Table I. Infrared and ^{1}H NMR Spectra

Compd	ν(CO),[a] cm^{-1}	τ(PCH$_3$),[b] ppm	J(P-CH),[d] Hz	τ(SCH$_3$),[d] ppm	J(P-SCH$_3$), Hz	J(H-SCH$_3$), Hz	τ(H), ppm	J(P-H), Hz
[[μ-SCH$_3$Fe(CO)$_2$P(CH$_3$)$_3$]$_2$H]$^+$PF$_6^-$	2049 s 2029 m 1994 s	8.19	10 d	8.20 dt	1.3	0.6	25.6	4
[[μ-SCH$_3$Fe(CO)$_2$P(CH$_3$)$_2$C$_6$H$_5$]$_2$H]$^+$PF$_6^-$	2049 s 2029 m 1996 s	7.89	10 d	8.58 dt	1.5	0.7	26.3	4
[[μ-SCH$_3$Fe(CO)$_2$PCH$_3$(C$_6$H$_5$)$_2$]$_2$H]$^+$CF$_3$COO$^-$	2047 s 2028 m 1996 s	7.34	9.5 d	8.74 dt	1.3	0.7	26.6	4.4
[[μ-SCH$_3$Fe(CO)$_2$P(C$_6$H$_5$)$_3$]$_2$H]$^+$CF$_3$COO$^-$	2046 s^c 2026 m 1997 s			8.89	e	e	27.3	e
	2051 m^c 2035 s 1996 s			8.89 8.72	e			

^{a} Measured in CH$_2$Cl$_2$ solutions. ^{b} Measured in CH$_2$Cl$_2$ solutions with TMS internal reference. ^{c} See text. ^{d} Key: d, doublet; dt, doublet triplet. ^{e} Unresolved.
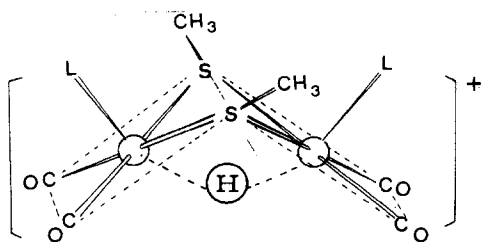

Figure 2. Proposed structure for [[μ-SCH$_3$Fe(CO)$_2$L]$_2$H]$^+$ complexes.

toward the metal–metal bond and this is a consequence of the steric strains due to the sharp Fe–S–Fe angle.[15] However, the introduction of the proton probably induces an opening of this angle and some steric crowding in the metal–metal bond area. Moreover, the behavior of the protonated complex with L = P(C$_6$H$_5$)$_3$ could provide some arguments in favor of the syn-exo hypothesis. Indeed, with this ligand, we have observed the only case of syn → anti isomerization; this ligand is the most overcrowded of the series and it is only when the bridges are syn-exo that this overcrowding can interfere with the bridge positions. So we suggest that the molecule has the structure syn-exo (Figure 2). However this isomerization could be the result of a more subtle electronic or steric effect and the structure with the SCH$_3$ groups in the syn-endo position cannot be definitively excluded.

Nucleophilicity of the Metal–Metal Bond and Donor Properties of the Phosphorus Ligands. From the Experimental Section, we have seen that the behaviors of complexes are quite different when $x = 0$, 1 or when $x = 2$, 3. In the first case, protonation gives stable and isolable materials. In the latter case, protonated species cannot be isolated. Moreover, when the trifluoroacetic acid is eliminated, only the starting material is recovered. These results are consistent with the observations concerning the protonation of mononuclear carbonyls; i.e., replacement of carbonyl group by phosphines increases the metal basicity.[16] However in our case the effect of a variation of basicity of ligand seems more pronounced because only a slight modification as the replacement of P(CH$_3$)$_2$C$_6$H$_5$ by PCH$_3$(C$_6$H$_5$)$_2$ induces a great change in the behavior of complexes toward the proton. This is certainly the result of the position of the ligands L trans to the metal–metal bond.

Registry No. I, 58150-42-8; II, 34215-24-2; III, 58150-43-9; IV, 31340-71-3; [[μ-(SCH$_3$)Fe(CO)$_2$P(CH$_3$)$_3$]$_2$H]$^+$PF$_6^-$, 58150-45-1; [[μ-(SCH$_3$)Fe(CO)$_2$P(CH$_3$)$_2$C$_6$H$_5$]$_2$H]$^+$PF$_6^-$, 58150-47-3; [[μ-(SCH$_3$)Fe(CO)$_2$PCH$_3$(C$_6$H$_5$)$_2$]$_2$H]$^+$CF$_3$COO$^-$, 58150-49-5; [[μ-(SCH$_3$)Fe(CO)$_2$P(C$_6$H$_5$)$_3$]$_2$H]$^+$CF$_3$COO$^-$, 58150-51-9.

