Attempts to prepare tris(chloromethyl)oxonium ion from **1** and bis(chloromethyl) ether[6] gave only **12**. Seemingly **1** attacks preferentially the chloromethyl ethers to form **13a,b**, which then easily ionizes to **11** or **12** and CH_2Cl_2.

$XCH_2OCH_2\overset{+}{Cl}CH_2Cl$

13a, X = H

13b, X = Cl

The demonstration of the formation of chloromethylhalonium ions and their effective chloromethylating ability opens up the question of the possible chloromethylating ability of related precursors, including methylene chloride, which, consequently, could be of a carcinogenic nature. We are carrying out further studies relating to the in vitro chloromethylating ability of these systems.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

References and Notes

(1) For part 18, see G. A. Olah, D. J. Donovan, H. C. Lin, H. Mayr, P. Andreozzi, and G. Klopman, *J. Org. Chem.*, **43**, 2268 (1978).

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(5) G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **89**, 2993 (1967).

(6) This highly carcinogenic compound should be handled with great care: *J. Natl. Cancer Inst.*, **43**, 481 (1969). All operations involving chloromethyl ethers were carried out in an efficient "carcinogenic hood" with appropriate precautions.

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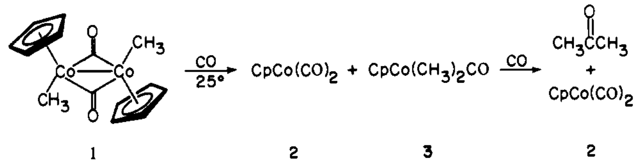
Reaction of a Bridged Binuclear Dialkylcobalt Complex with Carbon Monoxide and Phosphines. Observation of Competing Inter- and Intramolecular Metal to Metal Methyl Transfer

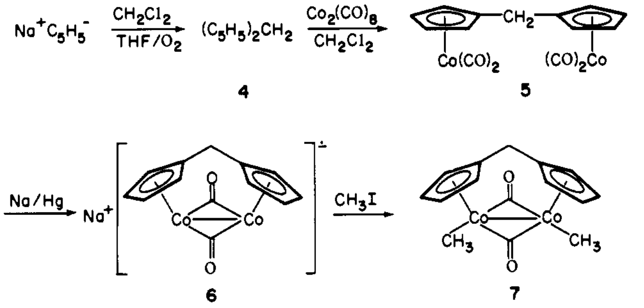
Sir:

Bis(η^5-cyclopentadienylcarbonylmethylcobalt) (**1**) reacts rapidly with carbon monoxide at ambient temperature, leading to a quantitative yield of η^5-cyclopentadienyldicarbonylcobalt (**2**) and acetone (Scheme I), a process in which a binuclear transition metal complex mediates the formation of two new carbon-carbon bonds. In a previous study,[1] we established that η^5-cyclopentadienylcarbonyldimethylcobalt (**3**) is an intermediate in this transformation. Labeling studies indicated that an intermolecular process was occurring, resulting in the formation of substantial amounts of acetone-d_3 upon carbonylation of equimolar mixtures of **1**-d_6 and **1**-d_0.

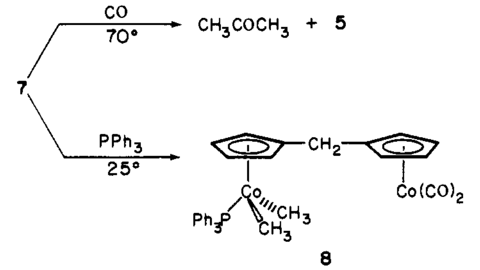
Scheme I



Scheme II



Scheme III



To determine whether this intermolecular process is on the direct pathway leading from **1** to **3**, we have now prepared **7** (Scheme II), a complex analogous to **1**, but having its two cyclopentadienyl rings joined by a methylene group. We find this structural modification allows us *to control the intramolecularity of the carbonylation reaction* by modifying reaction conditions. In addition, **7** undergoes a remarkable reaction with phosphines which sharply restricts mechanistic alternatives for these reactions.

