5.41 with area 10.7, the MoH_2 protons at τ 18.58 with area 2.0, and CH_3 around τ 9.38 (broad) with area 3.2, indicating the product should be formulated as $[(\pi\text{-}C_5H_5)_2MoH_2CH_3][SO_3F]$ which is analogous to known protonated species[9] but is unusual in containing CH_3 and H on the same metal center. By contrast, the products so far identified in the reaction of the parent hydride with alkyl halides are of the type $(\pi\text{-}C_5H_5)_2MoX_2^+$ (X = halide).[10]

In summary, CH_3SO_3F and similar strong carbocation sources provide a route to unusual and useful cationic metal alkyl compounds. The unique character of the products stems in part from the very low tendency of SO_3F^- and similar anions to coordinate to metals. A close parallel is noted between the methylation and protonation of metal atoms in mononuclear low oxidation state complexes; however, we have as yet been unsuccessful in extending this analogy by the methylation of metal–metal bonds of polynuclear metal carbonyls which are known to protonate.

Acknowledgment. This research was supported by the National Science Foundation through Grant GP 28878. We thank R. G. Pearson and J. MacDonald for helpful discussions.

[9] M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc., London*, 4854 (1961).

[10] R. L. Cooper and M. L. H. Green, *J. Chem. Soc. A*, 1155 (1967).

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Rates of Intramolecular Electron Transfer

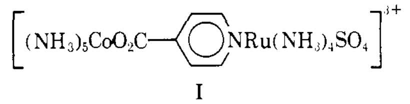
Sir:

The great majority of rates which have been measured for oxidation–reduction reactions involving electron transfer refer to inter- rather than intramolecular transfer. It is of special interest to measure intramolecular transfer rates because then the factors involved in assembling the reaction partners do not complicate the rate comparisons. Such first-order intramolecular transfer rates have been recorded for only a few systems: for outer-sphere electron transfer, in the reaction of $Fe(CN)_6^{4-}$ with $Co(NH_3)_5H_2O^{3+}$,[1] for inner-sphere electron transfer in the reaction of Fe^{2+} with nitriloacetatopentaamminecobalt(III),[2] and of Cu^+ with Ru(III) complexes which have as ligands carboxylates containing unsaturated carbon–carbon bonds.[3] In each of these cases, success depended on the high affinity of the reducing agent in associating with the oxidizing agent. But, in all of them, despite the rather high affinities for association, the combinations are labile and thus much ambiguity remains in respect to the structures of the activated complexes.

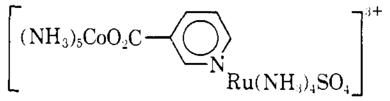
This ambiguity is much reduced for the systems to be described, where both the reducing and oxidizing metal ions, Ru(II) and Co(III), respectively, make substitution-inert bonds to the bridging group. The most direct approach in preparing "precursor complexes" of this class at significant concentrations by letting, say, $[Co(NH_3)_5O_2C\text{-}4\text{-}Py]^{2+}$ react with $Ru(NH_3)_5OH_2^{2+}$ fails because outer-sphere reduction of Co(III) is rapid compared to the rate at which the Ru(II)–N bond is formed.[4] A variety of attempts to prepare the Co^{III}–ligand–Ru^{III} complex, relying then on the ready reducibility of Ru(III) compared to Co(III) to generate the desired Co^{III}–ligand–Ru^{II} combination, have also failed. A procedure which promises to be successful for a very wide range of precursor complexes of this series is herewith described for a particular one of the four complexes so far prepared.

Equimolar quantities of $[Co(NH_3)_5O_2C\text{-}4\text{-}PyH](ClO_4)_3$[5] and *trans*-$[Ru(NH_3)_4SO_2Cl]Cl$[7] were dissolved separately in water and titrated with $NaHCO_3$ (1 equiv per mol for the former and two for the latter, the lability of the group trans to S(IV) is greatest when the latter has the form SO_3^{2-}). The two solutions were mixed and allowed to react for 2–5 min at room temperature. The resulting solution was filtered and added to an equal volume of concentrated HBF_4. After cooling at −5° an orange solid precipitated which was filtered and washed with ethanol and ether. The solid at this stage has the constitution $[Co(NH_3)_5O_2C\text{-}4\text{-}PyRu(NH_3)_4SO_2](BF_4)_4$ as shown by its elemental analysis. The sulfur dioxide ligated to Ru(II)[8] renders it so weakly reducing that electron transfer within the Co^{III}–Ru^{II} complex is very slow. The coordinated SO_2 was converted to coordinated SO_4^{2-} by dissolving the solid in the minimum amount of 1 *M* HCl and oxidizing with hydrogen peroxide. Immediately thereafter 5–10 volumes of acetone was added with stirring. The precipitate which formed on cooling was filtered and washed with ethanol and ether. The solid was purified by dissolving in water and reprecipitating from 1 *M* HCl with 2 volumes of acetone. The overall yield was *ca.* 60%.