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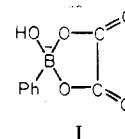of New York, Brooklyn, New York 11210

Effect of Chelate Ring Size on Boron Substitution Reactions. Complexation of Phenylboronic Acid with Malonic Acid

George Lorber and Richard Pizer*

We reported recently[1] on the reaction of phenylboronic acid, PhB(OH)$_2$, with oxalic acid to form the tetrahedral anionic complex I. The kinetic results are unusual from the point

I

of view of normal substitution processes in that ligand donor atom protonation is required for successful reaction, the more protonated ligands reacting more rapidly. On reaction, boron undergoes a change in coordination number from 3 (sp^2) to 4 (sp^3). One ligand donor atom occupies the fourth coor-

dination site and a hydroxide on boron is replaced by a second ligand donor atom to form the chelate ring. Hydrogen bound to ligand donor atoms is displaced even in very acidic media. The present study concerns the reactions of dicarboxylic acids of greater length in order to determine both the generality of the overall pattern of reactivity and the effect of chelate ring size on the kinetics of substitution.

Experimental Section

Malonic acid, succinic acid, phthalic anhydride (all Fisher reagent), and phenylboronic acid (Alfa) were used without further purification. pH studies were carried out on a Corning Model 12 research pH meter (±0.01 pH unit) in a nitrogen atmosphere. Temperature was maintained at 25° by a circulating water bath. Activity coefficients were calculated from the Davies equation.[2] The temperature jump has been described previously.[3] Depending on the pH, chlorophenol red (Fisher), bromophenol blue (Fisher), or orange IV (Allied Chemical) was used to monitor the reaction. The error in measured relaxation time (average of at least three photographed reaction traces) is at most ±10%. Further experimental details are given in ref 3.

Results

The stability constant and kinetic results are reported for the reaction of malonic acid at $\mu = 0.1$ M (KNO₃) and at 25°. The kinetics measurements were done by temperature jump and the stability constant was determined by two pH titration methods. For malonic acid $pK_{a1} = 2.58$ and $pK_{a2} = 5.25$ in excellent agreement with the literature values[4] ($pK_{a1} = 2.62$; $pK_{a2} = 5.25$; $\mu = 0.1$ M (NaClO₄)). The stability constant for the reaction PhB(OH)₂ + H₂Mal ⇌ PhB(OH)Mal⁻ + H₃O⁺ is 0.026. Complete equations describing the titration methods are described in the previous paper.[1] The fact that the six-membered chelate ring forms with malonic acid is in direct contrast to a previous report[5] which suggested that this and dicarboxylate complexes of longer chain length do not form. In pursuing this point we also investigated phthalic acid and succinic acid. In each case pH titration methods indicated complex formation but the stability constant was much less. No successful kinetic studies were carried out using these ligands.

The relaxation time for the reaction of malonic acid and its anions with PhB(OH)₂ is given by an equation of the form

$$1/\tau = k_1(A) + k_2(B) + k_3(C)$$

where k_1 refers to the reaction of fully protonated malonic acid, k_2 to the reaction of bimalonate, and k_3 to the reaction of the malonate dianion. A, B, and C are functions of the various equilibrium constants and of the equilibrium concentrations of reactants and products. The complete expression is identical with that given in the previous paper[1] for the reaction of oxalic acid. Since A, B, and C are pH dependent, varying pH over the widest possible range permits the accurate determination of k_1, k_2, and k_3. The results are that $k_1 = 350$ M^{-1} sec⁻¹ ± 10%, $k_2 = 150$ M^{-1} sec⁻¹ ± 10%, and $k_3 \leq 1$ M^{-1} sec⁻¹. Experimental and calculated relaxation times are given in Table I. These results are presented together with the results for the oxalic acid complexation in Table II.

Discussion

The first point to note is that the reactivity pattern is the same as that of oxalate. In particular, the dianion is unreactive. This lack of reactivity of dianions with boron acids may be due to a repulsion between the incoming anionic end of the ligand and a leaving negatively charged hydroxide. The incoming ligand is therefore not properly oriented for chelation and the three-coordinate boron compound that results on loss of hydroxide would rapidly hydrolyze to starting material. This is a direct consequence of the facile trigonal–tetrahedral interconversion of boron.[6-8]

In considering the reactivities of the fully protonated ligands, two effects are important. One is the acidity of the ligand;

