Table I. Partially Gasified Spherocarb + K_2CO_3: Dependence of the Extent of Methylation on Potassium Concentration

K/C	CH_3/K^a
0.015	0.28
0.032	0.21
0.044	0.19

[a] By ^{14}C radioassay (see text).

ppm is assigned to sp^2 aromatic carbon atoms of the lattice and is the only resonance detected in an unalkylated sample (Figure 1b). The two broad resonances in the aliphatic region are assigned to methyl groups covalently bonded to oxygen (~56 ppm) and to carbon (~18 ppm). The sample characteristics and chemical shift position of the oxygen derivative suggest that the most reasonable precursor for the $O{-}CH_3$ group is a surface phenolate salt. The carbon-bonded methyls could be reaction products of purely carbanionic species. Alternatively, methylation of carbon sites could result from charge delocalization of a nominal oxygen nucleophile.[13]

The degree of surface methylation, determined by radioassay, corresponds to one nucleophilic center for every 4–5 potassium atoms. Moreover, when the foregoing procedure is repeated for carbon samples with potassium concentrations ranging from 0 to ~10 atom % K, the ratio of added CH_3 groups to original potassium is approximately constant (see Table I). This result agrees with the picture of high and reproducible catalyst dispersion achieved by the formation of ionic bonds to surface complexes. The degree of dispersion agrees with the previous indications by HCl chemisorption/poisoning experiments.[6]

Very little alkylation ($CH_3/K < 0.02$) takes place on an impregnated carbon until it has been heated to more than 450 °C and K_2CO_3 decomposition/reaction has occurred. The methylation behavior of a sample that is rapidly cooled from gasification conditions is the same as that for a sample that is heated for an additional 30 min at 700 °C in argon. If the catalyst–carbon interaction were rate limiting, we would expect to see a significant change during this time. That we do not is an indication that the catalyst–carbon interaction occurs rapidly compared with gasification and the dispersion measured here is characteristic of the surface at steady state.

We have demonstrated by chemical derivatization that charge-transfer surface salt groups are involved in potassium-catalyzed gasification. Solid-state NMR of ^{13}C-enriched derivatives shows that the surface anions include oxygen functionalities, most probably phenolates. Quantitative analyses of ^{14}C-labeled derivatives show high catalyst dispersion with ~4 potassium ions per surface salt complex. The role of the surface salt complexes as intermediates in the mechanism will be the subject of future publications.

Acknowledgment. We thank M. I. Siskin for suggesting the experiment, R. L. Liotta for helpful discussions, and W. K. Robbins for the ^{14}C analyses.

Registry No. C, 7440-44-0; K_2CO_3, 584-08-7.

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(12) Solid-state ^{13}C NMR measurements were performed on a JEOL FX-60QS spectrometer by using high-power dipolar decoupling, cross-polarization (2.0-ms contact time), and magic-angle sample spinning. In these hydrogen-deficient solids, the aromatic band represents only a small fraction of total substrate carbon, yet the $O{-}CH_3/C{-}CH_3$ intensity ratio remains constant for contact times in this range. Further details of the NMR analysis will be reported elsewhere.

(13) Kornblum, N.; Berringan, P. J.; le Noble, W. J. *J. Am. Chem. Soc.* **1963**, *85*, 1141. Kornblum, R.; Seltzer, R.; Haberfield, P. *Ibid.* **1963**, *85*, 1148.

Additions and Corrections

Optimized Geometries of the Saddle-Point Rotamers of Formamide [*J. Am. Chem. Soc.* **1978**, *100*, 41]. ROMAN F. NALEWAJSKI.

The reported values of angle α for the 4-31G optimized geometries should be interpreted as being the corresponding values of the dihedral angle between the plane containing a hydrogen and N–C axis and the plane bisecting the line connecting the two hydrogens of the NH_2 group. Thus, the conformations resulting from the 90° and 270° twists have the HNH angles of 112.2° and 114.0°, respectively. These angles are slightly less than the 114.8° HNH angle found for ammonia in the 4-31G basis set calculations reported by Carlsen et al.[1] The more pyramidal distribution of the electron pairs around nitrogen is due to the twisting of the nitrogen lone pair out of interaction with the π system of carbonyl. This trend also follows from the MINDO calculations. Barriers to internal rotation for formamide, calculated from the energies of optimized conformations in the paper under discussion and the energy of the 4-31G basis optimized geometry of the untwisted molecule,[1] are 84.1 and 97.1 J mol^{-1} for the 90° and 270° rotamers, respectively. These values exceed the 70 ± 5 J mol^{-1} value expected for the barrier to internal rotation of the isolated formamide molecule anticipated from extrapolating experimental data.[2]

The author wishes to thank Professor Anthony J. Duben and Professor Leo Radom for bringing this error to his attention. Professor A. J. Duben had correctly suggested the possible nature of the error and accordingly reinterpreted the geometry relaxation effects at the 4-31G level.

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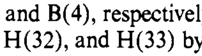
(1) N. R. Carlsen, L. Radom, N. V. Riggs, and W. R. Rodwell, *J. Am. Chem. Soc.*, **101**, 2233 (1979).

(2) A. J. Duben, personal communication.

Synthetic Applications of Conjugated Azocarbinols. Radical Chain Hydrophenylation and Hydrocyclohexenylation of Haloethenes [*J. Am. Chem. Soc.* **1981**, *103*, 7189]. YAU-MIN CHANG, RALPH PROFETTO, and JOHN WORKENTIN.*

Page 7191: In Table II, second column, line 13 should read Ph_3C (1.4×10^{-2} M),[g] ...

Page 7191, second column: The structural formula for **6**, **9**, and **10** should be



$$(C_6H_5)_2\underset{\displaystyle OR}{\underset{|}{C}}N{=}NC_6H_5$$

Page 7190: The heading for Table I should read: Reactions of **6** and **7** with Haloethenes.

Electron-Rich Carboranes. Studies of a Stereochemically Novel System, $(CH_3)_4C_4B_7H_9$, an 11-Vertex Arachno Cluster [*J. Am. Chem. Soc.* **1981**, *103*, 2675–2683]. DAVID C. FINSTER and RUSSELL N. GRIMES.*

Page 2679: In Table IV, first column (labeled "atom"), replace C(2), C(3), C(M2), C(M3), B(4), and B(6) by C(3), C(2), C(M3), C(M2), B(6), and B(4), respectively. Also replace H(21), H(22), H(23), H(31), H(32), and H(33) by H(31), H(32), H(33), H(21), H(22), and H(23).

Stereoselective Total Synthesis of 1α,25-Dihydroxycholecalciferol [*J. Am. Chem. Soc.* **1982**, *104*, 2945]. ENRICO G. BAGGIOLINI,* JEROME A. IACOBELLI, BERNARD M. HENNESSY, and MILAN R. USKOKOVIĆ.

Page 2948, left column, last line: "TMSI" is intended as *N*-(trimethylsilyl)imidazole and should be more appropriately abbreviated as "TSIM".