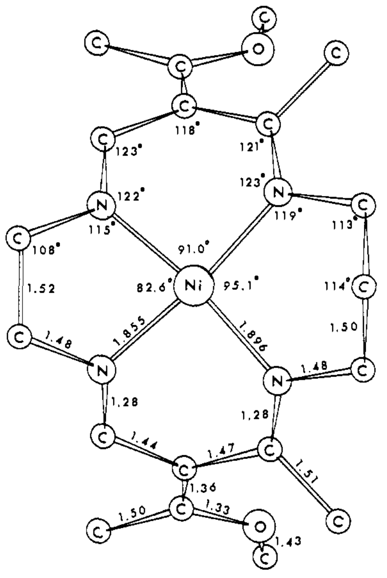

Figure 1. Bond lengths and angles in III. The angles and distances involving light atoms have been rounded off for clarity (av esd C–C 0.004 Å, C–C–C 0.3°).

by the C–N bonds. The conjugated system is not planar, the unsaturated chelate rings also adopting the boat form, with the C=N bonds approximately parallel, and the Ni and C segments tilted up 33 and 25°, respectively. The nickel atom lies 0.05 Å out of the plane of the nitrogen atoms.

The methoxyethylidene groups of III were found to undergo two types of reactions with nucleophiles. First, in addition to the previously reported hydrolysis leading to II (Scheme I), reactions with alcohols, ethylamine, and sodium ethoxide have been characterized. In acetonitrile solution III reacts with excess ethanol to form IV, indistinguishable from IV prepared by alkylation of II with triethyloxonium fluoborate. Yellow crystalline IV was isolated as a perchlorate salt, a 2:1 electolyte in acetonitrile, whose pmr spectrum (CD_3NO_2) shows $-OC_2H_5$(triplet, 6 H, $J \sim 7$ Hz at τ 8.54 and a quartet, 4 H, $J \sim 7$ Hz at τ 4.51 and no OCH_3. This reaction is reversible (IV → III in the presence of excess methanol). Excess ethylamine also reacts with III in acetonitrile giving V, a brown crystalline solid. This material (ν(N–H) at 3280 cm^{-1} in Nujol mull, a 2:1 electrolyte in acetonitrile) is readily characterized by its pmr spectrum (CD_3NO_2) (CH_3 triplet, 6 H, $J \sim 7$ Hz at τ 8.67 and a broad N–H singlet, 2 H at τ 2.54). No reaction was observed, however, upon exposure of III to excess ethyl mercaptan in CH_3CN solution after several days.

Another type of product was observed in the presence of strong bases, or bases which are either sterically hindered, or poor nucleophiles toward the carbon atom in question. Thus, upon addition of excess triethylamine, alkoxide, mercaptide anion, or sodium carbonate to III in acetonitrile, the amber solution turned dark red. This reaction, which is readily reversible on addition of excess acid was shown to involve deprotonation of III at the ethylidene methyl groups leading to VI. Treatment of III in acetonitrile solution with excess sodium ethoxide, followed by reduction of the solution volume, produced a dark green material, formulated as VI. The salient features of its pmr spectrum ($CHCl_3$) include the absence of a methyl singlet in the region expected for CH_3COCH_3 and the presence at τ 6.12 of a multiplet, 4 H, assigned to $CH_2{=}COCH_3$. Reaction of VI with deuteriotrifluoroacetic acid gave a product whose pmr spectrum was indistinguishable from that of III in the same solvent, except for reduction of the intensity of the methyl singlet at τ 7.47 to two-thirds of its initial value. The competition between these two kinds of processes, nucleophilic attack and deprotonation, is responsible for the selectivity toward nucleophiles exhibited by the compound. The increased electron density of the deprotonation product prevents its reaction with nucleophiles.

The selectivity toward nucleophiles displayed by III and its analogs affords a possible route to the attachment of additional chelate rings to the macrocyclic structure. It is especially significant that deprotonation can be effected on these derivatives for this both produces an anionic ligand and enhances the freedom of rotation about the bond connecting the newly constructed pendent group to the macrocycle proper. Synthetic applications of these new reactions are the subject of on-going studies.

