yielded 48 mg. Preparative thin-layer chromatography (Et_2O, R_f 0.64) yielded 30.0 mg (58%) of **77**.

Reaction of Geiparvarin with *n*-Propanethiol under Acidic Conditions. A solution of 28.0 mg (0.0705 mmol) of geiparvarin, 20 μL of *n*-propanethiol, and 1 mg of *p*-toluenesulfonic acid in 1.0 mL of benzene was stirred at room temperature for 115 h. Removal of solvent in vacuo yielded 34 mg. Preparative thin-layer chromatography [1:1 (v/v) Et_2O-CH_2Cl_2, R_f 0.50] yielded 14 mg (47%) of **80**. A second chromatography provided an analytical sample: IR 1695 (s), 1605 (s), 1595 (s), 1270 (m) cm^{-1}; NMR ($CDCl_3$, 250 MHz) δ 1.02 (t, t, $J = 7.3$ Hz, 3 H), 1.42 (s, s, 6 H), 1.66 (m, 2 H), 2.64 (m, 2 H), 3.30 (m, 1 H), 3.48 (m, 1 H), 4.20 (m, 2 H), 5.46, 5.54 (s, s, 1 H), 6.31 (d, $J = 10$ Hz, 1 H), 6.90 (m, 2 H), 7.44 (m, 1 H), 7.70 (d, $J = 10$ Hz, 1 H).

Anal. Calcd for $C_{22}H_{26}O_5S$: C, 65.63; H, 6.52. Found: C, 65.10; H, 6.49.

Reaction of Geiparvarin with *n*-Propanethiol under Basic Conditions. A solution of 9.9 mg (0.0303 mmol) of geiparvarin, 20 μL of *n*-propanethiol, and 1 drop of diisopropylamine in 1.0 mL benzene was stirred at room temperature for 70 h. Removal of solvents in vacuo yielded 11.1 mg. Preparative thin-layer chromatography (1:1 CH_2Cl_2-Et_2O, R_f 0.50) yielded 4.9 mg (40%) of **80**.

Hydroquinone Inhibition. A solution of 45.9 mg (0.273 mmol) of **11**, 130 μL of *n*-propanethiol, and 10 mg of 2,5-di-*tert*-butylhydroquinone in 3 mL of benzene was stirred at room temperature under N_2 for 67 h. Removal of solvents in vacuo yielded 60.0 mg of starting material.

A solution of 27.0 mg (0.1297 mmol) of **72**, 65 μL of *n*-propanethiol, and 10 mg of 2,5-di-*tert*-butylhydroquinone in 2 mL of benzene was stirred at room temperature under N_2 for 68 h. Removal of solvents in vacuo yielded 36.3 mg of starting material.

A solution of 130 mg (0.077 mmol) of **11**, 75 μL of *n*-propanethiol, 3 mg of *p*-toluenesulfonic acid, and 5 mg of 2,5-di-*tert*-butylhydroquinone in 1.4 mL of benzene was stirred at room temperature for 72 h. Removal of solvents in vacuo and thin-layer chromatography (Et_2O, R_f 0.38) yielded 7.3 mg (52%) of **76**.

A solution of 8.9 mg (0.0424 mmol) of **72**, 75 μL of *n*-propanethiol, 1.0 mg of *p*-toluenesulfonic acid, and 5 mg of 2,5-di-*tert*-butylhydroquinone in 1.4 mL of benzene was stirred at room temperature for 73 h. Removal of solvents in vacuo and preparative thin-layer chromatography (Et_2O, R_f 0.62) yielded 10.6 mg (82%) of **77**.

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Aromatic Substitution in the Gas Phase. Alkylation of Arenes by Gaseous $C_4H_9^+$ Cations

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Abstract: Butyl cations, obtained in the dilute gas state from the radiolysis of butane in the pressure range from 70 to 750 torr, have been allowed to react with benzene, toluene, and their mixtures or with trace amounts of *o*-xylene in the gaseous system. The gas-phase butylation yields invariably *sec*-butylarenes, remarkably free of isomeric byproducts, namely *n*- and *tert*-butylarenes. Other alkylation experiments, where gaseous butyl cations from the reaction of butane with radiolytically formed H_3^+ ions were used as reagent, confirmed the exclusive formation of *sec*-butylarenes. The butylation process displays the positional and substrate selectivity and the dependence of orientation on the pressure of the system, typical of other gas-phase ionic substitutions. At high pressures, ortho-para orientation predominates in the sec-butylation of toluene, with a ortho:meta:para ratio of 43:30:27 at 715 torr. As the pressure is reduced, a gradual shift in favor of the thermodynamically most stable meta-substituted arenium ion is observed, leading to a ortho:meta:para ratio of 31:48:21 at 70 torr.

