The reaction of 1.03 equiv of **7** with 1.00 equiv of benzoyl chloride and 4.0 mol % **1** in HMPA was conducted at 65 °C for 16 h. The isolation of **8** by radial chromatography (10% ethyl acetate/hexane) afforded **8** (mp 50–52 °C; $[\alpha]^{20}_{\mathrm{D}}$ $-0.314°$, $[\alpha]^{20}_{436}$ $-0.772°$ (CCl_4, *c* 30.0)), which had CD curves over a range of concentrations characteristic of the *R* isomer.[9] Alternatively the reaction of **3a** with 1.04 equiv of **7** in HMPA at 65 °C afforded **8** with 54% of the stereospecificity as the catalytic reaction.

A Baeyer–Villiger oxidation of **8** was carried out with 40% $CH_3CO_3H/BF_3{\cdot}Et_2O$ at 45 °C for 30 h[10] in order to determine the absolute configuration of **8**. Following purification by medium-pressure liquid chromatography (5% ethyl acetate/hexane), **9** showed $[\alpha]^{20}_{\mathrm{D}}$ $-0.10°$, $[\alpha]^{20}_{365}$ $-0.310°$ (CCl_4, *c* 9.0). The preparation of (*S*)-(+)-α-deuteriobenzyl benzoate, **10**, by acylation of **5** with benzoyl chloride/pyridine showed $[\alpha]^{20}_{\mathrm{D}}$ $+0.36°$, $[\alpha]^{20}_{365}$ 26° (CCl_4, *c* 9.0). The optical center of **5** is not affected by the acylation. Thus, **9** and **10** are enantiomers, and **9** must be (*R*)-(−)-α-deuteriobenzyl benzoate.

Since the Baeyer–Villiger oxidation is known to occur with retention of configuration at the saturated carbon of the ketone,[11] **8** must be of *R* configuration. Thus, the transmetalation occurs predominately with inversion of stereochemistry at the saturated carbon being transferred.

The optical purity of **9** is 21% (based on $[\alpha]^{20}_{365}$), which corresponds overall to 28% ee for the three reactions between **6** and **9**. There are points in the sequence between **6** and **9** where racemization is likely by processes other than the transmetalation step. The enolization of **8** as well as deuterium loss in a protic environment would lead to loss of optical purity. The loss of optical activity due to deuterium loss alone can be estimated from the deuterium content (mass spectrum): D_1:D_0 for **9** = 84.7:15.3 (= 98.4:1.6 for **10**). By assuming a deuterium isotope effect of 2 for the enolization process, then 42% of **8** racemized in the reactions from **7** to **9**.[12] Consequently, the highest possible optical purity that could have been realized for **8** was 43% ee, and therefore the transmetalation must have occurred with $\gtrsim$65% stereospecificity. By using α-dideuteriobenzyl phenyl ketone as a model, it was observed that 2.3% deuterium loss occurred in the radial chromatography, while no deuterium loss occurred in the Baeyer–Villiger reaction.

Other points in the reaction scheme where racemization could occur include the displacement of chloride from **6** by Bu_3SnLi. Although this occurs with >90% inversion with (*S*)-(+)-octyl chloride,[8] the displacement of a benzyl chloride by lithium triorganostannates is more likely to be accompanied by nonstereospecific free-radical processes, which would lower the optical purity of **7**.[13] Further, only a 52.6% stereospecificity for the reductive elimination of a methyl and an α-deuteriobenzyl group from palladium has been reported.[4] Taking these possibilities into account, it is likely that the amount of inversion occurring in the transmetalation step is relatively high.

In a polar solvent such as HMPA, inversion of configuration at carbon bonded to tin in transmetalation is analogous to the stereochemistry observed in acetonitrile for the bromine cleavage of a saturated carbon bonded to tin.[14] Accordingly, the transmetalation in this catalytic reaction can be compared to an electrophilic cleavage reaction in which the catalytic intermediate, **3**, is behaving as the electrophile.

Acknowledgment. This research was supported by Grant CHE-8003336 from the National Science Foundation. ^{31}P spectra were obtained from the Colorado State University Regional NMR Center funded by the National Science Foundation, Grant CHE-78-18581. Palladium chloride was provided under the Johnson-Matthey Metal Loan Program.