Following this procedure chloride salts containing the ions I to IV were prepared. Microanalyses for the salts, taken to be dihydrates, are reported in Table I.



I



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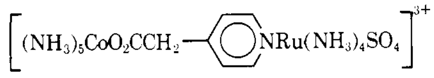
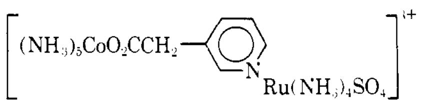


III



IV

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[1] D. Gaswick and A. Haim, *J. Amer. Chem. Soc.*, **93**, 7347 (1971).

[2] R. D. Cannon and J. Gardiner, *ibid.*, **92**, 3800 (1970).

[3] J. K. Hurst and R. H. Lane, *ibid.*, **95**, 1703 (1973).

[4] H. Taube, *Ber. Bunsenges. Phys. Chem.*, **76**, 964 (1972).

[5] This compound was prepared using a modification of the method of Gould and Taube[6] and supplied to us by E. K. Roberts. Other cobalt compounds were prepared by further modification of this method.

[6] E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964).

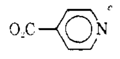
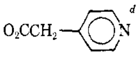
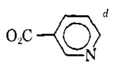
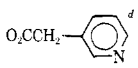
[7] (a) Gleu, K. W. Breuel, and K. Rehm, *Z. Anorg. Allg. Chem.*, **235**, 201, 211 (1938); (b) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).

[8] Details on the synthesis and substitution properties of Ru^{II}–SO_2 complexes will appear in a later publication.

Table I. Microanalyses for Salts I–IV, %

	C	H	N	Co	Ru	S	Cl
Calcd for I or II	10.7	5.2	20.8	8.8	15.0	4.8	15.8
Found for I	10.5	4.8	20.6	8.7	14.9	4.6	17.7
Found for II	10.2	4.7	20.3	8.8	14.8	4.7	15.5
Calcd for III or IV	12.2	5.4	20.4	8.6	14.7	4.7	15.5
Found for III	12.0	4.9	20.3	8.8	15.1	4.4	15.9
Found for IV	11.6	5.0	19.8				

Table II. Intramolecular Transfer in Systems of the Class [$Co^{III}O_2C \cdots NRu^{II}$[a]

Bridging ligand	[Co(III)–Ru(III)] × 10^3	[Eu^{2+}][b] × 10^3	Medium	k, sec^{-1}
 [c]	1.0	0.049	0.1 M Trifluoroacetic acid	~1 × 10^2
 [d]	2.3	0.095	1 M NaTos[e]	13 × 10^{-3}
	2.3	0.095	1 M HTos	16 × 10^{-3}
	0.2	0.02	0.4 M NaTos 0.05 M HTos	11 × 10^{-3}
	2.3	0.095	1 M NaCl	28 × 10^{-3}
	2.3	0.095	1 M HCl	51 × 10^{-3}
 [d]	2.0	0.095	0.4 M NaTos 7 × 10^{-4} M H^+	1.9 × 10^{-3}
	1.0	0.095	0.4 M NaTos 0.05 M HTos	1.7 × 10^{-3}
	2.0	0.095	0.4 M NaTos 0.05 M HTos	1.7 × 10^{-3}
	2.4	0.095	1 M HTos	1.6 × 10^{-3}
	2.4	0.095	1 M NaCl 1 × 10^{-4} M H^+	8.2 × 10^{-3}
	2.4	0.095	1 M HCl	11 × 10^{-3}
 [d]	2.3	0.095	1 M NaTos	0.86 × 10^{-3}
	2.3	0.095	1 M HTos	5.5 × 10^{-3}
	2.3	0.095	1 M NaCl	4.8 × 10^{-3}
	2.3	0.095	1 M HCl	34 × 10^{-3}

[a] At 25°. [b] In some cases $Ru(NH_3)_6^{2+}$ was used with no difference in rate. [c] Using stopped flow; other systems using Cary spectrophotometer. [d] The first readings were taken *ca.* 1 min after mixing, on extrapolating the observed optical densities to zero time, optical densities corresponding to 90% or more of those expected for the $\pi d-\pi^*$ transitions were calculated; at λ 400 nm. [e] Sodium toluenesulfonate.