Introduction

The study of gas-phase aromatic substitution by charged reagents generated in the dilute gas state with specifically designed radiolytic techniques has provided direct information on the intrinsic reactivity, selectivity, and steric requirements of free, unsolvated carbenium ions.[1-6]

This paper reports the extension of the study to aromatic alkylation by gaseous butyl ions, obtained directly from the γ radiolysis of butane in the pressure range from 70 to 750 torr or from the reaction of gaseous H_3^+ ions with butane and pentane, strongly diluted in H_2 gas. The interest of the investigation is twofold. In the first place, the mechanistic features of the gas-phase aromatic butylation can be directly evaluated and compared to those of related alkylation processes that occur both in the gas phase and in solution.

In the second place, the reaction with the aromatic substrate and the nature of the products formed represent a useful probe to sample the isomeric composition of the gaseous butyl ions and to gather additional information on the rate of interconversion of the $C_4H_9^+$ isomers.

Experimental Section

Materials. n-C_4H_{10} and H_2 were research grade gases obtained from Matheson Co., with a stated purity greater than 99.9 mol %, and were used without further purification. The aromatic substrates and pentane were GLC standards obtained from C.Erba Co., whose purity exceeded 99.8 mol %. The isomeric alkylarenes required as reference compounds for identification purposes in GLC were obtained from commercial sources (Aldrich Chemical Co. and C.Erba Co.) or prepared according to established procedures, their identity being confirmed by NMR and IR spectroscopy.

Procedure. The techniques used for the preparation of the samples and their irradiation have been described.[3,4] The dose, ranging from 2.0 to 4.0 Mrad, was delivered at the rate of 0.5 Mrad h^{-1} in a 220 Gammacell from Nuclear Canada Ltd., at the temperature of 24 °C. A small mole fraction (typically a few torr) of O_2 was used in all experiments as a thermal radical scavenger. The analysis of the products was carried out by GLC, using a Sigma 1 chromatograph equipped with a FID unit, on the following columns: (i) 10% EDO-1 on 100-120 mesh Chromosorb P-AW, 20 ft × $^1/_8$ in. o.d., operated at 0 °C for the analysis of the gases; (ii) 5% SP-1200 + 1.75% Bentone 34 on 100-120 mesh Supelcoport, 6

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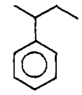
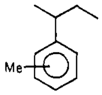
Table I. Alkylation of Arenes with Gaseous Butyl Ions

system composition, torr					relative yields,[a] %		isomeric composition[b] of *sec*-butyltoluenes, %			
C_5H_{12}	O_2	C_6H_6	C_7H_8	H_2			ortho	meta	para	k_T/k_B
750	5	1.7			100					
715	4	1.5	1.5		43	57	41	30	29	1.3
715	10	5.0	0.7		90	10	44	30	25	
710	5	5.0	4.8		18	82	44	32	24	1.0
710	8		2.7			100	42	30	28	
230	4	3.2	2.8		54	46	41	38	21	1.0
70	5	1.7	1.3		60	40	31	46	23	0.9
70	5	1.8	2.0		*b*	*b*	31	48	21	*b*
70	3.5		1.8			100	35	47	18	
70	2	2.0			100					
10	3	5.0		696	100					
15	3	2.0		690	100					
10.9[c]	3	1.8		737	*sec*-butylbenzene = 38%, 2-phenylpentane = 41%, 3-phenylpentane = 21%					
700	9	*o*-xylene = 0.82			*sec*-butylxylenes = 97.3%, *tert*-butylxylenes = 2.7%					

[a] Standard deviation of data ca. 10%. [b] Not measured. [c] C_5H_{12} instead of C_4H_{10}.

ft × $^1/_8$ in. o.d., operated at 100 °C; (iii) 0.1% SP-1000 on 80–100 mesh Carbopack C, 6 ft × $^1/_4$ in. o.d., glass column, operated at 205 °C. The yields of the products were deduced from the areas of their elution peaks, making use of individual calibration factors. Confirmation of the products identity was achieved by GLC–mass spectrometry, using a Hewlett-Packard 5982 A instrument, equipped either with a 300 ft × 0.02 in. i.d. squalane capillary column, operated at 65 °C, or with a 150 ft × 0.02 in. i.d. C20M capillary column operated at 95 °C, directly inserted into the ion source of the mass spectrometer switched in the EI mode. A Hewlett-Packard Model 5934A Data System was used for processing and classifying the raw experimental data. The same instrument, operated in the CI mode, was used to record the butane chemical ionization mass spectra of benzene and toluene in the restricted (0.1–0.5 torr) pressure range allowed by the dual ion source, working at a temperature of 150 °C.

