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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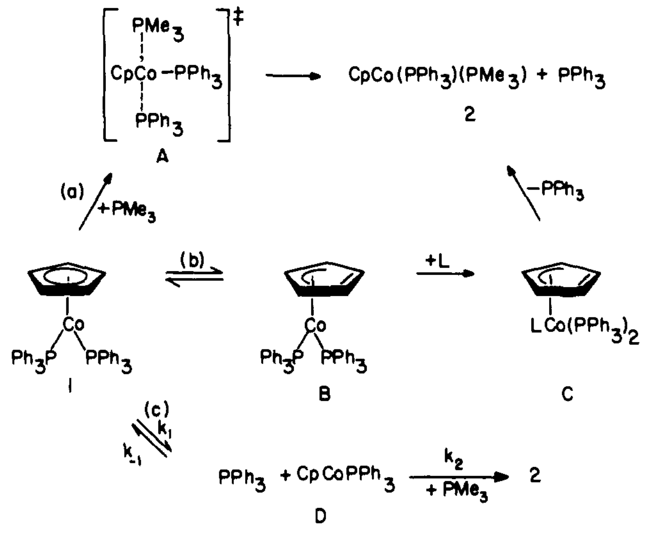
Scheme I



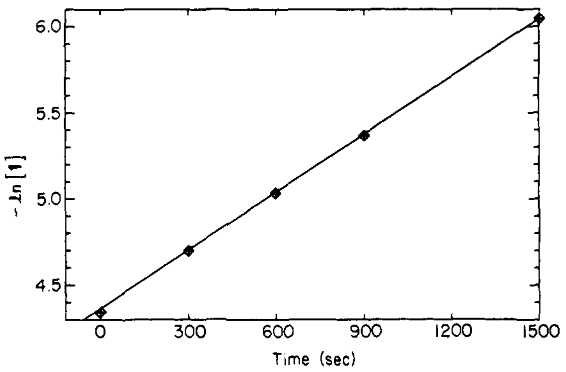


Figure 1. A plot of $-\ln$ [**1**] vs. time for the reaction of **1** with PMe$_3$ at -60 °C.

similar problem exists with d^2 Cp$_2$ML complexes[7]). If this is so, the CpCo(CO)$_2$ displacement discussed above may not be an isolated example, and other CpML$_2$ complexes should also find ways to avoid dissociative mechanisms for ligand replacement. We decided to test this hypothesis by examining the mechanism of ligand replacement in CpCo(PPh$_3$)$_2$ (**1**), a material quite closely related to CpCo(CO)$_2$. In contrast to results obtained on the latter complex, we have found there is apparently no energetic problem with dissociative ligand replacement in the bis(phosphine) **1**.

Results and Discussion

Complex **1** reacts cleanly with trimethylphosphine in toluene-d_8 to form the mixed complex **2** and PPh$_3$ (Scheme I). The reaction is so rapid that it is necessary to cool the reaction vessel to -60 °C in order to follow the conversion of starting material to products with the use of conventional NMR techniques. A second-order plot of ln ([PMe$_3$]/[**1**]) vs. time shows significant curvature, but a first-order plot of $-\ln$ [**1**] vs. time is nicely linear (Figure 1), indicating that the reaction is first order in [**1**] and zero-order in [PMe$_3$]. As shown in Figure 2 and Table I, the reaction rate is also strongly inhibited by added triphenylphosphine.

Three classic mechanisms, two associative and one dissociative, are shown in Scheme I. Mechanism a should exhibit bimolecular kinetics under all conditions and therefore cannot be operating. Mechanism b would give a rate law which could, under some conditions, be first order in [**1**] and zero order in [PMe$_3$]. However, if this mechanism were operative, inhibition by PPh$_3$ could be produced only by buildup of significant quantities of a complex such as C (L = PPh$_3$). No evidence for this complex was detected during the course of our NMR experiments.[8]

