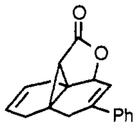
been converted to **7** in 64% overall yield via esterification with CH_2N_2 followed by treatment with DDQ.[4]

We have developed an efficient route from acid **6** to 1,6-methano[10]annulene derivatives bearing substituents on both the bridgehead and the 10-membered ring (Scheme II). Treatment of **6** with I_2/KI followed by DBU yielded lactone **8** in 92% yield. This lactone reacted with the appropriate cuprate reagents to produce acids **9a–e** in good yield.[10] Acids **9a–d** could be converted to the corresponding methyl esters **10a–d** by the action of $(MeO)_2SO_2/K_2CO_3$. Ester **10e** was obtained in 94% yield by treatment of **9e** with $BF_3 \cdot OEt_2$ in MeOH at reflux.[11] ^1H NMR data indicated that the substituent was introduced in formal S_N2 fashion during the cuprate reaction. This conclusion was verified crystallographically for **9a**;[12] the crystal structure also showed the expected endo configuration at the site of addition.

Bridged annulenes **11–13** were produced via DDQ oxidation of **10a–c**,[13] but attempts to oxidize esters **10d,e** in this way were unsuccessful. Both DDQ and *o*-chloranil caused **10e** to decompose, and no reaction was observed with *p*-chloranil. Annulenes **14** and **15** could, however, be prepared via the bromination/dehydrobromination route. Treatment of **9e** with Br_2 afforded a mixture of tribromo lactones in quantitative yield. Subsequent treatment of this mixture with *t*-BuOK produced only small quantities of **15**, but DBU (dioxane, reflux, 64 h) provided the desired annulene in 48% yield. An analogous series of reactions produced butyl analogue **14** in 34% yield.

One source of difficulty in these base-mediated eliminations is suggested by the observation that treatment of acid **9a** with I_2/KI followed by DBU led to the regioselective formation of γ-lactone **16** in 75% yield. If γ-lactones are produced by the action of Br_2 on **9d** and **9e**, as suggested by IR data, then subsequent elimination of the carboxylate must ultimately occur in 1,4 fashion. The modest yields of **14** and **15** via the bromination/dehydrobromination route, compared with the success of this route for conversion of **6** to **2**, may result from the harsh conditions required for this 1,4 elimination.



16

Treatment of **13** with KF (cat. HBr, DMF)[14] provided the desilylated phenol in 91% yield, the hydroxyl group of which could be alkylated under standard conditions[15] (e.g., 2 equiv of *n*-PrI, K_2CO_3, MeCN, reflux, 6 days; 98%). This type of alkylation, and other attachment strategies involving substituents on the 10-membered ring, should allow the incorporation of amphiphilic bridged annulenes into larger structures. The preparation and characterization of such molecules, based on the synthetic route we have presented here, are underway in our laboratory.

Acknowledgment. We thank Professor Reinhardt Brückner, Professor Howard W. Whitlock, and Mr. John Cochran for helpful suggestions and Ms. Elizabeth Gallo, Mr. Kevin Enzweiler, and Mr. Thomas Stein for technical assistance. This research was supported by the National Institutes of Health (GM-41825) and, in the initial phases, by Cambridge NeuroScience Research, Inc. S.H.G. thanks the Searle Scholars Program, the American Cancer Society (Junior Faculty Research Award), the National Science Foundation Presidential Young Investigator Program, the Eastman-Kodak Company, and Eli Lilly and Company for support.

Supplementary Material Available: Complete description of the synthesis of compounds **7**, **11**, and **15** (9 pages). Ordering information is given on any current masthead page.

---

(10) Success of cuprate additions to **8** is dependent upon the conditions under which the cuprate reagents are generated. Since optimum conditions vary with the cuprate used, reaction times and temperatures are listed below. Organolithium reagents, when not commercially available, were prepared via halogen metal exchange between the appropriate bromides and *n*-butyllithium. Solutions of the organolithium reagents were then added to a slurry of cuprous bromide–methyl sulfide complex in a 1:1 mixture of ether and methyl sulfide at 0 °C (Me_2CuLi), −78 °C [Ph_2CuLi, Bu_2CuLi, $(o\text{-}MeOC_6H_4)_2CuLi$], or −45 °C $\{[m\text{-}(t\text{-}BuMe_2SiO)C_6H_4]_2CuLi\}$. After 5 min ($Me_2CuLi$), 10 min ($Ph_2CuLi$, Bu_2CuLi), or 30 min [$(o\text{-}MeOC_6H_4)_2CuLi$], a solution of **8** in THF, equilibrated to the temperature of the cuprate, was added. After 60 min, a solution of $\{[m\text{-}(t\text{-}BuMe_2SiO)C_6H_4]_2CuLi\}$ was cooled to −78 °C before addition of **8**. After 2–3 h at low temperature, the reaction mixtures were allowed to come to room temperature overnight, and the crude product was isolated by aqueous workup. Copper salts were removed by ammonium chloride washes.