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Hydrogenation of Highly Hindered Compounds in the Study of Structure Sensitivity

Sir:

Of the many parameters which would be needed completely to characterize the surface of a metallic particle, there is one, the fraction of surface atoms which project in some degree from the surface at edges, vertices, or steps, which is of particular interest with respect to an important current problem in heterogeneous catalysis, structure sensitive (demanding) *vs.* structure insensitive (facile).[1] At present, it appears likely that the rates of some heterogeneous catalytic reactions depend primarily upon metallic surface area and are nearly independent of details of catalyst preparation (structure insensitive) whereas the rates of other reactions vary markedly with catalyst preparation (structure sensitive). A number of correlations of structure sensitive features with metallic particle size (presumably inversely related to the fraction of projecting atoms) in metallic catalysts have been proposed.[2,3] However, no such correlations have been attempted with two types of reactions of im-

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(2) R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, **60**, 1043 (1956).

(3) J. R. Anderson and Y. Shimoyama, Proceedings of the Fifth International Congress on Catalysis, North-Holland Publishing Co., Amsterdam, 1973, paper 48. See also, J. W. E. Coenen, R. Z. C. van Meerten, and H. Th. Rijnten, paper 46; J. K. A. Clarke, E. McMahon, and A. D. O. Cinneide, paper 47; and R. G. Oliver and P. B. Wells, paper 45.

portant potential applicability: reactions which because of steric hindrance between adsorbate and surface would be expected to occur more readily at projecting atoms than on atoms in densely packed crystal faces and competitive reactions which would specifically illuminate structure sensitivity for strengths of binding of reactants to the surface.

Balandin and Klabunovskii have investigated the hydrogenation of some highly hindered tripticenes which they suggest can occur only at protuberances from the surface.[4] However, for ease in purification, in chemical analysis, and in interpretation, di-*tert*-butylacetylene or *trans*-di-*tert*-butylethylene appears more attractive. They have been hydrogenated.[5,6] Models indicate that the absorbed species of the conventional mechanism of hydrogenation would involve substantial steric interaction between the *tert*-butyl groups and densely packed surfaces like (100) and (111) of fcc, but that there would be much less steric hindrance at steps or edges. We are examining these reactions alone and competitively and we have started with supported platinum catalysts of various degrees of dispersion.

We have assumed that cyclopentene and diethylacetylene adsorb with little or no steric hindrance and we have used them as reference compounds in rate comparisons and in competitive hydrogenations. Reactions were run in a miniature liquid-phase batch reactor of the Hussey[7] type with the Hussey technique of successive injections in which runs are sandwiched between two runs of a reference substance, in our case, cyclopentene. No runs were accepted unless both cyclopentene runs were strictly zero order and of the proper rate. Very careful purification of reactants and attention to detail is needed to avoid poisoning. Our experiences have led us to doubt the validity of rate measurement in any liquid-phase hydrogenation not using similar controls. In our experiments about 0.1 cm³ of acetylene or olefin, 1 cm³ of solvent (cyclohexane), 10–30 mg of catalyst, and a total pressure of 1 atm were employed.

Pt/SiO_2 catalysts were prepared by ion exchange of $Pt(NH_3)_4{}^{2+}$ with 200+ mesh large pore Davison silica gel, grade 59, following the recipes of Dorling, Lynch, and Moss.[8] The 0.5% Pt/SiO_2 was reduced in hydrogen at 300°; the 1.9% Pt/SiO_2 was additionally sintered in air at 450° before reduction. Dispersions were measured by hydrogen chemisorption (Table I) and the results were in good agreement with ref 8. The 1% Pt/Al_2O_3 was prepared by impregnation of 200+ mesh η-Al_2O_3[7] with diaminoplatinum dinitrite[7] followed by heating in oxygen at 500°, cooling in nitrogen to 350°, and reduction at that temperature by hydrogen. Pt/Al_2O_3 (1.1%), prepared similarly from γ-Al_2O_3 (Catapal, Continental Oil Co.), was reduced at 780°. Dispersions are given in Table I.

The course of hydrogenation of di-*tert*-butylacetylene was determined by removal and gas chromatographic analysis of samples. Both Pt/SiO_2 catalysts gave initial selectivities for *cis*-di-*tert*-butylethylene of 66%, for the trans ene of 21%, and for di-*tert*-butylethane of 13%. The more highly dispersed Pt/Al_2O_3 gave 80, 17, and 5%, the less highly, 77, 14, and 9%. As shown in Figure 1, further reaction of cis ene on Pt/SiO_2 is not completely inhibited by the acetylene but the degree of inhibition is much greater on the more highly dispersed Pt/SiO_2. Results on Pt/Al_2O_3 had the same general form and, in particular, the same effect of the degree of dispersion was noted. Isomerization of cis ene to trans ene is faster than its hydrogenation to ane, a situation unusual on platinum.[7] Hydrogenation of the trans ene is slow relative to that of the acetylene.