Results

Radiolytic Experiments. Alkylation of all aromatic substrates investigated represents a major reaction channel for the radiolytically formed $C_4H_9^+$ ions. Overall *G* values for the formation of butylarenes are affected by the competition for the charged reagent by nucleophiles other than the aromatic substrate(s).

Such nucleophiles can be intentionally added to the gas or are formed from its radiolysis, as in the case of water, butenes, etc., that are known to efficiently react with $C_4H_9^+$ cations.[7,8] As a consequence, *G* values increase with the concentration of aromatics and decrease with the energy absorbed by the system, which in turn depends on the n-C_4H_{10} pressure and the dose. Typical *G* values for the alkylation range from 1.6 to 2.5 in n-C_4H_{10} at 710 torr, in the absence of added nucleophiles. The overall $G(C_4H_9^+)$ value can be estimated around 4 (vide infra), and consequently the experimental results demonstrate that the alkylation of the arenes is indeed a major reaction channel of the carbenium ions. Addition of ionic interceptors, e.g., NH_3, causes a sharp decrease in the *G* value for the alkylation. As an example, addition of NH_3 (10 torr) to a gaseous system containing n-C_4H_{10} (710 torr) and C_7H_8 (1.0 torr) causes the *G* value for the formation of butyltoluenes to drop to 0.06, consistent with the ionic nature of the alkylation process.

Table I gives the relative yields of the identified products, the isomeric composition of the alkylated arenes, and the apparent ratio of the specific rate constants, k_T/k_B, deduced from the competition experiments. The major experimental features can be summarized as follows. (i) Alkylation of benzene and toluene with $C_4H_9^+$ ions, directly obtained from the radiolysis of n-C_4H_{10} or from the reaction of radiolytically formed H_3^+ ions with n-C_4H_{10}, gives exclusively *sec*-butylarenes, without detectable amounts of *n*-, iso-, or *tert*-butyl derivatives. Alkylation of *o*-xylene also gives predominantly (>97%) *sec*-butylxylenes, accompanied by traces (<3%) of *tert*-butylxylenes. (ii) Predominant (ca. 70%) ortho–para orientation occurs in the sec-butylation of toluene at high pressure, with a para:$^1/_2$ meta ratio of ca. 1.7. Increasing meta orientation is observed at lower pressures, reaching almost 50% at 70 torr. (iii) The apparent k_T/k_B ratio is near to unity in the pressure range investigated.

Butane CI Mass Spectra of Benzene and Toluene. The spectra were recorded in the pressure range from 0.1 to ca. 0.5 torr, at a ion-source temperature of 150 °C. Owing to instrumental limitations, in particular to the uncertainty in the measurement of the ion-source pressure, the results must be regarded as essentially qualitative. Nevertheless, the qualitative trends observed are of value for the following discussion. $C_4H_9^+$ is by far the most abundant (>90%) ion from pure butane in the pressure range investigated. On addition of traces (0.4 mol %) of C_6H_6 or C_7H_8, one observes formation of the correspondent protonated, $(M + 1)^+$, and alkylated, $(M + 57)^+$, species, whose intensity ratios at any given pressure depend significantly on the nature of the substrate.

Typically, at a pressure (very roughly) estimated around 0.3 torr, the $(M + C_4H_9)^+/(M + H)^+$ ratio is 0.90 for C_6H_6 and 0.21 for toluene. It is worth noting that the abundance of the $C_7H_7^+$ ion from toluene is very low (less than 2% of the protonated species), despite the exothermic character of the hydride ion abstraction by s-$C_4H_9^+$ from the side chain of C_7H_8.

