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

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

these reactions agree with the values determined on authentic samples of $(H_2O)_5CrCH_3{}^{2+}$.[16,17]

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

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

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]

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.

[3] A. Adin and J. H. Espenson, *Chem. Commun.*, 653 (1971).

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[5] S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson, *J. Chem. Soc.*, *Chem. Commun.*, 685 (1972).

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[8] A. van den Bergen and B. O. West, *ibid.*, 52 (1971).

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[10] H. A. O. Hill, J. M. Pratt, S. Risdale, F. R. Williams, and R. J. Williams, *Chem. Commun.*, 341 (1970).

[11] F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, **93**, 5283 (1971).

[12] G. N. Schrauzer, J. H. Weber, T. M. Beckham, and R. K. Y. Ho, *Tetrahedron Lett.*, 275 (1971).

[13] (a) W. Schmidt, J. H. Swinehart, and H. Taube, *J. Amer. Chem. Soc.*, **93**, 1117 (1971); (b) M. Ardon, K. Woolmington, and A. Pernick, *Inorg. Chem.*, **10**, 2812 (1971).

[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.

Scheme I

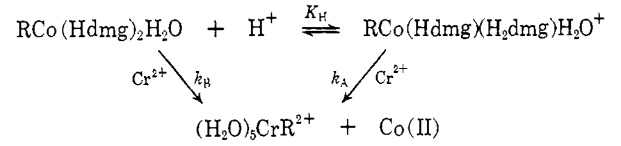

Table I. Kinetics of the Reactions of Alkylcobaloximes with Cr^{2+}_{aq} (25.0°) and Absorption Spectra of the Alkylchromium Ions

	Rate constants,[a] M^{-1} sec^{-1} k_A	k_B	Absorption spectra[b] of $(H_2O)_5CrR^{2+}$ λ_{max}, nm (ϵ, M^{-1} cm^{-1})
CH_3	23.0	14.5	530 (0.065), 392 (1.0), 258 (10.5)
CH_2CH_3	1.4×10^{-2}	1.3×10^{-2}	525 (0.037), 394 (1.0), 275 (6.1)
$CH_2CH_2CH_3$	1.38×10^{-3} [c]		522 (0.05), 394 (1.0), 275 (6.7)
$CH(CH_3)_2$	1.08×10^{-4} [c]		
$CH_2C(CH_3)_3$	6.1×10^{-5} [d]		387 (1.0),[e] 289 (4.1)
$CH_2C_6H_5$	7.3	5.0	355 (1.0), 297 (3.3), 274 (3.9), 243 (3.5)

[a] Rate constants as designated in Scheme I. [b] The spectrum is quoted relative to λ ~390 nm with values of ϵ, where known, as follows: CH_3 (240), C_2H_5 (166), and $CH_2C(CH_3)_3$ (204). [c] At $[H^+] \cong 0.4$ M. [d] At $[H^+] = 0.72$ M. [e] The spectrum of the neopentylchromium(III) ion is that determined by J. H. Espenson and D. A. Williams (independent observations) using an alternative synthesis.

constant, K_H.[3] Table I summarizes the values of the rate constants k_A and k_B along with the spectrum of each of the organochromium products.

The reaction appears to be applicable to methylcobalt (chelate) complexes outside the cobaloxime series; the methylchromium complex was also formed in the case of chelate = salen (k_2 = 76 M^{-1} sec^{-1}), bae (k_2 = 57 M^{-1} sec^{-1}), and Me_6 [14]-4,11-dieneN$_4$ ($k_2 \sim$ 4 M^{-1} sec^{-1}).[18]

In a formal sense eq 1 can be viewed as the transfer of radical R· to Cr^{2+}. We wish to consider four possible mechanisms. First, the reaction might occur by release of the radical from the original complex through homolytic scission of the Co–C σ bond, followed by capture of R· by Cr^{2+} ($R\cdot + Cr^{2+} \rightarrow CrR^{2+}$); the latter process is extremely rapid.[19] The second-order kinetics argues against this mechanism, however, as does the pronounced stability of the alkylcobaloximes toward reaction with acid,[20] and the ordering of rates for the different alkyl compounds (Table I) which does not at all follow the order expected for a homolytic scission reaction forming alkyl radicals.