Table I. Relaxation Spectra of PhB(OH)₂–H₂Mal Solutions

[PhB-(OH)₂]₀, M	[Mal]₀,[a] M	[HIn]₀,[b] M	pH	τ, msec Exptl	τ, msec Calcd
0.0788	0.0544	4.00 × 10⁻⁵	5.98	34	37
0.0862	0.1155	4.00 × 10⁻⁵	6.10	36	35
0.0862	0.1155	4.00 × 10⁻⁵	6.48	33	35
0.0844	0.0513	3.86 × 10⁻⁵	3.02	21	19
0.0844	0.0513	3.86 × 10⁻⁵	4.02	29	32
0.0856	0.0497	4.00 × 10⁻⁵	5.01	32	34
0.0856	0.0497	4.00 × 10⁻⁵	5.66	39	35
0.0430	0.0984	4.00 × 10⁻⁵	5.63	40	41
0.0760	0.0548	1.67 × 10⁻⁴	1.89	3.5	3.7
0.0760	0.0548	1.67 × 10⁻⁴	2.54	10	10
0.0434	0.1023	1.67 × 10⁻⁴	1.81	2.9	3.3
0.0434	0.1023	1.65 × 10⁻⁴	2.47	9.0	10
0.0846	0.1107	1.67 × 10⁻⁴	1.90	3.3	3.4
0.0846	0.1107	1.65 × 10⁻⁴	2.34	8.5	8.1
0.0876	0.1051	3.86 × 10⁻⁵	3.12	20	19
0.0876	0.1051	3.86 × 10⁻⁵	4.10	33	29
0.0862	0.0993	4.00 × 10⁻⁵	5.06	30	32
0.0862	0.0993	4.00 × 10⁻⁵	5.64	31	34

[a] This is the total initial concentration of malonic acid in solution as H₂Mal, HMal⁻, and Mal²⁻. [b] All solutions at pH 2.54 and below contain orange IV as the indicator. Between pH 3.02 and pH 4.10 bromophenol blue was used. Above pH 5.06 chlorophenol red was used. All reactions were followed at λ 580 nm.

Table II. Rate Constants for the PhB(OH)₂–H₂Ox and PhB(OH)₂–H₂Mal Reactions

Reaction	k, M^{-1} sec⁻¹	Reaction	k, M^{-1} sec⁻¹
PhB(OH)₂ + H₂Mal	350	PhB(OH)₂ + H₂Ox	2000
PhB(OH)₂ + HMal⁻	150	PhB(OH)₂ + HOx⁻	330
PhB(OH)₂ + Mal²⁻	≤1	PhB(OH)₂ + Ox²⁻	≤0.1

the other is chelate ring size. Our previous studies[1,3,9] of fully protonated ligands complexing with boron acids show that the most acidic ligand reacts fastest. On this basis alone, one would expect malonic acid to react more slowly than oxalic acid. However, the effect of chelate ring size may also be significant. Malonic acid reacts more slowly than oxalic acid by a factor of 6. It reacts faster than the less acidic α-hydroxy acids (which form five-membered chelate rings) by only a factor of 2. Ligand acidity parallels this order of reactivity but the relative magnitudes of the rate constants suggest that the formation of the larger chelate ring may also be kinetically significant. This is also reflected in the binoxalate and bimalonate rate constants. The very low stabilities of succinic and phthalic acid complexes support this suggestion. If ligand acidity were the primary factor determining forward rates, one would expect these acids to exhibit forward rate constants close to those of malonate itself. This would require unreasonably large reverse rate constants to account for the low complex stability. In kinetic studies of the hydrolysis of three-coordinate boron–diol esters such unusual kinetic instability of six- and seven-membered rings was not noted[10,11] (although the mechanism is surely different in three- and four-coordinate boron systems). Similarly, no dramatic thermodynamic differences between five- and six-membered chelate rings have been found.[11-13]

Recent studies of Ni²⁺ with dicarboxylates also indicate that slow rates are observed for the larger chelate rings,[14] and, in some cases, chelate ring closure does not occur[15] (both oxalate[16] and malonates[4,17] react normally). More pronounced effects would be expected with more labile ions.[18] An estimate can be made of the lability of the B–OH bond in tetrahedral boron systems from kinetic studies of the B(OH)₃ + OH⁻ ⇌ B(OH)₄⁻ reaction. The literature values differ,[6-8] but the highest value for the reverse rate constant (~10⁵ sec⁻¹)[6] is greater than the water-exchange rate of Ni²⁺. Effects of

chelate ring size may therefore be expected in substitution reactions of boron. Finally, as opposed to Ni^{2+} substitution reactions, complexes in aqueous solution in which only one end of the dicarboxylate coordinates are not known. Hydrolysis of such a species would presumably occur rapidly. These results strongly support the conclusion that low rates of complex formation are primarily responsible for the very low stability of larger ring systems in boron complexes of this type.

