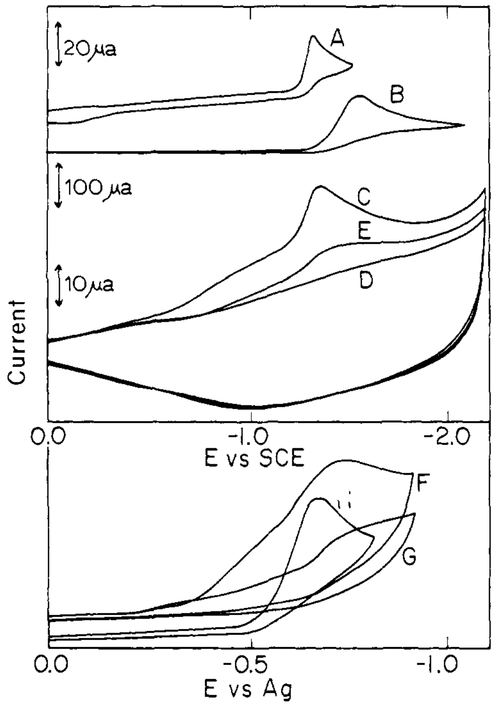

Figure 2. Cyclic voltammograms in 0.2 M Et_4NClO_4/CH_3CN. Curves A,B (0.1 V/s) and H(0.05 V/s) are free $py(CH_3)^+$ on unmodified electrodes. Curves C-E (0.50 V/s) and F, G (0.050 V/s) are $MO_2/py(CH_3)^+$.

by) these data. Given its rectifying properties,[13,14] the observed reoxidation reaction at TiO_2 may be somewhat unusual. We note, however, that the TiO_2 films used may be too thin for development of a full semiconductor space charge, that the reoxidation rate is quite slow, and that chemical modification as used here could introduce new surface states.

$SnO_2/py(CH_3)^+$ electrodes also exhibit a cathodic wave (curve F) ascribable to reduction of I. In this case, three-four repeat scans are required before the current falls to a steady background (curve G). The $SnO_2/py(CH_3)^+$ reduction peak is ~0.010 V negative of that for free $py(CH_3)^+$ (curve H) on unmodified SnO_2. The ESCA N 1s spectrum of reduced $SnO_2/py(CH_3)^+$ confirms reduction of the quaternary nitrogen; the X^- counterion spectrum also disappears. Although oxidations are observed on these heavily doped SnO_2 electrodes,[3] we have not observed reoxidation of a reduced $SnO_2py(CH_3)^+$ electrode to regenerate the cathodic peak of curve F.

The surface population Γ of $MO_2/py(CH_3)^+$ centers is estimable from the charge passed in the cyclic voltammograms for their electrochemical reduction. The estimate is complicated somewhat by the broad background current enhancement[16] which is observed on both electrodes and which vanishes after a reduction cycle. On $TiO_2/py(CH_3)^+$ assuming $n = 1$, $\Gamma = 2.0 \pm 0.2 \times 10^{-9}$ mol/cm^2 and 2.6×10^{-10} mol/cm^2 (average of five electrodes) based respectively on inclusion of, and correction for, this background. The corrected analysis on $SnO_2/py(CH_3)^+$ is 0.8×10^{-10} mol/cm^2. The corrected analysis is quite compatible with a molecular model estimate (~4×10^{-10} mol/cm^2) of monolayer coverage of $py(CH_3)^+$ on the MO_2 surfaces. Surface roughness (factor < 2X estimated by microscopic examination) and unmethylated surface pyridine are partially self-cancelling factors not included in this coverage estimate.

Electroreactivity of I requires a steric "floppiness" of the electroactive center allowing a close approach to the electrode, as the connecting chain is electronically insulating. Neighbor-neighbor steric interferences could thus interfere with the electron transfer event. That I is shown in fact to be electroactive, on two electrode materials, demonstrates that the strategy of immobilizing electron transfer sites on electrodes using flexible yet insulatig molecular architecture can be successful. Other examples of electrochemically active chemically modified electrodes, and a more detailed analysis of the $MO_2/py(R)^+$ electrodes, are subjects of continuing investigations.