(11) Esterification with $BF_3 \cdot Et_2O$: Marshall, J. L.; Erickson, K. C.; Folsom, T. K. *Tetrahedron Lett.* **1970**, 4011.

(12) Barrett, D. G.; Desper, J. M. Unpublished results.

(13) Optimal conditions for the oxidations were as follows: Compound **11**, **12** or **13** was stirred in the presence of 1.5 equiv of DDQ in dioxane at 60–70 °C for 24–48 h; a further 1.5 equiv of DDQ was then added, and the mixture was heated at reflux for 24 h. Along with the major product, a second annulene was usually isolated in ca. 5% yield upon chromatographic purification. Spectroscopic studies suggest this minor product to be the epimer at the bridge position.

(14) Sinhababu, A. K.; Kawase, M.; Borchardt, R. T. *Synthesis* **1988**, 710.

(15) Allen, C. F. H.; Gates, J. W., Jr. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 140.

Photoinduced Electron Transfer in Multimetal Complexes. Observations on Electronically Forbidden Back Electron Transfers

Tione Buranda, Yabin Lei, and John F. Endicott*

Department of Chemistry
Wayne State University
Detroit, Michigan 48202

Received September 20, 1991
Revised Manuscript Received June 15, 1992

There has been much recent interest in the use of light to promote charge separation in simple molecular systems.[1-6] One requirement for the generation of useful charge-separated intermediates is a relatively slow back-electron-transfer (BET) rate. A potential approach which has received little attention capitalizes on electronic selection rules to retard the BET rate. We have investigated this issue by using light-promoted reactions to generate a high-energy electron-transfer intermediate in complexes containing a light-absorbing ruthenium(II) complex (excited-state electron donor) covalently linked to cobalt(III) electron acceptors which form high-spin ($^4T_2$ in O_h symmetry) Co(II) products. While the resulting spin-forbidden and orbitally forbidden BET process might be expected to be relatively slow, the effects of such electronic factors on observed electron-transfer rates have long been a subject of discussion and controversy.[7,8] The work reported

---

(1) For reviews, see: (a) Fox, M. A., Chanon, M., Eds. *Photoinduced Electron Transfer. Parts A–D*; Elsevier: Amsterdam, 1988. (b) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Simon and Schuster: Heme Hempstead, England, 1990.

(2) Chen, P.; Duessing, R.; Graff, D. K.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 5850.

(3) Walker, G. C.; Barbara, P. F.; Doorn, S. K.; Dong, Y.; Hupp, J. T. *J. Phys. Chem.* **1991**, *95*, 5712.

(4) Doorn, S. K.; Stoutland, P. O.; Dyer, R. B.; Woodruff, W. H. *J. Am. Chem. Soc.* **1992**, *114*, 3133.

(5) Gust, D.; Moore, T. A.; Moore, A. L.; Gao, F.; Luttrull, D.; DeGraziano, J. M.; Ma, X. C.; Makings, L. R.; Lee, S.-J.; Trier, T. L.; Bittersmann, E.; Seeley, G. R.; Woodward, S.; Bensasson, R. V.; Rougée, M.; DeSchryver, F. C.; Van der Auweraer, M. *J. Am. Chem. Soc.* **1991**, *113*, 3638.

(6) (a) Knapp, S.; Dhar, T. G. M.; Albaneeze, J.; Gentemann, S.; Ponteza, J. A.; Holten, D.; Schugar, H. J. *J. Am. Chem. Soc.* **1991**, *113*, 4010. (b) Rodriguez, J.; Kirmaier, C.; Johnson, M. R.; Friesner, R. A.; Holten, D.; Sessler, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 1652.

(7) For general reviews, see: (a) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980. (b) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437. (c) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

0002-7863/92/1514-6916$03.00/0

Table I. Energetics of Electron-Transfer Pathways in Some Covalently Linked Transition Metal Complexes[a]

complex	k_{BET}(obsd), $s^{-1}/10^{10}$	ΔG° [b]	λ [c]	$\Delta G^{\ddagger}_{BET}$ [d]	k_{BET}(calcd),[e] $s^{-1}/10^{12}$
$(bpy)_2Ru((CN)Co(NH_3)_5)_2^{6+}$	0.3	12.3[f]	15 ± 3[f]	0.0–0.3 0.11	2–11
$(bpy)_2(CN)Ru((CN)Co(tetraen))^{3+}$	0.4	11.8	14 ± 2	0.0–0.03 0.09	2–11
$(bpy)_2(CN)Ru((CN)Co(terpy)(bpy))^{3+}$	0.3	8.0	11 ± 2	0.00–0.2	5–12
$(bpy)_2Ru((CN)Ru(NH_3)_5)_2^{6+}$ [g]	>2	11.3	3	(4)[h]	(2×10^{-7})
$(NC)_5Fe((CN)Ru(NH_3)_5)^-$	>300[i]	4.8[j]	5.4	0.02	1