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[9] The CD spectra of a 16.4 × 10^{-3} M methanol solution of **8** was a negative curve; $[\theta] = -10.3°$ (312 nm). A methanol solution of (*S*)-(+)-α-methyldeoxybenzoin also gave a negative curve. Since deuterium behaves in a dissignate manner, **8** is of *R* configuration by correlation. See: Sundaraman, P.; Gunter, B.; Djerassi, C. *J. Org. Chem.* **1980**, *45*, 4231. The use of a chiral shift reagent tris[3-((trifluoromethyl)hydroxymethylene)-*d*-camphorato]europium(III) did not provide a method of determining the enantiomeric excess of **8**. Others (Numan, H.; Wynberg, H. *J. Org. Chem.* **1978**, *43*, 2232) have reported that the direct determination of the optical purity of a ketone in which optical activity is solely due to deuterium substitution has never been realized.

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[12] The percentage of **8** racemized due to deuterium loss in enolization = (98.4 − 84.7)/0.984 = 13.9%. If the deuterium isotope effect ($k_{\mathrm{H}}/k_{\mathrm{D}}$ is approximately 2, then the percentage of racemization due to proton loss in enolization = 2 × 13.9% = 27.8%, and the overall percentage of **8** racemized through enolization is 42%.

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Fast Intramolecular Electron Transfer in Radical Ions over Long Distances across Rigid Saturated Hydrocarbon Spacers[1]

L. T. Calcaterra, G. L. Closs,*[†] and J. R. Miller*[‡]

Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439
Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

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Measurements[2-11] of electron-transfer rates in systems with donor and acceptor (D and A) groups linked by spacers (S) have tended to confirm the traditional notion that fast ET requires contact or near contact between the reactants. But fast long-distance intermolecular ET occurs in solids when reaction energetics are optimized.[12,13] We have embarked on a program of building molecules of the general structure D–S–A to test dependence of ET rates on distance, reaction energetics, and molecular structure, and report here the first results.

Radical anions of molecules I–III (Figure 1) were generated by reactions with solvated electrons (e^-_s) formed by a 30ps pulse of electrons from the Argonne Linac in 2-methyltetrahydrofuran (MTHF) at room temperature (296 ± 2 K) with a bimolecular rate constant of 1×10^{11} M^{-1} s^{-1}.[14] In each case the donor is

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[†] To whom correspondence should be addressed at The University of Chicago.

[‡] To whom correspondence should be addressed at Argonne National Laboratory.

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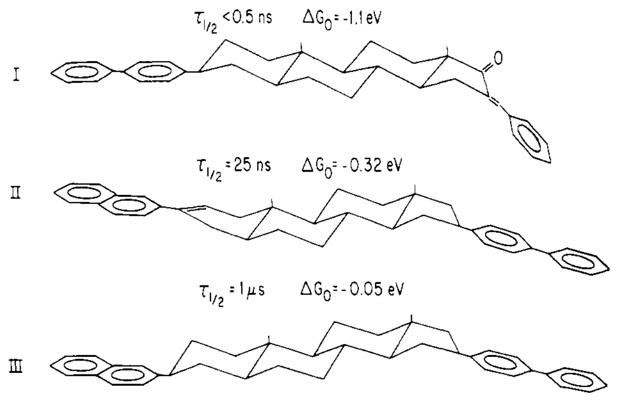


Figure 1. Structures of diended steroids with half-lives and free-energy changes for intramolecular transfer in their radical anions.

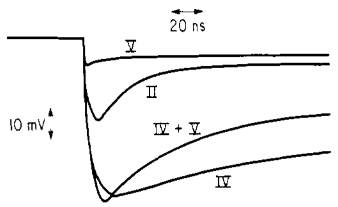
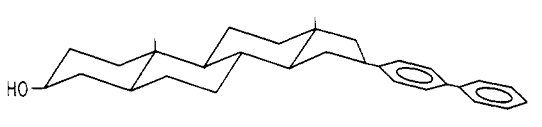


Figure 2. Oscilloscope traces for 1 mM solutions of the indicated compounds in MTHF at 296 K. The concentration of IV (but not V) was doubled in the mixture.

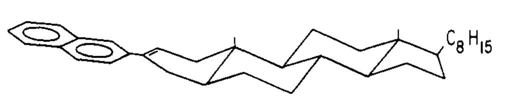
the negative ion of the biphenyl moiety donating an electron to the three different acceptors (cinnamoyl, 2-vinylnaphthyl, and 2-naphthyl, respectively).[15] Electron capture occurs at either end of the diended molecules with almost equal probability. What is measured is the kinetics of approach to equilibrium from this initial nonequilibrium state. The maximum ion concentration is 2×10^{-5} M, so only one electron attaches to each molecule.