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(15) The unusual shape of this background is due to the high sweep rate and current sensitivity plus the electrode's semiconductor properties.
(16) This background current is absent on some specimens and has been observed on modified electrodes bearing other electroactive groups.

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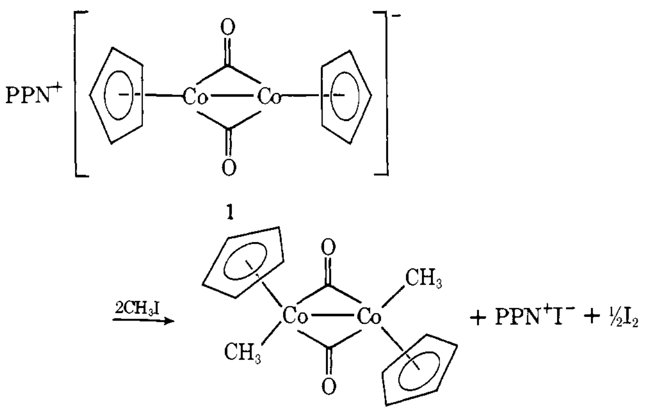
Synthesis of a Doubly Alkylated Binuclear Cobalt Carbonyl Complex. Generation of Acetone, a Process Involving the Formation of Two New Carbon-Carbon Bonds, in Its Thermal Decomposition

Sir:

The past few years have seen the development of several methods for carbon-carbon bond formation which employ mononuclear organometallic complexes as catalysts or stoichiometric reagents; recent mechanistic investigations have begun to elucidate the patterns by which these reagents operate.[1] The field of *binuclear* C-C bond forming processes is much less well-developed (despite the possible relevance of such processes to reactions promoted by clusters and heterogeneous catalysts[2]), partly because of the limited number of complexes available having alkyl groups bound to adjacent metal centers. In connection with this problem, we wish to report the preparation and thermal decomposition of a doubly alkylated binuclear complex (**2**). We find that this material decomposes under mild conditions in a reaction which forms *two* carbon-carbon bonds with surprising efficiency, and report preliminary data that provide an insight into the mechanism of this transformation.

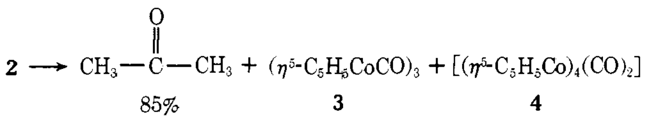
The bistriphenylphosphineiminium salt of bis-(η^5-cyclopentadienyl)dicarbonyldicobalt anion[3] (**1**) reacts completely with 2 equiv of CH_3I in 1 min in THF at room temperature. The IR band of **1** at 1690 cm^{-1} is replaced during this reaction by a bridging carbonyl band at 1820 cm^{-1}. Column chromatography on silica gel under scrupulously air-free conditions[4] allows isolation of a new (thermally very sensitive) neutral complex to which, on the basis of spectral and analytical data (Anal.[5a] Calcd for $C_{12}H_{16}O_2Co_2$: Co, 35.27; C, 50.32; H, 4.83%. Found: Co, 35.09; C, 50.49; H, 4.87%. Molecular weight: calcd, 334, found (cryoscopic in benzene), 341, 343. NMR (THF-d_8): δ −0.72 (6 H); 5.09 (10 H) ppm; (C_6D_6): δ −0.35 (6 H); 4.63 (10 H ppm)) we assign[5b] structure **2**. Presumably 1 equiv of PPN^+I^- and 0.5 equiv of I_2 are also formed in the alkylation.