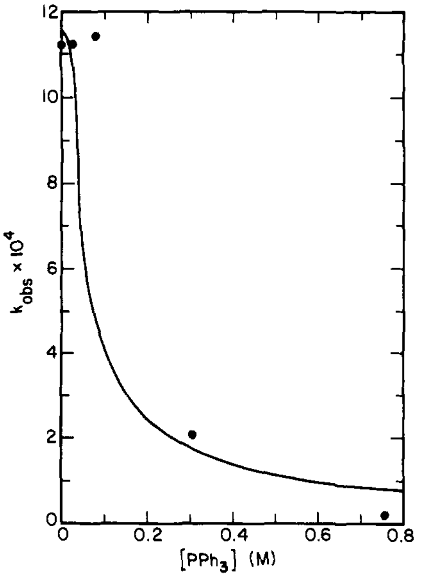


Figure 2. A plot of (k_{obsd}) vs. [PPh$_3$] for the reaction of **1** with PMe$_3$. Solid circles are experimental points; the curve is k_{obsd} calculated by assuming $k_1 = 1.15 \times 10^{-3}$ s^{-1} and $k_2/k_{-1} = 4$.

The simple dissociative mechanism outlined as path c in Scheme I gives the rate law shown in eq 1. At low [PPh$_3$] this should

$$R = \frac{k_1k_2[\mathbf{1}][\mathrm{PMe_3}]}{k_{-1}[\mathrm{PPh_3}] + k_2[\mathrm{PMe_3}]} \qquad (1)$$

reduce to a first-order rate law; as addition of PPh$_3$ increases the importance of the initial term in the denominator, inhibition should set in, as is observed. The form of the rate decrease can be modeled easily. Figure 2 shows the k_{obsd} vs. [PPh$_3$] data obtained and the best-fit curve calculated by using eq 1. The fit illustrated is obtained with $k_1 = 1.15 \times 10^{-3}$ s^{-1} and $(k_2/k_{-1}) = 4$. This value for k_1 corresponds to an activation free energy (ΔG^{*}) of 15.2 kcal/mol at -60 °C.

The intermediate involved in these substitutions undoubtedly has the empirical formula CpCo(PPh$_3$). However, the precise structure of this intermediate is not yet clear. The symmetry and d-orbital configuration of CpCo(PPh$_3$) is such that the simple *linear* complex has two degenerate highest occupied molecular orbitals which are only partially filled; i.e., the ground state of this species is predicted to be a triplet.[6] The presence of such an electronic structure in the transition state of a concerted pericyclic organic reaction indicates that a level crossing is encountered in the MO correlation diagram for the process; this normally is manifested in a high activation energy barrier.[9] Whether such barriers necessarily exist in organotransition-metal reactions, where filled and unfilled d-orbitals normally lie close together in energy, is not clear. What *is* clear from our data is that substitution is an especially facile process in CpCo(PPh$_3$)$_2$. Therefore, either (a) linear CpCo(PPh$_3$) is an intermediate in the reaction and its electronic configuration does not destabilize it appreciably or (b) the substitution reaction avoids the linear intermediate by some means, for example, by remaining in a bent configuration. Further (and more ingenious) experiments will be required to distinguish between these possibilities.

Experimental Section

General Data. All manipulations of oxygen- or water-sensitive materials were conducted under a prescrubbed recirculating atmosphere of N$_2$ in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or by using standard Schlenk or vacuum line techniques.

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$CpCo(PPh_3)_2$,[10] $CpCo(PPh_3)(PMe_3)$,[11] PMe_3,[12] and PPh_3-d_{15}[13] were all prepared by previously published methods. Toluene-d_8 was vacuum transferred from a purple sodium/benzophenone/tetraglyme ketyl solution.

NMR Experiments. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a high-field (180.09-MHz) instrument equipped with a Bruker magnet, Nicolet Technology Corp. Model 1180 data system and electronics assembled by Mr. Rudi Nunlist (U.C., Berkeley). Spectra were recorded at -60 °C, the probe being maintained at that temperature by a precooled nitrogen stream.