When any of the species I through IV is reduced by Eu^{2+} or $Ru(NH_3)_6^{2+}$, the color characteristic of the Ru(II)–N heterocyclic combination is produced.[9] In the present system Ru(III) is reduced much more rapidly than is Co(III) by these reagents.[10,11] The colored intermediate then disappears by a first-order process but with the kinetics slightly complicated by an effect to be described. Ru(III) is formed as a product of the reaction and this species in three of the systems oxidizes the Co^{III}–ligand–Ru^{II} intermediate rapidly compared to intramolecular electron transfer, thus depleting it as the reaction progresses.

$$Co^{III}\text{-}L\text{-}Ru^{II} + Ru^{III}\text{-}L = Co^{III}\text{-}L\text{-}Ru^{III} + Ru^{II}\text{-}L \quad (1)$$

The effect of this expected complication was minimized by having Co^{III}–L–Ru^{III} in large excess, and by basing the specific rate on the initial part of the reaction.

The results of the experiments on the rates of intramolecular transfer are presented in Table II.

In the case of I, the intramolecular transfer reaction is so rapid that its measurement is at the limit of the stopped flow method and is much more rapid than is loss of SO_4^{2-} from Ru(II) ($t_{1/2}$ for this reaction in $HO_2CPyRu(NH_3)_4SO_4$ is *ca.* 0.3 sec^{-1}). In the other cases, intramolecular transfer is much slower than SO_4^{2-} loss, and the rates in these cases then pertain to the $Ru^{II}(NH_3)_4H_2O$ entity as reducing agent. Direct comparison of the rates for I compared to the others is difficult, but it seems unlikely that, were the aquo form of I in hand, the rates would be a factor of more than 10 slower.[12] There seems therefore to be a wide disparity in rates for the nicotinate and isonicotinate cases, greater probably than for Cr^{2+} reacting with Ru(III) when nicotinamide and isonicotinamide function as bridging groups.[11]

As expected, insertion of a CH_2 group into the isonicotinate conjugated bond system causes a large rate decrease. What may perhaps appear to be astonishing is that the rate is measurable compared to the second-order intermolecular transfer ($k < 0.03$ M^{-1} sec^{-1}). Molecular models show that the carbonyl of the carboxyl comes close to the π cloud of the ring and thus the CH_2 linkage may actually be by-passed when Ru(II) reduces Co(III).

Comparisons of the results for IIa,[13] IIIa, and IVa are especially meaningful. Noteworthy is the fact that whereas k for IIIa is less than it is for I, for IVa it is, under most conditions, greater than for IIa. Molecu-

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[9] P. Ford, DeF. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).

[10] J. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).

[11] R. Gaunder and H. Taube, *ibid.*, **9**, 2627 (1970).

[12] Since only a small fraction of the initial absorbance is caught in this case, we cannot be certain that the specific rate does not apply to the aquo. If there were 5% aquation and reaction of residual sulfate were very rapid compared to aquo, we might in fact be observing electron transfer for the aquo.

[13] The "a" following the number denotes the aquo form of the binuclear complex.

lar models show that in IVa the metal ion centers can approach more closely than they do in IIa. We suggest that in IVa electron transfer is by an "outer-sphere" mechanism, in the sense that transfer does not make use of the bridging group, whereas in IIa the bridging group is implicated. This suggestion is supported by the fact that for IVa the rate is very sensitive to [H^+] whereas, for IIa (and for IIIa), it is not. An important path for the polarographic reduction of acetatopentaamminecobalt(III) involves H^+;[14] redox reactions at a mercury electrode in many respects have the characteristics of outer-sphere electron transfer processes in homogeneous systems.[15] In any case, the utility of the approach to the study of both inner and outer-sphere electron transfer appears to be demonstrated even in the limited series described.

Chloride ion enhances the rates for IIa, IIIa, and IVa, and more for IVa than it does for IIa or IIIa. The Ru^{II}–OH_2 position is labile enough so that a path for the overall reaction can involve Ru^{II}–Cl as reactant. The higher sensitivity of IVa compared to IIa and IIIa to chloride ion may indicate that an additional component contributes to the effect in IVa, the chloride ion in this case affecting the rate even short of entering the coordination sphere of Ru(II).

It should be pointed out that the effect of the product Ru(III) reacting with the Co^{III}–ligand–Ru^{II} species can be exploited in increasing the half-life for intramolecular electron transfer. By adding the Ru(III) product in known amount and by determining the equilibrium constant for reaction I, the half-life in the presence of the product can be used to calculate the intrinsic rate. An effort to take advantage of the reaction in question in compound I failed because of complications arising from sulfate complexation. The effect, however, is easy to observe qualitatively in any of the systems.

Enough has been done on the chemistry of Co(III) and Ru(II) to make it certain that bridging groups in great diversity can be used in extending the studies. For Co(III), besides carboxyl as the lead-in group, nitrile, imine, and saturated nitrogen can be used; for Ru, in addition to the last three, also donor sulfur. Thus, a systematic study of rates of intramolecular transfer as a function of the separation of the metal atoms and of the electronic properties of the bridging groups is possible using the approach applied in the four systems studied.