1

2

In THF or benzene, complex **2** decomposes thermally at room temperature. *The organic product of this reaction is acetone, formed in ≥85% yield.* The organometallic products are cobalt cluster complexes[6] **3** and **4**. In the presence of CO, reaction occurs much more rapidly; acetone is formed once again (100%), and in this case the only other reaction product is η^5-$C_5H_5Co(CO)_2$.



$$2 \longrightarrow \underset{85\%}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + \underset{\mathbf{3}}{(\eta^5\text{-}C_5H_5CoCO)_3} + \underset{\mathbf{4}}{[(\eta^5\text{-}C_5H_5Co)_4(CO)_2]}$$

Monitoring by NMR (Figure 1) or IR shows that acetone formation is not the first observable step in this reaction. A metastable intermediate having a single absorption in the IR at 2010 cm^{-1} and two sharp singlets in the NMR, one in the methyl (THF-d_8, δ 0.42; C_6D_6, 0.67 ppm (6 H)) and one in the cyclopentadienyl (THF-d_8, δ 5.00; C_6D_6, 4.44 ppm (5 H)] region, is formed initially from **2**, and is the source of acetone in a subsequent reaction. Although the intermediate appears to be too unstable to isolate in pure form, it may be generated in the absence of other materials in solution by running the decomposition of **2** under CO and stopping the process before very much acetone appears. Treatment of this solution of the intermediate with PPh_3 gives acetone and η^5-$C_5H_5Co(PPh_3)_2$,[7] which reacts with the η^5-$C_5H_5Co(CO)_2$ present in solution to give η^5-$C_5H_5Co(CO)(PPh_3)$.[8] On the basis of this conversion and the IR and NMR spectra of the intermediate, we assign to it[9] structure **6**.

Both the rate and products of decomposition of **2** are significantly altered by the presence of other ligands. As indicated above, under an excess of CO, **2** decomposes rapidly, leading (via **6**) *only* to acetone and η^5-$C_5H_5Co(CO)_2$. PPh_3 converts **2** to acetone (58%), η^5-$C_5H_5Co(CO)_2$ (<5%), η^5-$C_5H_5Co(CO)(PPh_3)$ (61%), **5**[10] (5%), and η^5-$C_5H_5Co(PPh_3)_2$ (9%).[11]

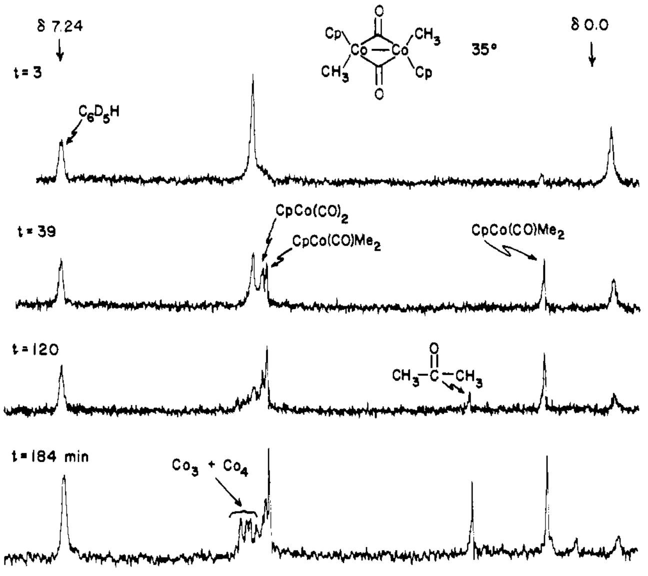
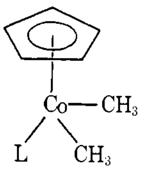


Figure 1. Decomposition of **2** in benzene-d_6, monitored by NMR. Initial concentration = 0.065 M.

The rate of decomposition of **2** is significantly accelerated by added ligand; **6** decomposes somewhat faster as well, but the effect is not large.