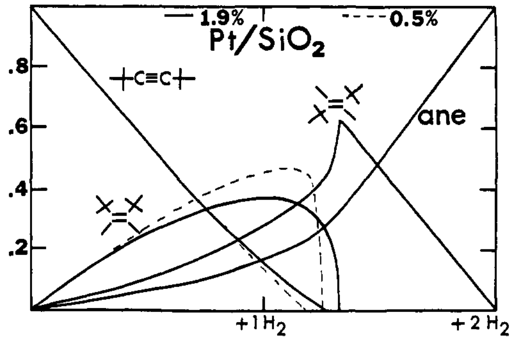

Figure 1. Hydrogenation of di-*tert*-butylacetylene: *x* axis, moles of H_2 added; *y* axis, hydrocarbon fraction.

Table I. Hydrogenations, Separate and Competitive at 20°

Catalyst	% dispersion	$S_{5/10}$[a]	k_5[b]	k_{10}/k_5[c]
0.5% Pt/SiO_2	54	90	15	0.68
1.9% Pt/SiO_2	14	240	12	0.78
1.0% Pt/η-Al_2O_3	100	60	2.7	0.36
1.1% Pt/γ-Al_2O_3	31	140	7.3	0.85

[a] The selectivity for hydrogenation of cyclopentene *vs.* di-*tert*-butylacetylene in competitive experiments. We list the initial value of $(\ln (C_5{}^\circ/C_5))/(\ln (C_{10}{}^\circ/C_{10}))$. [b] Turnover number in molecules of cyclopentene hydrogenated per second per surface Pt at a hydrogen pressure of 1 atm. [c] Ratio of initial rate of hydrogenation of the acetylene alone to that of cyclopentene alone.

The table shows rates of hydrogenation of cyclopentene and di-*tert*-butylacetylene singly and the selectivity ratio when the two are hydrogenated competitively. The rate of hydrogenation of the acetylene alone is not much less than that of cyclopentene but, competitively, the acetylene reacts very much more slowly. In competitive hydrogenations, the initial overall rates were very near those of cyclopentene alone. On the Pt/η-Al_2O_3, the rate ratio k_6/k_{10} for diethylacetylene *vs.* di-*tert*-butylacetylene is 1.15 and the selectivity ratio $S_{5/6}$ is 0.14. Thus, although the two acetylenes hydrogenate at about the same rate, $S_{6/10}$ would be 430 in competitive runs with the two assuming[7] that $S_{6/10} = S_{5/10}/S_{5/6}$.

The turnover numbers for hydrogenation of cyclopentene and the acetylene do not vary greatly among the catalysts but the numbers are lower on Pt/Al_2O_3 than on Pt/SiO_2 particularly on the highly dispersed Pt/Al_2O_3. The reactions are clearly structure sensitive, but the effect of structure sensitivity appears less in overall rates than in selectivity factors, in variation from catalyst to catalyst of the strength or rate of adsorption of the acetylene *vs.* cis ene and *vs.* cyclopentene. On the cata-

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lysts reported here, the more highly hindered reactant, di-*tert*-butylacetylene, is a better competitor *vs.* cyclopentene and the cis ene on the catalyst of highest dispersion, that is, on the catalysts in which there is presumably a higher proportion of projecting platinum atoms. However, it appears that other factors are also involved.

Transport of hydrogen between gas and solution is not limiting in our experiments nor are there serious concentration gradients in the pores of the catalysts. We examined the more highly dispersed Pt/SiO_2 in mesh sizes 120–140, 200–270, and 400+. The selectivity ratio $S_{5/10}$ was the same for all; k_5 was somewhat smaller for mesh 120–140 but equal for the other two.

More platinum catalysts must be examined before firm conclusions can be drawn but clearly the reactions in question and competitive reactions in general will be useful in studying structure sensitivity.[9]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

(9) We will be happy to furnish those interested in using these reactions with descriptions of methods which we have found to be satisfactory for purification and oxygen-free storage of solvents and reactants.

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Alkyl Transfer from Cobalt to Chromium[1]

Sir:

A subject of some current interest is the cleavage of the Co–C σ bond in organoaquocobaloximes[2] including reactions in which the alkyl group R is transferred to another metal.[3–12] Several mechanisms must be invoked to explain these observations, because the alkyl group in such reactions may be transferred (in a formal sense at least) as a carbanion, as a radical, and as a carbonium ion.