Acknowledgment. Financial support for this research by the National Science Foundation under Grants No. GP 24726 and GP 28142 is gratefully acknowledged. We also wish to thank Dr. E. Kirk Roberts for supplying $[Co(NH_3)_5O_2C\text{-}4\text{-}PyH](ClO_4)_3$ and Glenn Tom for his assistance in the cyclic voltammetry experiments.

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(14) A. Vlcek, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., McMillan, New York, N. Y., 1961, p 590.

(15) H. Taube, "Proceedings of the Robert A. Welch Foundation: Topics in Modern Inorganic Chemistry," W. O. Milligan, Ed., Houston, Texas, 1963, p 7.

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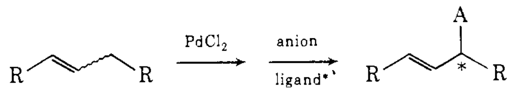
New Synthetic Reactions. Asymmetric Induction in Allylic Alkylations

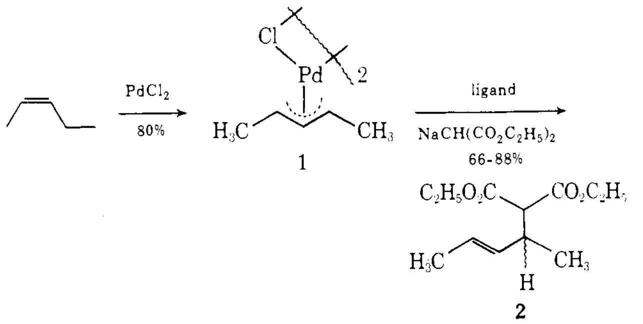
Sir:

The development of direct methods for asymmetric creation of a new carbon–carbon bond continues to present a major challenge.[1,2] The application of organometallics in such cases has had mixed results.[3–5] In most cases, reasonable optical inductions (up to 33%) are observed only when exceedingly low temperatures and certain optically active solvents are employed.[3] A unique feature of the allylic alkylation procedure is its potential in chiral synthesis. We wish to report that alkylation of a π-allylpalladium complex to form a sp^3–sp^3 carbon–carbon bond[6] leads to surprisingly high optical yields without resorting to chiral solvents and at temperatures from −40 to +25° (eq 1, where the asterisk indicates chiral center).



(1)

A simple system of relatively high symmetry was examined to provide a vigorous test of the potential for optical induction inherent in the method. The alkylation involved reaction of *syn,syn*-1,3-dimethyl-π-allylpalladium chloride dimer (**1**) (prepared by treatment of *cis*-2-pentene with palladium chloride, sodium chloride, cupric chloride, and sodium acetate in acetic acid[7]) and diethyl sodiomalonate. Experimentally, the ligand and π-allylpalladium species are mixed in THF at the stated temperature after which a solution of diethyl sodiomalonate in THF is added. A wide range of ligands including triphenylphosphine, trimethyl phosphite, 1,2-bis(diphenylphosphino)ethane, and *N,N,N′,*-*N′*-tetramethylethylenediamine (but not *N,N,N′,N′*-tetramethyl-2,3-dimethoxy-1,4-butanediamine[3]) promoted alkylation in isolated yields ranging from 66 to 88%. Use of the optically active ligands (+)-2,-



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(1) For reviews see J. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971; H. Pracejus, *Fortschr. Chem. Forsch.*, **8**, 493 (1967); D. R. Boyd and M. A. McKervey, *Quart. Rev., Chem. Soc.*, **22**, 95 (1968); J. Mathiew and J. Weill-Raynal, *Bull. Soc. Chim. Fr.*, 1211 (1968).

(2) For some recent interesting examples, see S. Yamada, K. Hiroi, and K. Achiwa, *Tetrahedron Lett.*, 4233 (1969); S. Yamada and G. Otani, *ibid.*, 4237 (1969); U. Eder, G. Sauer, and R. Wiechert, *Angew. Chem., Int. Ed. Engl.*, 10, 496 (1971).

(3) D. Seebach, H. Dörr, B. Bastani, and V. Ehrig, *Angew. Chem., Int. Ed. Engl.*, **8**, 982 (1969).

(4) B. Bogdanovic, B. Henc, B. Meister, G. Pauling, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **11**, 1023 (1972).

(5) G. Consiglio and C. Botteghi, *Helv. Chim. Acta*, **56**, 460 (1973).

(6) B. M. Trost and T. J. Fullerton, *J. Amer. Chem. Soc.*, **95**, 292 (1973).

(7) In addition, an approximately 10% relative yield of *syn*-1-ethyl-π-allylpalladium chloride dimer is formed in this reaction.