This study presents additional evidence for two previous conclusions: ligand donor atom protonation is required for reaction and the rate of substitution increases with increasing ligand acidity. In addition, these results indicate that chelate ring closure is a significant rate-limiting step in boron substitution processes involving chelate rings of six atoms or larger. This last conclusion also supports the suggestion[1,3] that there is a close formal similarity between these boron substitution reactions and other labile substitution processes.

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Substituent Effects on the Oxidation–Reduction Reactions of Nickel Para-Substituted Tetraphenylporphyrin in Nonaqueous Media

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In nonaqueous media, porphyrins and metalloporphyrins may be oxidized in two single-electron-transfer steps to yield π-cation radicals or dications or reduced in two single-electron-transfer steps to yield π-anion radicals or dianions.[1-3] In several metalloporphyrins, such as those containing Cr, Mn,
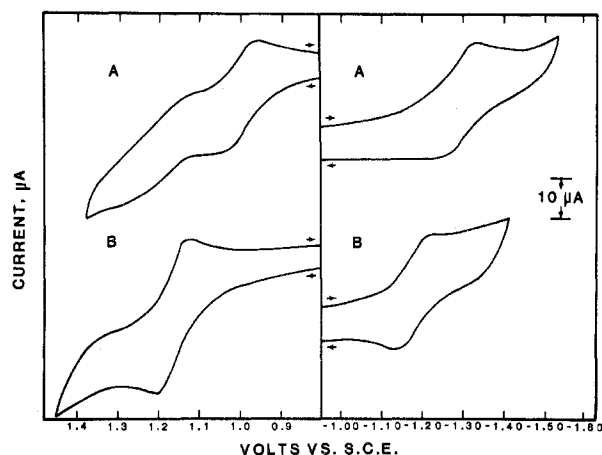
Figure 1. Cyclic voltammograms of (A) 0.2 mM Ni(p-CH$_3$)TPP and (B) 0.2 mM Ni(p-COOCH$_3$)TPP in 0.1 M TBAP, CH$_2$Cl$_2$; scan rate 0.050 V/s.

Fe, Co, Ni, and Ag, the central metal may also be oxidized or reduced[4-7] to yield complexes of metal oxidation states +1, +2, +3, or +4. Differentiation of metal from ring oxidation is often accomplished by optical and ESR spectra or electrochemical techniques.[1-7] During a comprehensive electrochemical study of solvent and substituent effects on a number of different transition metal para-substituted tetraphenylporphyrins, certain trends were noted which could be used as a basis for deciding whether a given electrode reaction is that of the porphyrin ring or the central metal.[8]

We have observed that, by attachment of an electron-donating or -withdrawing group at the para position of the four phenyl groups of several metallotetraphenylporphyrins, the half-wave potentials for both ring and metal redox reactions would shift in a manner predicted by the Hammett linear free energy relationship[9]

$$\Delta E_{1/2} = 4\sigma\rho \tag{1}$$

where σ is the total polar substituent constant which is dependent on the kind and position of the four substituents, and ρ is the reaction constant which is given in volts and expresses the susceptibility of the electrode reaction to the total polar effect of the substituents. Its value depends on the kind of electroactive group and the composition of the solvent and supporting electrolyte, as well as the temperature.

In this note we present a new electrochemical criterion for differentiating between metal and ring reactions based on the magnitude of the Hammett reaction constants.

Experimental Section

Nickel *meso*-tetraphenylporphyrin and its para-substituted derivatives were synthesized by the method of Adler.[10] Tetrabutyl-ammonium perchlorate, TBAP (Southwestern Analytical, Inc.), was recrystallized from methanol and dried at reduced pressure at room temperature over P4O10. Methylene chloride, "Distilled-in-Glass", Burdick and Jackson Laboratories, Inc., was used as received.

Cyclic voltammograms were obtained with a three-electrode system using a PAR Model 174 polarographic analyzer, in conjunction with a Houston Instruments Model 2000 X-Y recorder. The working electrode was platinum, and a platinum wire served as the auxiliary electrode. A commercial saturated KCl calomel electrode (SCE) was the reference electrode. This was separated from the bulk of the solution by a fritted-glass compartment. Deaeration was accomplished by bubbling solvent-saturated high-purity nitrogen through the solutions for 10 min prior to analysis. N2 blanketed the solution during analysis.

Controlled-potential coulometry was accomplished on a large platinum gauze electrode using a PAR Model 173 potentiostat, Model 179 digital coulometer, and time base X-Y recorder. The coulometric cell was similar to that used for cyclic voltammetry and has been