Hydroboration Kinetics. 10.[1] Kinetics, Mechanism, and Selectivity for Hydroboration of Representative Alkenes with Borinane

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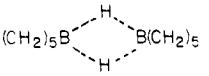
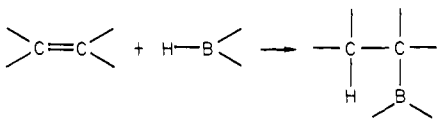
Abstract: The kinetics of hydroboration of representative alkenes with borinane dimer



have been studied at 0 °C in *n*-heptane. With many alkenes the reaction shows three-halves-order rate behavior, indicating a fast dissociation of the borinane dimer, followed by the rate-limiting step involving the monomer and the alkene. With a few alkenes the reaction was too fast for accurate rate measurements. The rate data indicate a possible generalization of the earlier conclusions for the mechanism of hydroboration of alkenes by 9-borabicyclo[3.3.1]nonane dimer, $(9\text{-BBN})_2$. The relative rates calculated from the rate constants agree well with those determined competitively. A comparison of the reactivity of borinane toward various classes of alkenes with those of other hydroborating agents, such as 9-BBN, disiamylborane, dibromoborane–methyl sulfide, and thexylchloroborane–methyl sulfide, shows that borinane is similar to 9-BBN in its selectivity and differs markedly from that of disiamylborane, dibromoborane–methyl sulfide, and thexylchloroborane–methyl sulfide.

The hydroboration reaction (eq 1) is a clean, facile, and stereospecific addition of the H–B< bond to the carbon–carbon double bond of an unsaturated substrate.[4] Its synthetic utilities



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have been extensively explored,[5] but much less is known regarding its mechanism. Several mechanistic pathways have been proposed,[6] and a considerable number of MO calculations have been made[7] to shed light on the transition state for this reaction. Unfortunately, the verification of these mechanistic proposals by kinetic studies was seriously impeded until recently by experimental difficulties arising from the complexities of this reaction. For example, the reaction of diborane with an alkene proceeds through several consecutive steps of comparable rates.[6d] In order to avoid this difficulty, the kinetics of the reaction of disiamylborane dimer, $(Sia_2BH)_2$, with alkenes was studied.[8] This reaction exhibited second-order kinetics for a typical alkene such as cyclopentene (eq 2), indicating that the disiamylborane dimer must be attacked by the alkene.[8]

$$-\mathrm{d}[(Sia_2BH)_2]/\mathrm{d}t = k[(Sia_2BH)_2][C_5H_8] \quad (2)$$

However, the kinetics of hydroboration of alkenes with 9-borabicyclo[3.3.1]nonane dimer, $(9\text{-BBN})_2$, differed markedly from those of $(Sia_2BH)_2$.[1] With $(9\text{-BBN})_2$, no second-order kinetics were observed. With faster reacting alkenes, such as 1-hexene, 2-methyl-1-pentene, and cyclopentene, the reaction showed kinetics which were first order—first order in $(9\text{-BBN})_2$, zero order in alkene; with less reactive olefins, such as cyclohexene, the kinetics displayed were three-halves order—one-half order in $(9\text{-BBN})_2$ and first order in alkene. This was rationalized by a dissociation mechanism (eq 3 and 4). With faster reacting

$$(9\text{-BBN})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ 9\text{-BBN} \quad (3)$$

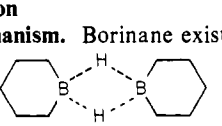
$$9\text{-BBN} + \text{alkene} \xrightarrow{k_2} B\text{-alkyl-9-BBN} \quad (4)$$

alkenes, the dissociation step (eq 3) is slower than the subsequent reaction between the monomer and the alkene (eq 4), giving first-order kinetics. With less reactive alkenes, the second step is slower than the first, leading to a three-halves-order reaction. In cases where these two steps are of comparable speed, intermediate kinetic behavior was observed.