NMR experiments were carried out as follows. Various amounts of PPh_3-d_{15} (see Table I) were weighed into standard 5-mm NMR tubes fused to 14/20 ground-glass joints. The sample tubes were taken into the drybox and each prepared in the following manner. A standard solution of $CpCo(PPh_3)_2$ was prepared by dissolving 0.052 g (0.080 mmol) of that compound in 2.00 mL of toluene-d_8; 0.250 mL of that solution was transferred into each NMR tube by syringe. Toluene-d_8 was added to the tubes to bring the total volume of the solution in each tube to 0.50 mL. In turn, each tube was capped with a Teflon needle valve, taken out of the drybox and placed on a vacuum line. The samples were degassed by three freeze-pump-thaw cycles on the vacuum line and charged with PMe_3 while frozen at −196 °C. The phosphine was added by expansion into a 25.85-mL known volume bulb (above the sample tube) to a pressure of 4.79 torr (as measured by using an MKS Baratron capacitance manometer) followed by vacuum transfer of the contents of the bulb into the NMR tube. The tube was sealed with a flame and stored at −196 °C until ready for use. At that time, the tubes were thawed at −78 °C and shaken at that temperature before being dropped into the precooled NMR probe. Spectra were taken under computer control until completion of each reaction.

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Complete Substitution Stereochemistry of Solvolysis of 1-Methyl-2-adamantyl Tosylate and 4-Methyl-*exo*- and 4-Methyl-*endo*-4-protoadamantyl 3,5-Dinitrobenzoate

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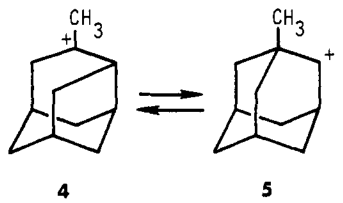
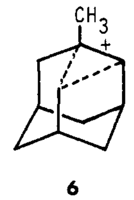
Abstract: Formation of 1-methyl-2-adamantanol in the solvolysis of 1-methyl-2-adamantyl-*4-d* tosylate (**14**-OTs/**15**-OTs), 4-methyl-*exo*-4-protoadamantyl-*5-d* 3,5-dinitrobenzoate (**10**-ODNB/**11**-ODNB), and 4-methyl-*endo*-4-protoadamantyl-*5-d* 3,5-dinitrobenzoate (**12**-ODNB/**13**-ODNB) in 60% aqueous dioxane has been found in each case to occur with >97% stereoselectivity. The pathway without rearrangement (from **14**-OTs/**15**-OTs) produces retention of configuration, while the routes involving rearrangment (from **10**-ODNB/**11**-ODNB and **12**-ODNB/**13**-ODNB) afford inversion of configuration at the migration origin. Concurrent displacement with rearrangment from the 1-methyl-2-adamantyl reactant proceeds with migration only of the substituted bridge backside to the tosylate. These and earlier published data constitute a complete stereochemical description of representative solvolysis of the title reactants. The new results strongly complement previous evidence for a bridged cation intermediate, **6**.

Introduction

The 4-alkyl-4-protoadamantyl and 1-alkyl-2-adamantyl systems are closely connected in solvolysis.[1-8] 4-Methyl-*exo*-4-protoadamantyl 3,5-dinitrobenzoate (**1**-ODNB) and 1-methyl-2-adamantyl tosylate (**2**-OTs) are hydrolyzed in 60% acetone[4] and in 60% dioxane[8] to comparable mixtures of the two corresponding alcohols plus 4-methylprotoadamantene and 4-methyleneprotoadamantane, and the same products are formed from 4-methyl-*endo*-4-protoadamantyl 3,5-dinitrobenzoate (**3**-ODNB)[4,8] (Scheme I). The Wagner-Meerwein related carbenium ions, **4** and **5**, derived from these reactants would be expected to be similar in energy, since the more stable charge locus[9] in **4** weighs against the relatively strain-free tricyclic constitution[10] of **5**. This balance raises the possibility that a single-bridged ion, **6**, may be favored over an equilibrium between the two localized ions.



4 **5**



6

Schleyer and co-workers[4,5] in 1974 presented detailed evidence for the direct formation of **6** in the aqueous acetone solvolysis of both **1**-ODNB and **2**-OTs. *endo*-Protoadamantyl reactant **3**-ODNB was considered also to react via **6** following unassisted ionization. These conclusions were based on product, kinetic, stable-ion, and stereochemical results, including the exclusive formation of exo alcohol **1**-OH over the epimeric **3**-OH, an observation subsequently made also for aqueous dioxane by Majerski et al.[8] Complementary rate and product data for other 1-substituted adamantyl tosylates were reported by Lenoir in 1973.[2,3]

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