Dicyclopentadienylmethane (**4**) was prepared[2] as a mixture of isomers and converted into the binculear tetracarbonyl **5** by the route outlined in Scheme II. As might be expected if decomposition of **1** involves initial dissociation into mononuclear fragments, complex **7** is less reactive than **1**, and requires temperatures near 70 °C to achieve carbonylation at a reasonable rate. Under these conditions, the chemistry of **7** is quite comparable with that of **1**, and acetone and tetracarbonyl complex **5** are produced in quantitative yield. Unlike **1**, however, the carbonylation can be made to follow a predominantly intra- or intermolecular pathway by varying the concentration

Table I. Isotope Labeling Data Obtained in Crossover Experiments on the Reaction of Mixtures 7-d_0 and 7-d_6 with CO and PPh_3

starting complex									
total concn, M	7-d_0, %	7-d_6, %	entering ligand	T, °C	acetone products,[a] %			molecularity	
					d_0	d_3	d_6	% intra-	% inter-
0.25	53	47	CO[b]	70	40	28	32	44	56
0.05	55	45	CO[b]	70	52	5	43	90	10
0.25	46	54	PPh_3[c]	25	38	16	46	67	33
0.05	49	51	PPh_3[c]	25	49	1	50	98	2
0.25	69	31	PPh_3[c]	70	69	3	28	93	7

[a] In the carbonylation reactions, where acetone was formed as direct product, it was either isotropically analyzed by GC/MS or purified by preparative GC and then subjected to subsequent MS analysis. In the PPh_3 reaction, product **8** was first diluted to a concentration $\leq$0.05 M and then carbonylated to generate acetone for analysis (the run at 0.05 M **7** precludes the possibility of significant label scrambling during the carbonylation of **8** at these concentrations). [b] Toluene solvent. [c] Benzene solvent.

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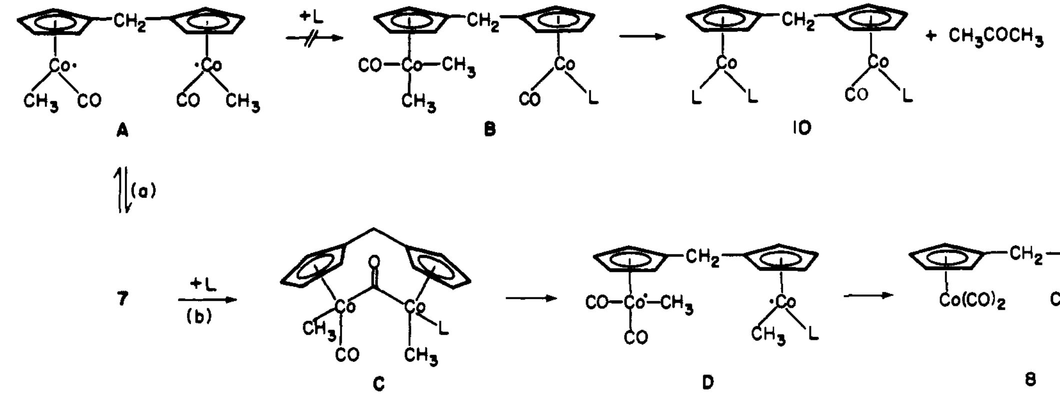
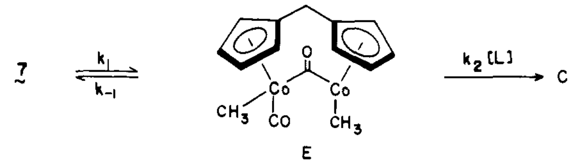
Scheme IV



Scheme V



$$k_{obs} = \frac{-d[\mathbf{7}]}{dt} = \frac{k_1[L]}{(k_{-1}/k_2)+[L]}$$

of starting complex **7**. Thus, as shown in Table I, approximately equimolar mixtures of **7**-d_0 and **7**-d_6 (labeled methyl groups) at 0.05 M total concentration of **7** gives acetone in a reaction which is 90% intramolecular. At saturation (0.25 M), however, 44% of the reaction takes place by an intermolecular path, presumably analogous to that[1] occurring in **1**.