This difference in the behavior of $(9\text{-BBN})_2$ and $(Sia_2BH)_2$ precluded the postulation of a generalized mechanism of hydroboration. It appeared that a study of the kinetics of hydroboration of alkenes with a third hydroborating agent might clarify the problem. It was hoped that the results with a third system might indicate which of the two systems, $(9\text{-BBN})_2$ or $(Sia_2BH)_2$, was anomalous. Recently, an effective way of obtaining borinane in pure form was developed.[9] Therefore, we undertook a study of the kinetics of the reaction of borinane with representative alkenes.

Results and Discussion

Kinetics and Mechanism. Borinane exists as a dimer (**1**)



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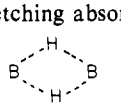
which shows a strong stretching absorption at 1560 cm^{-1}.



(1) (a) For a review of the mechanism of hydroboration and reference to the previous studies in this series, see: Brown, H. C.; Chandrasekharan, J.; Wang, K. K. *Pure Appl. Chem.* **1983**, *55*, 1387-1414. (b) Wang, K. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 5303-5306.

(2) Postdoctoral research associate on Grant CHE 79-18881 of the National Science Foundation.

(3) Postdoctoral research associate on Grant CHE 76-20846 of the National Science Foundation.

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(5) (a) Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972. (b) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Synthesis via Boranes"; Wiley-Interscience: New York, 1975. (c) Cragg, G. M. L. "Organoboranes in Organic Synthesis"; Marcel Dekker: New York, 1973.

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Table I. Effect of Concentrations on the Rate Constants for the Hydroboration of *cis*-2-Butene, Cyclopentene, and 1-Methylcyclopentene with Borinane[a]

init concn, M				
alkene	$(borinane)_2$	10^4k_1, s^{-1}	$10^4k_{3/2}$, $M^{-1/2}\ s^{-1}$	10^4k_2,[b] $M^{-1}\ s^{-1}$
		cis-2-Butene		
0.200	0.100	7.02	16.3	78.5
0.200	0.050	14.2	14.8	94.3
0.100	0.050	4.74	15.1	99.3
		Cyclopentene		
0.200	0.100	6.67	15.4	72.5
0.200	0.050	14.9	15.1	96.8
0.100	0.050	4.75	16.0	108
		1-Methylcyclopentene		
0.400	0.100	4.59	3.37	15.9
0.200	0.100	1.49	3.53	16.8
0.200	0.050	3.30	3.40	22.0

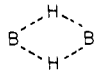
[a] In *n*-heptane at 0 °C. [b] Second-order rate constant.

Table II. Rate Constants for the Hydroboration of *cis*-2-Butene (0.100 M) with $(Borinane)_2$ (0.05 M)[a]

time, s	*cis*-2-butene,[b] M	$10^4k_{3/2}$,[c] $M^{-1/2}\ s^{-1}$	time, s	*cis*-2-butene,[b] M	$10^4k_{3/2}$,[c] $M^{-1/2}\ s^{-1}$
0	0.100		1326	0.0494	14.3
246	0.0858	14.5	1806	0.0397	14.5
606	0.0684	15.5	2286	0.0322	14.9
846	0.0610	14.8	2766	0.0262	15.4
1086	0.0545	14.6			

[a] In *n*-heptane at 0 °C. [b] The concentration of borinane dimer is one-half that of *cis*-2-butene. [c] Calculated from the equation $k_{3/2}t = 2^{1/2}[(b-2x)^{-1/2} - b^{-1/2}]$ where b is the initial concentration of *cis*-2-butene and $(b-2x)$ is the concentration at time t.

Therefore, the kinetics of the hydroboration of alkenes with borinane dimer was followed by monitoring the decrease in absorbance of the



vibration using a quantitative IR spectrometer.[1b] Our preliminary experiments indicated that the reaction of borinane with alkenes is very rapid, much more rapid than the corresponding reactions with 9-BBN. Fortunately, with many olefins, the rates could be measured accurately at 0 °C in *n*-heptane, utilizing relatively dilute solutions.