[a] Energies in $cm^{-1}/10^3$); temperature 25 °C in acetonitrile except as indicated. [b] Based on cyclic voltametric measurements except as indicated. [c] Nuclear reorganizational parameter; $\lambda = \lambda_s + \lambda_v$, where λ_s originates from solvational changes and λ_v from metal–ligand bonding changes (refs 7). Calculated values from ref 8g and work in progress. The error limits are based on the propagation of error in the calculated values. [d] Based on $\Delta G^{\ddagger} = (\lambda/4)(1 + \Delta G^{\circ}/\lambda)^2$; refs 7. Range of values based on the error limits for λ. [e] $k_{BET}(\text{calcd}) = \kappa_{nu}\nu_{eff}$, $\kappa_{nu} = \exp(-\Delta G^{\ddagger}_{BET}/RT)$; see refs 7. Range of values based on the range of $\Delta G^{\ddagger}$ values. [f] Estimate based on $Co(NH_3)_6^{3+,2+}$ parameters: refs 8a,d,g. [g] Prepared and characterized as described by Bignozzi et al.: Bignozzi, C. A.; Roffia, S.; Scandola, F. *J. Am. Chem. Soc.* **1985**, *107*, 1644. [h] The classical model often predicts too large an activation barrier for the "Marcus inverted region" ($|\Delta G^{\circ}| > \lambda$); refs 7. [i] Ref 4. [j] Ref 3.

here is among the strongest evidence to date that electronic factors can inhibit thermally activated electron transfer.

We used three cyanometalates of $Ru(bpy)_2(CN)_2$ in these studies: (a) $(bpy)_2Ru((CN)Co(NH_3)_5)_2^{6+}$; (b) $(bpy)_2(CN)Ru((CN)Co(tetraen))^{3+}$; and (c) $(bpy)_2(CN)Ru((CN)Co(terpy)(bpy))^{3+}$. Irradiations at the ruthenium(II) metal-to-ligand charge-transfer (MLCT) bands of these complexes in solution showed no evidence of the usual ruthenium emission.[9,10] The transient species, generated by an 18-ps, 532-nm excitation of the complex in water or acetonitrile, absorbed much less in the 400–500-nm (Ru(II) → bpy MLCT) region and more strongly at longer wavelengths than did the substrates. These transients decayed smoothly to regenerate the substrate absorbancies in about 1 ns.[11] The observed absorbance changes demonstrate photoinduced charge separation followed by simple BET to form the original Ru(II)–Co(III) ground states.[12]

The BET processes in these Ru–Co systems have very small activation barriers ($\Delta G^{\ddagger}$ (calcd) $\leq 300\ cm^{-1}$; see Table I). Simple electron-transfer models suggest that the BET process should be about 1000 times faster than observed (Table I). Simple cyano-bridged, Fe–Ru and Ru–Ru (Table I) systems, in which no electronic retardation is expected, exhibit much faster BET rates.[3,4] Thus, the relatively small observed values of k_{BET} for the Ru–Co systems implicates an electronic retardation factor of $\kappa_{el} \sim 10^{-3}$–10^{-4} for the $(^2T_2)Ru(III)$–$(^4T_2)Co(II) \rightarrow (^1A_1)Ru(II)$–$(^1A_1)Co(III)$ electron-transfer process.

The apparent acceptor independence of k_{BET} was unexpected. While the large driving forces of the BET process should lead to very small values of the classical activation energy and little variation in the nuclear retardation factor $\kappa_{nu} = \exp(-\Delta G^{\ddagger}/RT)$, the $(^4T_2)Co(II) - (^2E)Co(II)$ energy difference should vary in these complexes,[13,14] leading to significant variations in κ_{el}.[15] That this is not the case may be due to a cancellation of contributions. It is also possible that the sensitivity of κ_{el} in these rigid systems to donor–acceptor orbital symmetry (σ-donor and π-acceptor orbitals are involved here) modulates variations expected from spin–orbit coupling.