Discussion

The Reagent. Radiolytic and mass spectrometric studies[9,10] indicate that butyl ions are formed in the irradiation of butane, either directly

$$n\text{-}C_4H_{10} \rightarrow C_4H_9^+ + H + e^- \tag{1}$$

or via fast, exothermic hydride ion transfer from butane to fragment ions, R^+ ($R = C_2H_3, C_2H_5, C_3H_7$, etc.)

$$R^+ + n\text{-}C_4H_{10} \rightarrow RH + C_4H_9^+ \tag{2}$$

The occurrence of processes (eq 2) can be directly observed in the CI mass spectrum of pure n-C_4H_{10}, from the gradual disappearance of the fragment ions in favor of the one at *m*/*e* 57, as the pressure of the alkane is raised. In a similar fashion, irradiation of diluted solutions of n-C_4H_{10} in H_2 leads to formation of butyl ions, either directly

$$H_3^+ + n\text{-}C_4H_{10} \rightarrow C_4H_9^+ + 2H_2 \tag{3}$$

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or via reaction 2, as well established by radiolytic and mass spectrometric studies.[11-13]

Neither energetic considerations nor kinetic mass spectrometric evidence dictate that butyl ions from processes 1–3 must originally possess the secondary structure II.

$$\underset{\text{I}}{CH_3CH_2CH_2\overset{+}{C}H_2} \quad \underset{\text{II}}{CH_3\overset{+}{C}HCH_2CH_3} \quad \underset{\text{III}}{(CH_3)_3C^+}$$

On the contrary, there is evidence[14] for the occurrence of a fast I → II isomerization, exothermic[15] by 18 kcal mol^{-1}. In the presence of butane, the isomerization can take place intermolecularly via process 2, when $R = n\text{-}C_4H_9$.

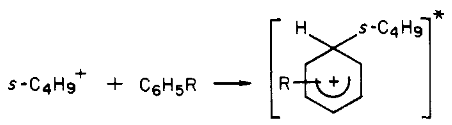
However, intramolecular isomerization cannot be excluded and must be specifically invoked when *n*-butyl ions are formed in systems containing higher alkanes, e.g., pentane. In any case, the failure to detect n-butylated products shows that the I → II isomerization is complete before a reactive encounter with the aromatic substrate can occur, i.e. within 10^{-8}–10^{-7} s.

In contrast, no appreciable II → III isomerization takes place, despite the higher stability[15] of III, $H_f° = 167$ kcal mol^{-1} with respect to II, $H_f° = 183$ kcal mol^{-1}, as shown by the negligible yield of tert-butylated products. This cannot be traced to the scarce reactivity of the arenes toward III, since at least toluene and *o*-xylene were shown to efficiently condense with *tert*-butyl ions in the gas phase.[2,5] Consequently, the present results show that II must survive for at least 10^{-8}–10^{-7} s in butane or H_2, without appreciable rearrangement to III.

This finding can be rationalized on the grounds that isomerization I → II requires, only a H^- shift, while process II → III involves a carbon skeleton alteration, with a methyl group shift.

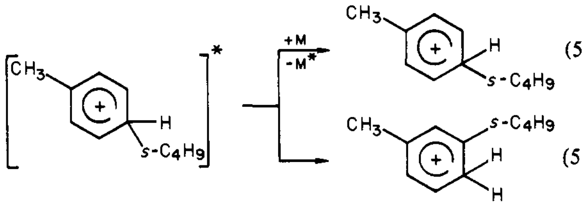
The present results corroborate previous mass spectrometric[16,17] and radiolytic[10] evidence pointing to the stability of II in the gas state, in contrast with its facile isomerization to III observed in solution.[18] In conclusion, under the conditions prevailing in the present study, the alkylation, whose ionic character is ensured by the presence of a radical scavenger and demonstrated by the dramatic effects of NH_3 on the yields, is carried out by *sec*-butyl cations, generated via processes 1–3 and thermalyzed by a large number of unreactive collisions with the bath gas molecules, before attacking the aromatic substrate. The reagent involved is energetically and structurally well-defined, as a result of mass spectrometric[15] and theoretical[19,20] investigations.

The Alkylation Process. Several exothermic reaction channels are open to the *sec*-butyl cation in its attack on the substrate. In particular, the condensation process (4) is characterized[21] by a



(4)

ΔH° value of ca. −22 kcal mol^{-1} in the case of benzene. The excited arenium ions undergo collisional deactivation or isomerization to a more stable structure, e.g., eq 5, the competition being



(5a)

(5b)

regulated by the density and the nature of the third body. Eventually, the arenium ions loose a proton to a gaseous base contained in the system, yielding the observed *sec*-butylarenes.