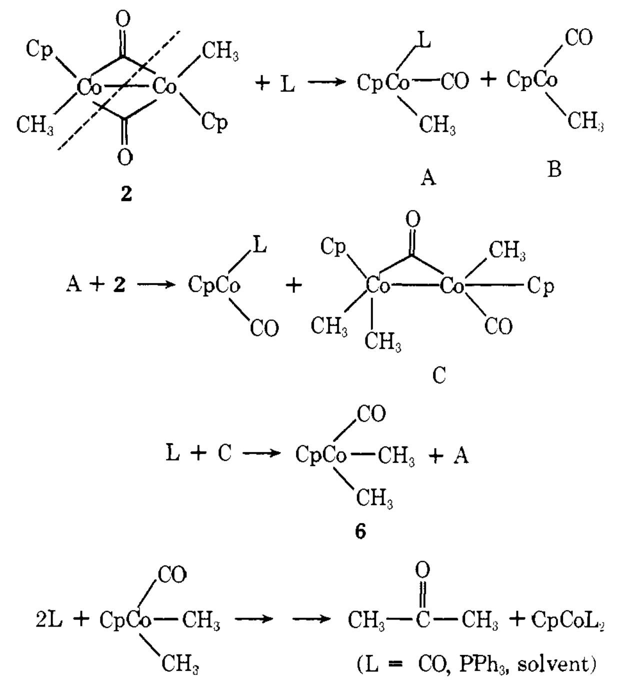
5, L = PPh_3

6, L = CO

The intra- or intermolecularity of the acetone-forming reaction was investigated using the following crossover experiments. A sample containing a mixture of 50% **2** prepared from CH_3I, and 50% **2**-d_6 prepared separately from CD_3I, was allowed to decompose in benzene-d_6 or diethyl ether. After complete decomposition, the acetone product was reduced to isopropyl alcohol by treatment of the crude reaction mixture with $LiAlH_4$ (to prevent adventitious exchange of the acidic acetone α-hydrogens) and the isopropyl alcohol isolated by preparative VPC. Mass spectrometric analysis of this material revealed an isotope distribution of 26 ± 2% d_6, 47 ± d_3, and 27 ± 2% d_0 species. This distribution, along with the absence of significant amounts of d_1, d_2, d_4, and d_5 species, demonstrates that acetone is formed in an *intermolecular* process which involves carbon atom scrambling rather than simple hydrogen exchange. In a second experiment, solutions of pure **2**-d_0 and **2**-d_6 were allowed to react until intermediate **6** was formed, and then mixed. After complete conversion to acetone, the mixture was worked up as described above and found to contain a 47 ± 2% d_0, 7 ± 2% d_3, and 45 ± 2% d_6 isotope distribution. Thus the methyl scrambling process must occur *before*, rather than after, intermediate **6** is generated.

The mechanism of this process is obviously complicated and further studies will be required to elucidate it completely. However, an attractive working hypothesis consistent with our present results is the chain pathway outlined in Scheme I. This postulates initial ligand-induced dissociation of **2** to Co^{II} intermediates A and B. The 19-electron complex A should by a very powerful methyl radical donor; while it is possible that methyl transfer from A to B occurs, attack of A upon a second molecule of **2**, which is present in much higher instantaneous concentration, seems more likely. This generates alkylated complex C, which could decompose (with ligand assistance)

Scheme I



to give intermediate **6** and a molecule of A to continue the chain process.[12]

In conclusion, acetone formation from **2** is a very efficient process, but clearly occurs with concomitant cleavage of the metal-metal bond.[13] We are currently working on the preparation of complexes related to **2** having other alkyl groups; a comparison of their chemical behavior with that of **2** will be reported at a later date.

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(4) The chromatography was carried out inside a Vacuum Atmospheres recycling inert atmosphere box (N_2 atmosphere). Using benzene as eluent, R_f (**2**) = 0.56; other materials formed in this reaction and collected without decomposition from the column were η^5-$C_5H_5Co(CO)_2$ (R_f = 0.61) and (η^5-$C_5H_5CoCO)_3$ (R_f = 0.42).

(5) (a) C and H analyses were performed by Dr. S. Rottschaefer in the Caltech Analytical Laboratory. Cobalt analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Cryoscopic molecular weights were measured by Dornis u. Kolbe Microanalytisches Laboratorium, Mülheim, Germany. (b) We cannot at present rule out the possibility that the methyl groups are bridging rather than terminal; see, e.g., E. O. Fischer, et al., *Angew. Chem., Int. Ed. Engl.*, **12**, 943 (1973).

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(9) We have recently found that the known,[10] stable phosphine complex **5**, under 1 atm of CO in THF, gives a quantitative yield of acetone and η^5-$C_5H_5Co(CO)_2$ under the influence of UV irradiation (at 25 °C) or heat (~70 °C). Complex **6** is a detectable intermediate (NMR) in the photochemical reaction (E. Evitt and R. G. Bergman, unpublished observations).

