 5.65 (d, J = 9 Hz, 4 H), 4.60 (m, 4 H), 4.40 (t, J = 5.5 Hz, 2 H); ^{11}B NMR ($CDCl_3$) δ −24.6; mass spectral m/e, 322 (M^+, $C_{18}H_{28}{}^{11}B_2{}^{56}Fe$); uv ($C_2H_5OH$) $\lambda_{max}{}^{nm}$ 214 (35000), 274 (2170), 312 (1320), 362 (660). **4b** has also been produced analogously from **2d** with methyllithium and presumably the synthesis could be extended to other 1-substituted analogs by varying the alkyllithium. Compounds **4a** and **4b** have recently been reported by Herberich.[3] Thus this synthesis provides a point of convergence for the two methods for producing borabenzenes.

Like the previously reported complexes, data indicate that the 1-substituted-borabenzene is a η^6-ligand.[1-3] π-Boron coordination to iron is suggested by the air-stability of **4** in contrast to their pyrophoric conjugate acids **6** and by the large upfield shift of **4** relative to **6** in the ^{11}B NMR spectra. Similarly the ^1H NMR chemical shift values show a considerably smaller range than those of η^5-cyclohexadienyl iron complexes.[7]

The ^{57}Fe Mössbauer spectrum of **4a** has been measured. The isomeric shift relative to $Na_2Fe(CN)5NO{\cdot}2H_2O$ is identical with that of ferrocene, 0.72 mm/sec, while the quadrupole splitting is 1.97 mm/sec, somewhat smaller than that of ferrocene (2.40 mm/sec). A similar reduction in the magnitude of the quadrupole splitting has been observed for ferrocenes with strongly electron withdrawing substituents.[9] This suggests 1-phenylborabenzene withdraws somewhat more electron density from the iron than do the cyclopentadienyl rings of ferrocene, although the equality of the isomeric shift makes it improbable that there is any large electronic difference at iron.

The ionization potentials of **4** have been measured by He(I) ionization. See Table I. The vertical ionization potentials are approximately 0.8 eV greater than ferrocene[10] and indeed are similar to those of the electron withdrawing ferrocene 1,1′-diacetylferrocene.

Friedel-Crafts acetylation of **4b** with acetylchloride, aluminum chloride in methylene chloride at 0° gave a 20% yield of a monoacetyl product, **7b**: mass spectral m/e, 280 (M^+, $C_{14}H_{18}{}^{11}B_2{}^{56}FeO$); ir ($CDCl_3$) 1662 cm^{-1}; H NMR, τ 9.35 (s, 3 H), 9.13 (s, 3 H), 7.63 (s, 3 H), 5.90 (d, J = 8 Hz, 1 H), 5.50 (d, J = 9 Hz, 1 H), 5.34 (d, J = 9 Hz, 1 H), 4.8–4.3 (m, 5 H), 4.08 (d, J = 6 Hz, 1 H). Since only three α-protons are observed as higher field doublets, the acetyl group must occupy the 2-position. Bis(1-*tert*-butylborabenzene)iron was recovered unchanged upon attempted acetylation even at higher temperatures.

The four α-protons of **4b** exchange when treated with trifluoroacetic acid-d_1 at 25°. No further exchange was found even after 24 hr at reflux. Exchange is slower in CF_3CO_2D–benzene mixtures. In competition experiments ferrocene reacts more rapidly than **4b**, which exchanges at approximately the same rate as mesitylene. Thus on an approximate reactivity scale, ferrocene is three orders of magnitude more reactive than **4b.**[12]

The lower reactivity of the **4b** relative to ferrocene is consistent with its higher ionization potential. On the other hand the low reactivity of the β and γ positions relative to the α position may reflect a lower stability of the corresponding intermediates for substitution. Perhaps boron-cross-conjugated diene–iron complexes, which must be intermediates for substitution at the β and γ positions, are of higher energy than the terminal boron-conjugated diene–iron complex which would be the intermediate for α-substitution.[13]

Acknowledgments. This work was partially supported by grants from the National Science Foundation. We would also like to thank Professor Herberich for discussing his work with us prior to publication.

References and Notes

(1) G. E. Herberich, G. Greiss, and H. F. Heil, *Angew. Chem., Int. Ed. Engl.*, **9**, 805 (1970); G. E. Herberich and G. Greiss, *Chem. Ber.*, **105**, 3413 (1972).

(2) G. E. Herberich and H. J. Becker, *Angew. Chem., Int. Ed. Engl.*, **12**, 764 (1973); **14**, 184 (1975).

(3) G. E. Herberich, *Chimia*, **26**, 475 (1972); G. E. Herberich, H. J. Becker, and G. Greiss, *Chem. Ber.*, **107**, 3780 (1974).

(4) A. J. Ashe, III, and P. Shu, *J. Am. Chem. Soc.*, **93**, 1804 (1971).

(5) A. J. Ashe, III, and P. Shu, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, No. ORGN 53.

(6) Satisfactory combustion analyses have been obtained on all new compounds.

(7) However, see R. Van Veen and F. Bickelhaupt, *J. Organomet. Chem.*, **43**, 241 (1972).

(8) D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4458 (1962).

(9) A. V. Lesikan, *J. Chem. Phys.*, **40**, 2746 (1964); R. A. Stukan, S. P. Gubin, A. N. Nesmeyanov, V. I. Gol'danskii, and E. F. Makarov, *Theor. Exp. Chem.* (*USSR*), **2**, 581 (1966).

(10) In parallel to these observations, it has been reported that the ionization potential of 3 is 1 eV greater than that of cobaltocene. G. E. Herberich, G. Greiss, H. F. Heil, and J. Muller, *Chem. Commun.*, 1328 (1971).

(11) S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard, and C. F. Pygall, *J. Chem. Soc., Faraday Trans. 2*, 1847 (1972).

(12) See A. N. Nesmeyanov, D. N. Krysanov, V. N. Śetkina, N. V. Kislyakova, and N. S. Kochetkova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1932 (1962). Apparently the relative rates of acetylation parallel those of deuterium exchange; see H. C. Brown and G. Marino, *J. Am. Chem. Soc.*, **81**, 5611 (1959); M. Rosenblum, J. O. Santer, and W. G. Howells, *ibid.*, **85**, 1450 (1963).

(13) A similar effect is observed with tricarbonyl(diene)iron complexes: R. E. Graf and C. P. Lillya, *J. Am. Chem. Soc.*, **94**, 8282 (1972).

(14) A. P. Sloan Fellow, 1973–1976.

Arthur J. Ashe, III,*[14] Elizabeth Meyers
Paul Shu, Thomas Von Lehmann
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104

J. Bastide
Physikalisch-Chemisches Institut der Universität Basel
4056 Basel, Switzerland

Received June 23, 1975

Zeugmatographic High Resolution Nuclear Magnetic Resonance Spectroscopy. Images of Chemical Inhomogeneity within Macroscopic Objects[1]

Sir:

Two- and three-dimensional images of objects, including living organisms, may be generated from their NMR signals in magnetic field gradients.[2,3] These "zeugmatographic" techniques may be combined with high resolution pulsed Fourier transform NMR spectroscopy to make possible noninvasive nondestructive spatially resolved chemical analyses of the interiors of objects.

We describe here one simple illustrative example of such