We wish to report that organocobaloximes react with Cr^{2+}_{aq} with essentially quantitative transfer of the alkyl group to chromium (eq 1). The Cr(III) product is $(H_2O)_5CrR^{2+}$, of which the methyl complex was the only previously known simple alkyl derivative.[13,14]

$$RCo(Hdmg)_2H_2O + Cr^{2+}_{aq} + 2H^+ = Co^{2+} + (H_2O)_5CrR^{2+} + 2H_2dmg \quad (1)$$

The product in the case of the methyl derivative can be isolated from the reaction solutions at low [H+] in *ca.* 60% yield using ion-exchange chromatography (Dowex 50W-X2, Li^+ form, elution with 0.35 *F* $LiClO_4$). The actual yields are much higher—at least 80% $(H_2O)_5CrCH_3^{2+}$ based upon spectral analysis of the product solutions—but considerable quantities are lost to acid hydrolysis (eq 2) during the ion-exchange isolation.

$$(H_2O)_5CrCH_3^{2+} + H_3O^+ = Cr(H_2O)_6^{3+} + CH_4 \quad (2)$$

The identity of the methylchromium complex was established by comparison of the visible–uv spectrum[15] and the rate and products of the acid hydrolysis reaction with that of the authentic complex.[13,14] Also, methane was the only volatile product of acid hydrolysis which could be detected mass spectroscopically, and methyl bromide the only volatile product detected upon reaction of the product with $Br_{2(aq)}$ (eq 3). The rate constants of these reactions agree with the values determined on authentic samples of $(H_2O)_5CrCH_3^{2+}$.[16,17]

$$(H_2O)_5CrCH_3^{2+} + Br_2 + H_2O = Cr(H_2O)_6^{3+} + CH_3Br + Br^- \quad (3)$$

The reactions have also been studied for R = CH_2CH_3, n-C_3H_7, $CH_2C_6H_5$, $CH_2C(CH_3)_3$, $CH(CH_3)_2$, and 2-octyl. Ion exchange isolation of the organochromium product was successful for the first three compounds but has not been attempted for the neopentyl and 2-octyl derivatives. The isopropylchromium(III) ion hydrolyzes rapidly enough so that the complex could not be isolated in this manner.

The reactions were studied at 25° in aqueous perchloric acid solutions having an ionic strength of 1.0 *M*. The reaction follows a second-order rate expression (eq 4), the rate constant for both the neutral and protonated forms of the cobaloxime being determined from the dependence of the apparent second-order rate constant upon [H+], which was consistent with the known protonation constants of the coordinated oxime function.[3]

$$-d[RCo(Hdmg)_2H_2O]/dt = k_2[RCo(Hdmg)_2H_2O][Cr^{2+}] \quad (4)$$

The kinetic data are in accord with the mechanism shown in Scheme I, and were fit to this mechanism using the independently determined values of the protonation

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(1) Work performed in the Ames Laboratory-USAEC with partial support from the National Science Foundation.

(2) Cobaloxime is the trivial name for the bis(dimethylglyoximato) complexes of cobalt.

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(14) Although R = CH_3 was the only simple alkyl derivative known, various other organochromium compounds of this formula have been prepared including the benzyl [J. K. Kochi and D. B. Buchanan, *J. Amer. Chem. Soc.*, **87**, 859 (1965)], various haloalkyls [F. A. L. Anet, *Can. J. Chem.*, **37**, 58 (1959); D. Dodd and M. D. Johnson, *J. Chem. Soc. A*, 34 (1968)], and other substituted alkyls.[13a]

(15) The Cr(III) product had the following uv–visible spectrum, given as λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 530 (15.7), 392 (240), and 158 (2510) in comparison with the literature values 550 (9.6), 392 (196), and 258 (2160). However, the latter values were determined by Ardon, *et al.*,[14] on a sample eluted with 0.35 *F* $HClO_4$ such that partial decomposition according to eq 3 was inevitable, leading to low values of ϵ. On repeating this preparation using $LiClO_4$ as the eluting agent, the spectrum of $(H_2O)_5CrCH_3^{2+}$ was 538 (11.5), 392 (246), and 258 (2400).

(16) The Cr(III) product reacted with perchloric acid according to eq 2 with a pseudo-first-order rate constant of 5.0×10^{-3} sec^{-1} (25.0°, 1.00 *M* H^+, $\mu = 1.09$ *M*). Under the same conditions the specific rate of the authentic complex is 5.2×10^{-3} sec^{-1}.[13a]

(17) The Cr(III) product and authentic $(H_2O)_5CrCH_3^{2+}$ both react with Br_2(aq) according to eq 3; the second-order rate constant is 2.1×10^6 M^{-1} sec^{-1} (25.0, $\mu = 1.00$ *M*): J. H. Espenson and D. A. Williams, unpublished observations.