Second, one can envisage a Cr(II) catalysis of this homolysis which accounts for the form of the rate expression but to which the other objections apply (as well as the inherent chemical unreasonableness of Cr(II) catalysis of such a dissociation).

Third, we consider a concerted process in which the transfer of a carbanion from cobalt to chromium accompanies electron transfer from chromium to cobalt. Fourth, we consider a process rarely if ever encountered in organic reactions,[21] involving bimolecular homolytic substitution at saturated carbon (S_H2 mechanism). These latter mechanisms both appear to be in accord with the data at hand. Based upon the marked decrease in rate with substitution at the α carbon, it is tempting to suggest that the reaction occurs with inversion of configuration at carbon.

Additional experiments are in progress to define the mechanism more completely, and to resolve the question of the stereochemical change at the α carbon atom.

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(18) T. S. Roche and J. F. Endicott, *J. Amer. Chem. Soc.*, **94**, 8622 (1972), indicated that the products of reaction of this methyl complex with Cr^{2+} were $Cr(H_2O)_6^{3+}$ and CH_4, but their studies were made at 1 M H^+ where the acid hydrolysis of $CrCH_3^{2+}$ occurs relatively rapidly.

(19) H. Cohen and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 320 (1972).

(20) Were the alkylcobaloximes subject to thermal homolysis, $R(Co) \rightleftharpoons R\cdot + (Co^{II})$, as is the case photochemically [G. N. Schrauzer, L. P. Lee, and J. W. Sibert, *J. Amer. Chem. Soc.*, 92, 2997 (1970)], acidic solutions would be quite unstable, which is not the case. This conclusion is not altered by postulating a high recombination rate between R· and (Co^{II}), provided the latter are free entities whose reaction rate cannot exceed the limit of diffusion control, because the decomposition of the Co(II) compound by perchloric acid is exceedingly rapid: A. Adin and J. H. Espenson, *Inorg. Chem.*, 11, 686 (1972).

(21) K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971, pp 72–90.

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Synthesis, Stereochemistry, and Bonding of Tetrapyridinemagnesium(II) Bis(π-cyclopentadienyltricarbonylmolybdate($-$I)) and Related Compounds

Sir:

It was suggested in a recent communication[1] that direct magnesium–transition metal bonding occurs quite generally in a broad class of "mixed metal" complexes. While such metal–metal bonds might well exist in selected cases, results from this laboratory provide an alternative bonding pattern for these bimetallic complexes.[2] We describe herein the preparation and spectroscopic properties of a series of complexes with the general formula $m_2Mg(py)_4$ (m = metal carbonyl group; py = pyridine) and the crystal and molecular structure of one of these, $Mg[h^5\text{-}C_5H_5Mo(CO)_3]_2(C_5H_5N)_4$ (**1**).

By analogy with the mMgX (X = Cl, Br) systems[2,3] complex **1** was prepared by a metal exchange reaction of magnesium and the corresponding m_2Hg derivative in tetrahydrofuran (THF). The highly insoluble THF complex that initially precipitated was converted to **1** by recrystallization from pyridine.[4,5] The other com-

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(2) S. W. Ulmer, Ph.D. Thesis, Cornell University, 1972.

(3) J. M. Burlitch and S. W. Ulmer, *J. Organometal. Chem.*, **19**, P21 (1969).

(4) Stirring a THF solution (25 ml) of $Hg[Mo(CO)_3C_5H_5]_2$ (1 mmol) with magnesium (10 mg-atoms, 80 mesh) for 8 hr at 25° under argon produced a light green solid which was collected, dried under vacuum, and recrystallized from boiling, dry, deaerated pyridine (15–20 ml). Extremely air-sensitive, yellow crystals of **1** were obtained in 65% yield. Alternatively **1** may be prepared by directly carrying out the exchange reaction in pyridine or in a solution of pyridine and toluene.[5] *Anal.* Calcd: C, 52.00; H, 3.61; N, 6.75. Found: C, 52.14; H, 3.57; N, 6.49.

(5) J. M. Burlitch and R. C. Winterton, unpublished observations.