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(11) The complex formed in greatest amount is the thermodynamically most stable material [η^5-$C_5H_5Co(CO)(PPh_3)$], which suggests that the yields of these materials may not reflect the kinetic product distribution of the phosphine induced reaction. This possibility is currently under investigation.

(12) Short-lived intermediates such as A and C may, of course, avoid 19-electron metal configurations by temporarily reducing the number of electrons donated by the η^5-C_5H_5 ligands. When L = solvent (no PPh_3 or CO present), $CpCoL_2$ and CpCo(CO)L are not stable and decompose to the cluster complexes observed as final products.

(13) Two somewhat related reactions are worthy of mention here. In the first, $[Ru(CO)_4SiMe_3]_2$ has been prepared[13a] and shown to undergo PPh_3-induced decomposition to $(PPh_3)_2Ru(CO)_3$ and $(PPh_3)_2Ru(CO)_2(SiMe_3)_2$. Later work has shown[13b] that the kinetics of this process are consistent with an initial reversible metal-metal bond cleavage step followed by coordination of a ligand (a similar overall process is shown as the first line of Scheme I). The second reaction is the decomposition of the cobalt(I) complex $CH_3Co(CO)_4$; although no yields are reported, acetone appears to be the only volatile organic product of this reaction.[13c,d] In contrast to the behavior of cobalt(II) complex **2**, however, the presence of free CO appears to *inhibit*, rather than accelerate, the formation of ketone;[13d] and $CH_3COCo(CO)_4$ is observed instead; (a) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 2559 (1969); (b) U. P. Fawcett, A. J. Pöe, and M. V. Twigg, *J. Organomet. Chem.*, **51**, C17 (1973); (c) W. Hieber, W. Beck, and E. Lindner, *Z. Naturforsch. B*, **16**, 229 (1961); (d) W. Beck and R. E. Nitzschmann, *Chem. Ber.*, **97**, 2098 (1964).

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(15) National Institutes of Health Postdoctoral Research Fellow, 1974–1975.

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Calculation of Polar Substituent Parameters by ab Initio Molecular Orbital Methods. Proton Affinities of Substituted Primary Amines[1]

Sir:

Progress toward the interpretation of structure-energy relationships in physical organic chemistry has been greatly aided by the evolution of techniques for the precise measurement of equilibrium constants for proton transfer reactions in the gas phase,[2,3] and by the development of simple nonempirical molecular orbital methods [4]with which it is possible to reliably calculate the energies of such processes. The widespread use of linear free energy relationships based upon standard proton transfer reactions in aqueous solution has been tempered (or even made hazardous) in fundamental understanding by aqueous solvent effects now known to range up to $\sim 10^{40}$ for proton transfer between neutral bases.[5]

Gas phase proton transfer equilibria between meta- and para-substituted benzoic acids have been correlated with σ^0 values;[6] proton transfer equilibria between para-substituted α-methyl styrenes and between para-substituted benzaldehydes even more closely follow σ^+ parameters.[7] Thus, for "chemically inert" type substituents in the benzene system, solvent may strongly attenuate the substituent effect (factors of 2–10 have been reported[3]), but the nearly fixed order of substituent effects is maintained in the gas phase and in aqueous solution.

We report here the results of the first study of the relationship of gas phase proton transfer equilibria and the polar substituent parameters, σ_I. Gas phase proton transfers between β-substituted ethylamines are ideally suited *in part* to definitive determinations of polar effects of substituents in the absence of solvent. This follows from the relatively simple nature of the strongly basic functional group; i.e., both free base and conjugate acid involve the single atomic (N) position with classically saturated (nonconjugating) structures and nearly the same hybridization. However, conformational effects (i.e., chelation), arising because of the flexibility of the molecular skeleton,[8] complicate the use of the β-substituted ethylamines for this purpose. This situation is compounded in the gas phase by the polarizability effect[2e,3,9] (i.e., preferential stabilization of BH^+ by the interaction of the charge with the polarizable substituent and molecular framework) as well as effects of internal H-bond chelation between substituent and the am-