In cases where the rates could be measured accurately, the reaction displayed three-halves-order kinetics. Changing the initial concentrations of either reactant did not alter the three-halves-order rate constant significantly but changed the calculated first- and second-order rate constants considerably (Table I). Table II shows the results of a typical kinetic run. The fact that this reaction shows three-halves-order rate behavior is definite evidence in favor of a dissociation mechanism analogous to that observed for $(9\text{-BBN})_2$. This mechanism will lead to three-halves-order kinetics when the dissociation step (eq 5) is faster than the subsequent reaction between the monomer and the alkene (eq 6).

$$(borinane)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2borinane \qquad (5)$$

$$borinane + alkene \xrightarrow{k_2} B\text{-alkylborinane} \qquad (6)$$

These results support the position that hydroboration with dimeric R_2BH probably occurs via a dissociation–hydroboration mechanism similar to that for $(9\text{-BBN})_2$. Obviously, the mechanism proposed for the $(Sia_2BH)_2$ system is not applicable to hydroboration in general. Moreover, it is possible that the results obtained in that study[8] are not entirely reliable. The kinetics were followed by a relatively tedious quenching method, and there were many experimental difficulties.[8] A conclusive study of the kinetics of hydroboration of alkenes with $(Sia_2BH)_2$ employing the quantitative IR procedure is being undertaken.

Table III. Comparison of Three-Halves-Order Rate Constants and Relative Rates by the Competitive Method for the Reaction of Alkenes with Borinane[a]

alkene	$10^4k_{3/2}$, $M^{-1/2}\ s^{-1}$	relative rates
2-methyl-1-pentene[b]		135
cyclooctene[b]		115
1-hexene[b]		100
cycloheptene$_b$		20.1
1-methylcyclooctene[b]		16.8
3,3-dimethyl-1-butene[b]		15.7
cis-3-hexene	21.5	12.0
cis-2-butene	15.6	5.40
cyclopentene	15.5	7.53
2-methyl-2-butene	12.3	4.97
trans-2-butene	10.8	3.55
trans-3-hexene	9.5	4.00
1-methylcyclopentene	3.43	1.48
2,3-dimethyl-2-butene	0.326	0.142
cyclohexene	0.251	0.093
1-methylcyclohexene	0.049	0.015

[a] In *n*-heptane at 0 °C. [b] The reaction is too fast to measure its rate constant accurately.

An elegant way of checking the dissociation mechanism (eq 5 and 6) is to compare the relative rates of hydroboration of pairs of alkenes determined competitively with those calculated from the rate constants. The ratios of the three-halves-order rate constants should agree well with the ratios of the relative reactivities obtained by the competitive method.[1a] Table III lists the three-halves-order rate constants and the relative reactivities obtained by the competitive method. It can be seen that there is a good agreement between the relative rates obtained by the two methods. For example, k(1-methylcyclopentene)/k(2,3-dimethyl-2-butene) is 10.5 by comparison of the rate constants and 10.4 by the competitive method.

Although there is a similarlity in the mechanism of hydroboration by 9-BBN dimer and by borinane dimer, some intrinsic differences are perceptible. First, the reaction of borinane dimer with alkenes is much faster than that of $(9\text{-BBN})_2$. Second, $(9\text{-BBN})_2$ shows three-halves-order rate behavior only with very unreactive alkenes, such as cyclohexene, 2,3-dimethyl-2-butene, etc., while borinane dimer shows three-halves-order kinetics even with more reactive alkenes, such as cyclopentene, *cis*-2-butene, etc. This may indicate that there is a larger rate difference between the dissociation step and the subsequent hydroboration step in the case of borinane dimer than in the case of $(9\text{-BBN})_2$.