Acknowledgment. Partial support of this research from the Division of Chemical Sciences, Office of Basic Energy Research, U.S. Department of Energy, is gratefully acknowledged. We are very grateful to the Notre Dame Radiation Laboratory and Dr. Richard Fessenden for providing us with access to the picosecond flash photolysis system, and to Dr. John Chateauneuf for assisting us with this instrument.

Supplementary Material Available: Figure 1 depicting transient spectra of some RuCNCo complexes (1 page). Ordering information is given on any current masthead page.

---

(8) Recent discussions of various aspects of these issues can be found in the following: (a) Hammershoi, A.; Geselowitz, D.; Taube, H. *Inorg. Chem.* **1984**, *23*, 979. (b) Larsen, S.; Ståhl, K.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 3033. (c) Newton, M. D. In *The Challenge of d and f Electrons*; Salahub, D. R., Zerner, M. C., Eds.; ACS Symposium Series 394; American Chemical Society: Washington, DC, 1989; p 378. (d) Newton, M. D. *J. Phys. Chem.* **1991**, *95*, 30. (e) Ramasami, T.; Endicott, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 389. (f) Endicott, J. F. *Acc. Chem. Res.* **1988**, *21*, 59. (g) Endicott, J. F.; Brubaker, G. R.; Ramasami, T.; Kumar, K.; Dwarakanath, K.; Cassel, J.; Johnson, D. *Inorg. Chem.* **1983**, *22*, 3754.

(9) (a) Lei, Y.; Buranda, T.; Endicott, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 8821. (b) Lei, Y. Ph.D. Dissertation, Wayne State University, 1989.

(10) We observed greater than 95% emission quenching at both 298 and 77 K.

(11) A figure depicting characteristic transient spectra is in the supplementary material (see paragraph at end of paper). More complex behavior was observed for $(bpy)_2Ru((CN)Co(NH_3)_5)_2^{6+}$ in DMSO.

(12) The $(^3CT)Ru(bpy)^{22+}$ excited states of these dicyano species all exhibit strong absorbancies in the 430–460-nm region.[9] This absorption does not exist in Ru(III) complexes.

(13) The ^2E state has been estimated to be $13.7 \times 10^3\ cm^{-1}$ above the ground $^4T_2$ state in $Co(NH_3)_6^{2+}$,[14] this energy difference is about $3.5 \times 10^3\ cm^{-1}$ in $Co(bpy)_3^{2+}$.

(14) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1984.

(15) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767.

One-Electron Activation and Coupling of Ethene by Rhodium(II) Porphyrins: Observation of an η^2-Ethene–Metalloradical Complex

Andrew G. Bunn and Bradford B. Wayland*

Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

Received April 6, 1992

A series of rhodium(II) porphyrin (d^7, $s = {}^1/_2$) complexes where the ligand steric demands are incrementally increased has been used in studying metalloradical reactions of ethene. (Tetramesitylporphyrinato)rhodium(II),[1] $(TMP)Rh^{\bullet}$, and complexes with smaller ligand steric requirements react with ethene to form two-carbon alkyl bridged complexes, $(por)Rh–CH_2CH_2–Rh(por)$.[2-5] Replacing the methyl substituents of TMP with ethyl and isopropyl groups results in rhodium(II) complexes that produce ethene coupling and permit observation of an intermediate η^2-ethene–metalloradical complex, $[(por)Rh(CH_2{=}CH_2)]^{\bullet}$.

[Tetrakis(1,3,5-triethylphenyl)porphyrinato]rhodium(II), $(TTEPP)Rh^{\bullet}$, in benzene solution when exposed to ethene ($P_{C_2H_4} \sim 0.25$ atm) produces a four-carbon alkyl bridged complex, $(TTEPP)Rh–CH_2CH_2CH_2CH_2–Rh(TTEPP)$ (**1**) (eq 1). Compound **1** is formed quantitatively within the time required to record

$$2(TTEPP)Rh^{\bullet} + 2CH_2{=}CH_2 \rightleftharpoons (TTEPP)Rh{-}CH_2CH_2CH_2CH_2{-}Rh(TTEPP) \quad (1)$$

(1) Wayland, B. B.; Sherry, A. E.; Poszmik, G.; Bunn, A. G. *J. Am. Chem Soc.* **1992**, *114*, 1673.

(2) Ogoshi, H.; Setsume, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869.

(3) (a) Wayland, B. B.; Feng, Y.; Ba, S. *Organometallics* **1989**, *8*, 1438. (b) Sherry, A. E. Ph.D. Dissertation, University of Pennsylvania, 1990.

(4) Del Rossi, K. J.; Wayland, B. B. *J. Chem. Soc., Chem. Commun.* 1986, 1653.

(5) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

0002-7863/92/1514-6917$03.00/0