In addition to condensation, proton-transfer and hydride ion abstraction processes need to be considered. Protonation of the aromatic substrate

$$s\text{-}C_4H_9^+ + C_6H_5R \rightarrow C_4H_8 + C_6H_6R^+ \qquad (6)$$

is almost thermoneutral or slightly endothermic for benzene, depending on the particular C_4H_8 alkene formed, and exothermic for toluene.[22]

The difference between the two substrates is clearly brought out by their butane CI mass spectra, where the $C_6H_7^+$ ion is a minor species, comparatively much less (<1:5) abundant than its $C_7H_9^+$ counterpart at the same C_4H_{10} pressure. Abstraction of a hydride ion from toluene by the *sec*-butyl ion

$$s\text{-}C_4H_9^+ + C_6H_5CH_3 \rightarrow n\text{-}C_4H_{10} + C_6H_5CH_2^+ \qquad (7)$$

is energetically allowed,[23] with a $\Delta H°$ value of −12 kcal mol^{-1}, and could represent an additional competitive process with respect to alkylation of toluene. However, from the extremely low abundance of the $C_7H_7^+$ ions in the n-C_4H_{10} CI mass spectra of toluene, it appears that process 7 is insignificant in comparison to alkylation (eq 4) and especially to protonation (eq 6).

Positional and Substrate Selectivity. A word of caution is required before discussing the positional selectivity data concerning toluene. There are secondary isomerization processes (eq 5b) that affect the initial (kinetically controlled) population of the arenium ions, in favor of the thermodynamically most stable isomer, the meta-substituted methyl-*sec*-butylbenzenium ion. The kinetically most significant data are those measured at the higher pressures, which are likely to reflect most faithfully the original selectivity of the electrophile, owing to the efficiency of collisional stabilization. The isomeric distribution emerging from the experiments carried out in the range from 715 to 750 torr is typical of gas-phase aromatic substitution by moderately stable carbenium ions, in particular it is very close to that measured in the gas-phase alkylation of toluene with free s-$C_3H_7^+$ ions, namely, 46% ortho, 30% meta, and 24% para, measured in propane at 720 torr.[5,24] Consequently, the steric requirements of the free, unsolvated *sec*-butyl cation appear, as expected, very close to those of s-$C_3H_7^+$, as shown in particular by the extent of ortho-substitution, only slightly higher for the latter reagent.

The pressure dependence of the isomeric composition of products is also very similar for s-$C_4H_9^+$ and s-$C_3H_7^+$, as shown by the para:$^1/_2$ meta ratio, that passes from 1.7 at 715 torr to 0.9 at 70 torr in the *sec*-butylation and from 1.5 at 720 torr to 0.9 at 50 torr in the isopropylation. The substrate selectivity, characterized by a k_T/k_B ratio near to or even lower than unity, similar

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(21) Value arrived at from $H_f°$ of *sec*-butylbenzenium ion = 181 kcal mol^{-1}, calculated by assuming that the PA of the ipso position of *sec*-butylbenzene corresponds to that of an unsubstituted position of benzene. The latter is taken as 180 kcal mol^{-1}, according to: (a) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445–476. The $H_f°$ value of *sec*-butylbenzene was taken from: (b) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.

(22) Taking into account the PA of benzene,[21a] the $H_f°$ value of s-$C_4H_9^+$[15] and those of 1-butene, *cis*-2-butene, and *trans*-2-butene, the proton transfer (6) appears to be almost thermoneutral if *trans*-2-butene is formed and slightly endothermic if 1-butene and *cis*-2-butene are formed. The thermoneutral character of the process is also confirmed by the PA of *trans*-2-butene, 180 kcal mol^{-1}, given by: (a) Shuang-Ling Chong; Franklin, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 6347–6351. The higher PA of toluene, 188.5 kcal mol^{-1} [21a] makes process 6 exothermic in all cases.

(23) Value calculated from the $H_f°$ value of $C_6H_5CH_2^+$, corresponding to 213 kcal mol^{-1}, according to: (a) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3290–3294; (b) Rossi, M.; Golden, D. M. *Ibid.* **1979**, *101*, 1230–1235.

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to those measured in other gas-phase alkylations[6] is prima facie inconsistent with the clear electrophilic character of the substitution. Such an apparent anomaly is easily removed if one considers the alternative reaction pathway, i.e., protonation (eq 6), that competes with alkylation (eq 4) and whose efficiency is largely different for the two substrates, as suggested by energetic considerations and demonstrated by the CI experiments. Indeed, taking into account that a much larger fraction of the *sec*-butyl ions undergoes proton transfer to toluene than to benzene, the correct order of overall nucleophilic reactivity of the two substrates is largely restored. However, its precise determination remains difficult, since quantitative extension of the CI data to the radiolytic experiments, carried out at much higher pressures, would be undoubtedly arbitrary.