Structural Effects. It has been found that various hydroborating agents exhibit different selectivity characteristics toward the different classes of alkenes.[11] A comparison of the reactivity of borinane[12] toward several types of alkenes with that of 9-BBN,[13] Sia_2BH,[8] dibromoborane–methyl sulfide,[14] and thexylchloroborane–methyl sulfide[11] ($ThxBHCl{\cdot}SMe_2$) will be highly useful in understanding the discriminatory power of borinane among several kinds of unsaturated centers.

A. Terminal Alkenes. In the hydroboration of terminal alkenes with borinane, the boron atom is placed predominantly on the terminal carbon atom.[15] Increasing the bulk of the group connected to the double bond decreases the rate of hydroboration.

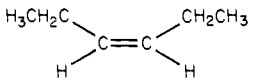
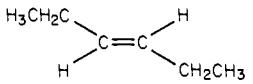
(11) Sikorski, J. A.; Brown, H. C. *J. Org. Chem.* **1982**, *47*, 872.
(12) The relative reactivity values for borinane and Sia_2BH were determined at 0 °C while those for 9-BBN and $ThxBHCl{\cdot}SMe_2$ were determined at room temperature.
(13) (a) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 5297–5301. (b) Brown, H. C.; Nelson, D. J.; Scouten, C. G. *J. Org. Chem.* **1983**, *48*, 641–643.
(14) Brown, H. C.; Chandrasekharan, J. *J. Org. Chem.* **1983**, *48*, 644–648.
(15) Brown, H. C.; Negishi, E. *J. Organomet. Chem.* **1971**, *26*, C67–C69.

	$CH_3(CH_2)_3$-CH=CH_2	$(CH_3)_3$-C-CH=CH_2
borinane	1.0	0.16
9-BBN	1.0	0.23
Sia_2BH	1.0	0.047
$Br_2BH\cdot SMe_2$	1.0	0.20

Borinane seems to be similar to 9-BBN in its susceptibility to the steric effect, differing markedly from Sia_2BH. Borinane reacts with terminal alkenes faster than with internal alkenes, as observed with other reagents also.

	1-hexene	*cis*-3-hexene
borinane	1.0	0.12
9-BBN	1.0	0.007
Sia_2BH	1.0	0.02
$ThxBHCl\cdot SMe_2$	1.0	0.11
$Br_2BH\cdot SMe_2$	1.0	0.42

B. Cis and Trans Isomers. Borinane reacts with *cis*-2-butene faster than with *trans*-2-butene. A similar rate ratio is also found between *cis*- and *trans*-3-hexene. A possible reason for the higher reactivity of *cis*-alkenes may be the relief of steric strain during hydroboration. Borinane is much less selective between the geometrical isomers of an alkene as compared to Sia_2BH or $ThxBHCl\cdot SMe_2$, comparable in behavior to 9-BBN and $Br_2BH\cdot SMe_2$.

borinane	3.0	1.0
9-BBN	2.2	1.0
Sia_2BH	10.0	1.0
$ThxBHCl\cdot SMe_2$	92.0	1.0
$Br_2BH\cdot SMe_2$	1.9	1.0

C. Cyclic Alkenes. Cyclohexene (chx) is uniquely unreactive toward hydroboration as compared to its lower and higher ring homologues. Thus, cyclopentene (cp) cycloheptene (chp), and cyclooctene (coc) are all much more reactive than cyclohexene. This has been attributed to the greater ring strain on the former three cycloalkanes, strain which is relieved on hydroboration.[16] Borinane is quite similar to other hydroborating agents in discriminating among these cycloalkenes.

	cp	chx	chp	coc
borinane	1.0	0.012	2.7	15.0
Sia_2BH	1.0	0.0071	19.0	41.0
$ThxBHCl\cdot SMe_2$	1.0	0.032	5.5	40.0
9-BBN	1.0	0.0095	1.1	0.96
$Br_2BH\cdot SMe_2$	1.0	0.063	4.0	19.5