Treatment of **1** with triphenylphosphine gave a complicated reaction, leading to lowered (but still significant) yields of acetone, as well as several carbonylphosphine complexes. We believe this is partly due to the fact that the rate of reaction of **1** with phosphine is comparable with that of its spontaneous thermal decomposition. In contrast, complex **7**, stable at room temperature in solution, reacted at a convenient rate with triphenylphosphine, giving a very clean reaction. This led to *no* acetone. Only one product was formed, an organometallic complex which had infrared absorptions in the metal carbonyl region (2015, 1958 cm^{-1}; THF) very similar[3] to that of $CpCo(CO)_2$, and NMR absorption in the methyl region (δ 0.40, d, J = 6 Hz (C_6D_6)) very similar[4] to that of $CpCo(CH_3)_2PPh_3$ (**9**). Isolation and characterization by standard methods demonstrated that this complex has structure **8** (Scheme III). In analogy to the carbonylation of **9**, heating **8** with CO led to acetone and tetracarbonyl complex **5**.

Despite the cleanliness of the reaction of **7** with PPh_3 and its quantitative yield, *the intramolecularity of the reaction is still dependent upon the concentration of starting complex*, just as in the carbonylation. Data once again obtained with mixtures of **7**-d_6 and **7**-d_0 are summarized in Table I.

The two most reasonable mechanistic alternatives for these processes are outlined in Scheme IV. Our initial hypothesis (path a) involved unbridging both carbonyls followed by metal-metal bond cleavage (as observed with **1**), to give intermediate A, However, reaction of A with an entering ligand, followed by methyl transfer from one metal to the other, simply cannot be the route to product (at least in the reaction of **7** with PPh_3), because this would lead to B, and B must necessarily give[1] complex **10** and acetone. In fact the appearance of two CO groups bound to one cobalt in the product of the PPh_3 reaction, in a system where the mixed phosphinecarbonyl is known to be more stable,[5] *requires that one cobalt atom retain its bonding to both carbonyls during the entire reaction*. This restrictive requirement leaves little reasonable alternative other than path b, at least in general outline. Here metal-metal cleavage must preserve one carbonyl bridge, giving bis-18-electron complex C.[8] Cleavage of the remaining metal-carbonyl bond must occur now only at the "right-hand" metal atom, leading to D. In the intramolecular process, this intermediate transfers a methyl radical from the formally 19-electron cobalt to its 17-electron neighbor, leading to **8**. At high concentrations, the methyl group may be transferred to a 17-electron cobalt in another molecule of D, generating intermolecular product.[6]

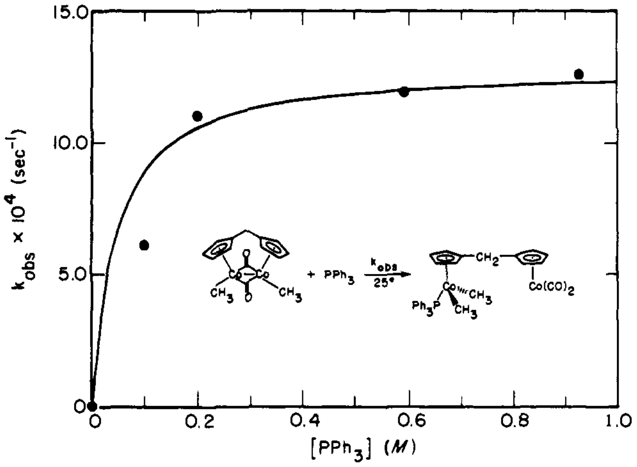


Figure 1. Dependence of the pseudo-first-order rate constant for reaction of **7** with excess PPh_3 upon the concentration of PPh_3.