Comparison with Solution Chemistry Results. In the specific case of *sec*-butylation there are very few data from the enormous body of experimental work concerning the Friedel–Crafts reactions of butenes, butanols, butyl halides, and other precursors of the *sec*-butyl cation that can be regarded as kinetically significant. Reaction of *n*- and *sec*-butyl chloride with benzene, catalyzed by $AlCl_3$, yields *sec*-butylbenzene as the major, and frequently the only, alkylated product, sometimes accompanied by smaller amounts of isobutylbenzene.[25] Alkylation of benzene with *n*-butyl alcohol in the presence of BF_3 also gives *sec*-butylbenzene.[26] Alkylation of benzene and toluene with sec-butyl alcohol, catalyzed by $AlCl_3$, H_2SO_4, polyphosphoric acid, etc., investigated in CH_3NO_2 under conditions (low temperatures, <25 °C, low concentrations of the catalyst, low conversions) designed to reduce secondary isomerization, yields exclusively *sec*-butylarenes without appreciable amounts of iso- and *tert*-butyl derivatives.[27] All these solution chemistry results are analogous to those obtained in the gas phase as to the nature of the butylated product(s). The isomeric composition of the *sec*-butyltoluenes formed under conditions that limit secondary isomerization,[27] namely, ortho:meta:para $\simeq$ 40:20:40, is also reasonably close to that measured in the gas phase in the high-pressure range.

Isomerization occurs in solution at higher temperatures and/or catalyst concentrations, leading to a "thermodynamically" controlled orientation, with up to 70% of the meta isomer.

The trend is qualitatively analogous to that observed at low pressures in the gas phase, except for the effects of solvation, which increase the intrinsic steric requirements of the alkyl ion and lead to a much lower proportion of the ortho isomer, whose percentage drops to less than 5% in the solution chemistry experiments carried out under "isomerizing" conditions.[27]

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Phosphine Substitution in (η^5-Cyclopentadienyl)bis(triphenylphosphine)cobalt(I): Evidence for a Dissociative Mechanism

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Abstract: The substitution of trimethylphosphine for triphenylphosphine in (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt(I) (**1**) to form (η^5-cyclopentadienyl)(trimethylphosphine)(triphenylphosphine)cobalt(I) was studied at −60 °C by NMR spectrometry. Kinetic measurements show the process to be first order in **1** and zero order in PMe_3; added PPh_3 strongly inhibits the reaction rate. This information indicates the reaction proceeds by rapid reversible phosphine dissociation through the unsaturated $CpCo(PPh_3)$ intermediate. The rate for generation of that intermediate, k_1, is 1.15×10^{-3} s^{-1} while the ratio of rate constant k_2 (for conversion of intermediate to products) to k_{-1} (return to starting materials) is 4 at −60 °C. Possible structures for CpCo(L) are discussed in light of recent indications that the linear structure has a triplet ground state.

Introduction

It has been known for almost 20 years that rapid ligand exchange in $CpCo(CO)_2$ and $CpRh(CO)_2$ occurs by an associative (S_N2) mechanism[1,2] rather than by dissociation of a carbonyl group to give a (possibly linear) CpMCO intermediate. Although there was some indication initially[3] that CpCo(CO) could be produced on photolysis of $CpCo(CO)_2$, recent evidence indicates[4] that the products of this irradiation are $CpCo(CO)N_2$ and η^3-$CpCo(CO)_3$.

It seems possible[5] that the apparent difficulty of generating d^8 complexes having CpML structures (especially in thermal reactions) might be due to the fact that such complexes are forced by symmetry[6] to have open-shell electronic configurations (a

Table I. Observed Rate Constants for the Reaction of PMe_3 with $CpCo(PPh_3)_2$ in the Presence of Added PPh_3 at −60 °C

$[1]^a$	$[PMe_3]^a$	$[PPh_3]^b$	k_{obsd}, s^{-1}
0.02	0.012	0.000	1.12×10^{-3}
0.02	0.013	0.025	1.12×10^{-3}
0.02	0.012	0.076	1.14×10^{-3}
0.02	0.012	0.307	2.06×10^{-4}
0.02	0.013	0.757	1.65×10^{-5}

[a] In mol/L. [b] Concentration of triphenylphosphine-d_{15} in mol/L. Deuterated material used to avoid swamping the NMR receiver by the triphenylphosphine proton signals.

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