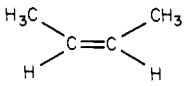
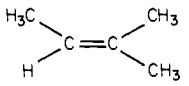
D. Effect of α-Methyl Groups. Introduction of a methyl substituent at C_2 (α to the site of hydroboration) in a terminal alkene increases the rate of hydroboration with borinane modestly. A similar factor is observed in the case of 9-BBN. On the other hand, Sia_2BH shows a much lower reactivity with 2-methyl-1-pentene, as compared to 1-hexene, while the exact opposite is observed for $Br_2BH\cdot SMe_2$. It appears that a dominant role is played by electronic factors in the case of $Br_2BH\cdot SMe_2$ and steric factors in the case of Sia_2BH. In the case of borinane and 9-BBN, both electronic and steric factors seem to exert comparable influence on the rate of hydroboration.

	2-methyl-1-pentene	1-hexene
borinane	1.3	1.0
9-BBN	1.9	1.0
Sia_2BH	0.049	1.0
$ThxBHCl\cdot SMe_2$	0.41	1.0
$Br_2BH\cdot SMe_2$	21.0	1.0

Addition of an α-methyl group to an internal alkene has little effect on the rate of hydroboration with borinane or 9-BBN while there is a significant rate decrease in the case of $ThxBHCl\cdot SMe_2$.

(16) Dauben, W. G.; Pitzer, K. S. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed., Wiley: New York, 1956; Chapter 1.

On the other hand, introducing and α-methyl group on a cyclic alkene significantly reduces the rate of hydroboration with borinane or 9-BBN.

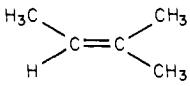
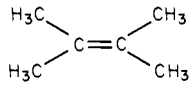
borinane	1.1	1.0
9-BBN	1.1	1.0
$ThxBHCl\cdot SMe_2$[17]	33.0	1.0
$Br_2BH\cdot SMe_2$[18]	0.20	1.0

However, the rate difference is more marked for $ThxBHCl\cdot SMe_2$. With $Br_2BH\cdot SMe_2$, a rate increase is observed.

	cp	1-Me-cp	chx	1-Me-chx	coc	1-Me-coc
borinane	5.1	1.0	6.2	1.0	6.8	1.0[19]
9-BBN	4.8	1.0	6.1	1.0		
$ThxBHCl\cdot SMe_2$	15.0	1.0	45.0	1.0		
$Br_2BH\cdot SMe_2$	0.13	1.0	0.25	1.0		

Again, borinane shows a close resemblance to 9-BBN.

Finally, introducing a fourth methyl group at the site of hydroboration of 2-methyl-2-butene leads to a considerable rate decrease in the case of borinane, 9-BBN, and $Br_2BH\cdot SMe_2$.

borinane	35	1.0
9-BBN	140	1.0
$Br_2BH\cdot SMe_2$	34	1.0

Conclusion

The mechanism of hydroboration of alkenes with borinane dimer has been established through kinetic studies. The reaction proceeds through a dissociation of borinane dimer, followed by subsequent reaction of the monomer with the alkene. The mechanism is analogous to that of hydroboration by $(9\text{-BBN})_2$. This similarity allows one to generalize the mechanism of hydroboration of alkenes with dimeric monofunctional hydroborating agents.

A comparison of the reactivity of borinane toward different types of alkenes with those of other monofunctional hydroborating agents, such as 9-BBN, Sia_2BH, $ThxBHCl\cdot SMe_2$, and $Br_2BH\cdot SMe_2$, shows that borinane is similar to 9-BBN in its selectivity and differs markedly from the other monofunctional borane reagents examined. It seems that cyclic hydroborating agents have a significantly different selectivity than acyclic reagents such as disiamylborane, probably attributable to the much greater steric requirements of the latter reagents. In such acyclic reagents, only dialkylboranes of relatively high steric requirement possess the stability for utilization as simple hydroborating agents.