Kinetic studies provide further details concerning the intimate mechanism of the first step of this reaction scheme. Two distinct possibilities exist for the generation of species C: either **7** and phosphine react in a direct associative process or reaction proceeds through an unstable unsaturated intermediate, such as E, which is then trapped by phosphine to yield C. The dependence of the reaction rate upon phosphine concentration dramatically confirms the latter hypothesis. Reactions of **7** with excess phosphine show pseudo-first-order kinetics in the conversion of **7** into **8**. As $[PPh_3]$ is raised from relatively low absolute concentrations, the observed reaction rate becomes independent of phosphine (Figure 1). This is exactly the behavior expected by the reaction scheme shown in Scheme V. Analysis of the kinetic data yields $k_1 = 1.28 \times 10^{-4}$ s^{-1} and $k_{-1}/k_2 = 4.3 \times 10^{-2}$ M^{-1}.

This study emphasizes that, even when organometallic reactions are kinetically well-behaved and give one product in quantitative yield, it is critically important to carry out crossover experiments to test their intramolecularity. In this case such experiments, combined with the specific nature of the transformation involved, have allowed us to delineate especially sharply the mechanism of a carbon–carbon bond-forming reaction mediated by a binuclear organotransition metal complex.

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(5) Allowing **8** to react with excess PPh_3 under the reaction conditions (sealed tube) yielded the complex analogous to **8** having the $Co(CO)_2$ group replaced by a $Co(CO)(PPh_3)$ group.
(6) An alternative possibility involves methyl transfer from D to a second molecule of **7**, initiating a chain process of the type suggested in ref 1. We cannot rigorously rule out this process; however, no evidence for this type of autocatalysis was evident in our kinetics experiments.
(7) Hertz Foundation Fellow, 1977–present.
(8) NOTE ADDED IN PROOF. A binuclear intermediate very similar to C, also containing a single carbonyl bridge but no metal–metal bond, was observed recently in a study of photosubstitution of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$: Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2753.

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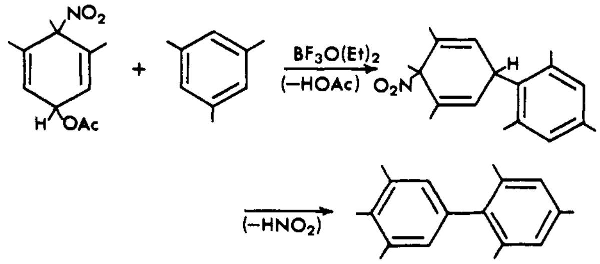
Ipso Nitration. Use of Ipso Nitration Products as Sources of Carbon Electrophiles in Regiospecific Syntheses of Aromatic Derivatives

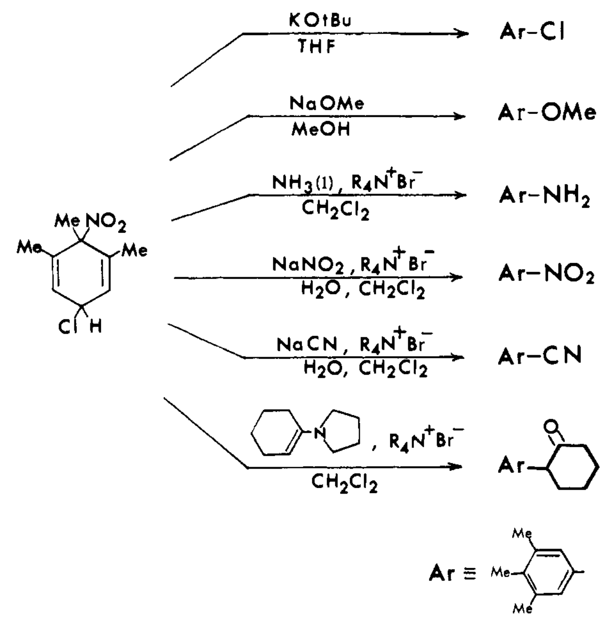
Sir:

Ipso nitration products can be used under conditions of acid catalysis to mount electrophilic substitutions on reactive aromatics.[1-3] The general pattern is exemplified by reaction of 4-nitro-3,4,5-trimethylcyclohexadienyl acetate (**1**) with mesitylene in the presence of boron trifluoride etherate to give the hexamethylbiphenyl derivative in better than 90% yield (eq 1). The more general use of these derivatives as sources of carbon electrophiles requires conversion of the acetate function into a leaving group that does not require strong acid media for activation. One obvious strategy is the conversion of nitrodienyl acetates into nitrodienyl halides. We report here convenient ways to accomplish such transformations and demonstrate the utility of nitrodienyl halides, formal 1,4-adducts of nitryl halides and aromatic, in regiospecific syntheses of a range of aromatic derivatives.



(1)

Scheme I



Compound **1** was readily converted into 4-nitro-3,4,5-trimethylcyclohexadienyl chloride (**2**) by passing a stream of hydrogen chloride through a suspension of **1** in pentane-ether (10:1) for 5 min at −10 °C followed by an additional 5-min reaction period at the same temperature.[4] Colorless, crystalline **2** was isolated in quantitative yield by vacuum evaporation of the solvents and the acetic acid byproduct, mp 61–62 °C dec.[5] Thermal decomposition of **2** at 200 °C yields mainly 1,2,3-trimethylbenzene plus some 5-chloro-1,2,3-trimethylbenzene and 4-nitro-1,2,3-trimethylbenzene. Spectral studies indicate that **2** has a half-life of <60 s upon solvolysis in 50% ethanol,[6] and product studies reveal both 5-hydroxy- and 5-ethoxy-1,2,3-trimethylbenzene with $<1\%$ of the 5-chloro derivative. Reaction of **2** in methanolic sodium methoxide gave 5-methoxy-1,2,3-trimethylbenzene in $>90\%$ yield with trace amounts of the 5-chloro derivative. Reaction of **2** with potassium *tert*-butoxide in tetrahydrofuran gave 5-chloro-1,2,3-trimethylbenzene in 85% yield.

Treatment of methylene chloride solutions of **2** with liquid ammonia gave no significant yield of 5-amino-1,2,3-trimethylbenzene, but, upon addition of tetrabutylammonium bromide to the same reaction mixture, a 78% yield of the 5-amino derivative was obtained. The reaction of a stirred solution of **2** (0.16 M) in methylene chloride with an aqueous solution of sodium nitrite (3.5 M) and tetrabutylammonium bromide (2.5 M) at 0 °C for 6 h gave a 60% yield of 5-nitro-1,2,3-trimethylbenzene. Similarly, the reaction of **2** in methylene chloride with aqueous sodium cyanide and tetrabutylammonium bromide gave 5-cyano-1,2,3-trimethylbenzene in 75% yield. Finally, reaction of **2** with the pyrrolidine enamine of cyclohexanone and tetrabutylammonium bromide gave, after acid hydrolysis, a 50% yield of 5-(2-cyclohexanoyl)-1,2,3-trimethylbenzene. These results are summarized in Scheme I.[7,8]

We have been unable to convert 4-methyl-4-nitrocyclohexadienyl acetate into the corresponding nitrodienyl chloride, but reaction with hydrogen bromide proceeds readily to yield the labile nitrodienyl bromide. Direct reaction of crude preparations of this nitrodienyl bromide in methylene chloride with aqueous sodium nitrite and tetrabutylammonium bromide gives *p*-nitrotoluene in 60% yield, based on nitrodienyl bromide, with no detectable *o*-nitrotoluene.

The loss of nitrite from **1** in aqueous solvents is known to be facile. Strong acid catalysis is required for the departure of

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