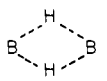
Experimental Section

General procedures for the manipulation of boron reagents have been outlined in Chapter 9 of ref 5b. All glassware, syringes, and needles were oven-dried at 140 °C for several hours. The glassware was assembled hot and cooled under a stream of dry nitrogen. Syringes were assembled and fitted with needles while hot and cooled as assembled units.

Materials. Borinane was prepared from 1,4-pentadiene as described elsewhere.[9] Except for *cis*- and *trans*-2-butene, all alkenes were purified by distillation over LAH in a nitrogen atmosphere. Thier purities were confirmed to be >99% by GC analysis. Solutions of *cis*- and *trans*-2-butene were prepared in dry *n*-heptane and were standardized as follows: an aliquot was allowed to react with a known excess of standard borinane solution at 0 °C. After completion of the reaction, the unreacted borinane was estimated by the quantitative IR technique.

n-Heptane was purified by stirring over H_2SO_4 for several days, followed by distillation over LAH in a nitrogen atmosphere.

Kinetics Procedure. The quantitative IR method[10] was used to follow the kinetics. The decrease in the absorbance of the



stretching vibration at 1560 cm^{-1} was measured with a Miran 1A variable filter infrared spectrometer from Wilks Scientific Corp. A typical procedure is as follows: dry *n*-heptane (17.12 mL, cooled to 0 °C) and a solution of borinane in *n*-heptane (7.34 mL of 0.341 M in dimer at 0 °C) were taken in an oven-dried, nitrogen-cooled, 50-mL flask equipped with a connecting tube. The resulting solution was allowed to equilibrate at 0.0 °C ± 0.05 in a constant-temperature bath. The reaction was started by adding cyclopentene (0.44 mL). The reaction mixture, 0.200 M in cyclopentene and 0.100 M in borinane dimer, was pumped through a 0.1-mm Wilks NaCl IR cell at a rate of 4 mL/min using a FMI pump. The IR cell was kept at the reaction temperature by circulating water at 0 °C through a cell holder. The absorbance was recorded as a function of time on a strip chart recorder. After the reaction was complete, the background absorbance of the pure solvent was noted. The calculations of the rate constants were made by the procedure given in ref 1b.

Relative Reactivities. The procedure to determine the relative reactivity of alkenes A and B is as follows: 5.0 mmol each of alkenes A and B and a suitable internal standard (*n*-octane, 0.4 mL) were added to *n*-heptane (15 mL) in an oven-dried, nitrogen-cooled reaction flask fitted with a connecting tube. Several minute aliquots (1 μL) were removed and analyzed by GC to determine the response factors of the two alkenes using an SE-30 column (6 ft × 0.25 in.) on Chromosorb W. The mixture was cooled to 0 °C, and borinane (5.0 mmol) in *n*-heptane was added. The reaction temperature was kept at 0 °C. After the reaction was over, samples were removed and analyzed by GC to determine the amounts of unreacted alkenes. From the initial and final quantities of alkenes, the relative reactivity was calculated by using the Ingold–Shaw expression[20] (eq 7)

$$\frac{k_A}{k_B} = \frac{\ln [A]_o - \ln [A]_f}{\ln [B]_o - \ln [B]_f} \quad (7)$$

where $[A]_o$ and $[A]_f$ are the initial and final quantities in mmol of the alkene A and $[B]_o$ and $[B]_f$ are the corresponding quantities (in mmol) of the alkene B. The alkene pairs studied were 2-methyl-1-pentene/cycloheptene, 1-hexene/cycloheptene, cyclooctene/cycloheptene, cycloheptene/*cis*-3-hexene, *cis*-3-hexene/cyclopentene, cyclopentene/2-methyl-2-butene, 2-methyl-2-butene/*trans*-3-hexene, *trans*-3-hexene/1-methylcyclopentene, 1-methylcyclopentene/2,3-dimethyl-2-butene, 2,3-dimethyl-2-butene/cyclohexene; cyclohexene/1-methylcyclohexene, 1-methylcyclooctene/cycloheptene, *cis*-2-butene/2-methyl-2-butene, 2-methyl-2-butene/*trans*-2-butene, cycloheptene/3,3-dimethyl-1-butene.

(17) Value reported for *cis*-2-pentene vs. 2-methyl-2-pentene; ref 13.
(18) Value for *cis*-3-hexene vs. 2-methyl-2-butene.

Acknowledgment. Financial assistance from the National Science Foundation (Grant CHE 79-18881) is gratefully acknowledged.

Registry No. 1, 40209-82-3; 9-BBN, 280-64-8; Sia_2BH, 1069-54-1; $ThxBHCl{\cdot}SMe_2$, 75067-06-0; $Br_2BH{\cdot}SMe_2$, 55671-55-1; 2-methyl-1-pentene, 763-29-1; cyclooctene, 931-88-4; 1-hexene, 592-41-6; cycloheptene, 628-92-2; 1-methylcyclooctene, 933-11-9; 3,3-dimethyl-1-butene, 558-37-2; *cis*-3-hexene, 7642-09-3; *cis*-2-butene, 590-18-1; cyclopentene, 142-29-0; 2-methyl-2-butene, 513-35-9; *trans*-2-butene, 624-64-6; *trans*-3-hexene, 13269-52-8; 1-methylcyclopentene, 693-89-0; 2,3-dimethyl-2-butene, 563-79-1; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1.

(19) The hydroboration product of 1-methylcyclooctene with diborane undergoes rapid isomerization around the cyclooctane ring (Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 2544–2557). With borinane and 1-methylcyclooctene, no isomerization of the organoborane is observed, even after prolonged intervals of time (48 h) at the reaction temperature (0 °C). Again, isomerization does not occur during the hydroboration of this alkene with 9-BBN (Taniguchi, H.; Brener, L.; Brown, H. C. *Ibid.* **1976**, *98*, 7107).
(20) Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, 2918.

Steric and Electronic Effects in Ligand Substitution of Metal Carbonyls. Rapid Kinetics of Labile Carbonylmanganese Complexes by Transient Electrochemical Techniques

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Abstract: The ligand substitution kinetics of a series of carbonylmanganese cations $MeCpMn(CO)_2L^+$ with L = 3- and 4-substituted pyridine ligands are measured for a variety of phosphine nucleophiles N of differing steric and electronic properties. The unified free energy relationship in eq 17 is shown for the first time to accommodate all the extensive rate data, if the steric effect is evaluated by Tolman's cone angles for the phosphines, and the electronic effects are evaluated by the acid–base dissociation constants of the pyridine ligands and the phosphine nucleophiles. The range of second-order rate constants k_1 for ligand substitution of $MeCpMn(CO)_2L^+$ extends over four decades from 3.0 to 2×10^4 M^{-1} s^{-1}. The strong dependence of log k_1 on both the electronic and steric effects of the pyridine ligand L and the phosphine nucleophile N points to an associative S_N2 mechanism for this ligand substitution. The measurement of the fast rates of ligand substitution by transient electrochemical techniques is based on the novel electrocatalysis of the neutral precursor $MeCpMn(CO)_2L$ in the presence of added phosphine nucleophiles, as described in Scheme I. The analysis of the electrochemical kinetics for this mechanism by Feldberg's method for the computer simulation of the cyclic voltammograms and by Saveant's adimensional evaluation of the CV peak currents is described in detail.

The mechanism of ligand substitution of metal carbonyls is central to the successful catalysis of a variety of important processes leading to the reduction of carbon monoxide.[1,2] As such, ligand exchange in metal carbonyls and their derivatives has received extensive mechanistic scrutiny.[3-5] The generally accepted mechanisms for the displacement of the ligand L from a series of metal carbonyls $L{-}M(CO)_n$ by added nucleophiles N such as amines, phosphines, etc., involve diamagnetic intermediates,

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