Figure 2 shows oscillograms observing decay of optical absorbance of the radical anion of the biphenyl moiety (Ph_2^-) in II at 400 nm. The decay of Ph_2^- in 10^{-3} M solution is due mainly to intramolecular ET: $D^-SA \rightarrow DSA^-$. The much slower intermolecular ET ($k = 5 \times 10^9$ M^{-1} s^{-1}) has been measured with the model compounds IV and V. The traces in Figure 2 show an initial fast rise due to the formation of Ph_2^- generated by electron capture ($\tau \sim 10$ ns). The decay observed for IV, containing only the biphenyl moiety, is due to reaction of Ph_2^- with solvated protons and radicals created from the initial solvent hole ($MTHF^+$).[16]

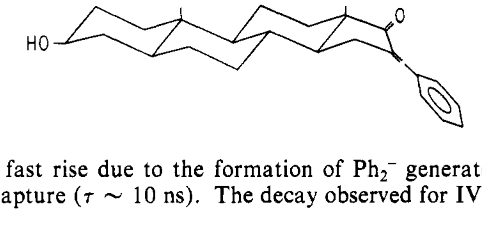
IV



V



VI



The concentration-independent rate constant of the intramolecular ET in II indicated in Figure 1 was extracted from the data with small corrections being made for intermolecular ET and reactions with products from the counterion. When I was subjected to pulse radiolysis under the same conditions as II, electron transfer was found to be complete within the present time resolution of our instrumentation (0.5 ns). ET in III is much slower, proceeding with a forward rate constant of 1×10^6 s^{-1}.

While intramolecular ET processes have been measured by several groups before,[2-11] the long, rigidly fixed distances in I–III are without parallel. The fast rates over these long distances are surprising in view of the insulating nature of the σ-bonded framework of the spacer. The LUMO of the spacer lies about 5 eV above the HOMO of the Ph_2^-.[17] Therefore, the probability of finding the electron in the spacer region is negligible, and the ET reactions must be described as long-range electron tunneling.

Quantum mechanical descriptions of ET[18] express the rate constant $k(r)$ as a product of the square of the electronic coupling $V(r)$ and a Franck–Condon weighted density of states (FCWD), where $V(r)$ decreases exponentially with distance between the reactants. The FCWD depends on reaction exothermicity, temperature, and the reorganization energies λ_v and λ_s of the reactants and surrounding solvent. It is maximized when reaction exothermicity equals the reorganization energy, $\lambda = \lambda_v + \lambda_s$, which has been found to be ≈ 1 eV for intermolecular ET reactions in MTHF at low temperatures.[13,19] Using information from the low-temperature ET experiments, we roughly estimate that the FCWD for ET in II ($\Delta G° = -0.32$ eV) will be smaller than for ET in I ($\Delta G° = -1.1$ eV) by a factor of ≈ 70. However, this estimate is very sensitive to the reorganization energies, which are not well-known for liquid MTHF, and assumes that $V(r)$ is similar in I and II, because of the similar separations of the π systems. The estimate is in accord with the measurements that indicate that ET is at least 50 times faster in I than II. These reorganization energies also predict that the ET rate in II should be midly temperature ($E_a \approx 0.1$ eV) and solvent dependent, while ET in I is expected to be nearly activationless. The slow rate in III is almost certainly due to the small exothermicity, although the distance between acceptors is also larger than in I and II.

Measurements in rigid MTHF at 77 K were used to probe the dependence of intermolecular ET rates on the distance between Ph_2^- and VI, which have only disordered solvent molecules between them (no linkage). At 15 Å center to center,[20] the same distance as in I, ET occurs in ≈ 5 ns, whereas intramolecular ET in I is at least 10 times faster. This small discrepancy may arise from the oversimplified models used in this comparison, or it may result from through-bond interactions in I that are absent in the rigid matrix system.

An understanding of how distance, energy, and molecular structure control rates of long-distance electron transfer will be essential to understanding photosynthesis and to designing efficient molecular systems for photochemical energy storage. The measurements reported here show that ET can be very fast indeed, even at large distances.

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[14] e_s^- gives similar rate constants with our various derivatized steroids, close to the value of 1.1×10^{11} M^{-1} s^{-1} measured earlier for e_s^- + biphenyl in THF by Bockrath: Bockrath, B.; Dorfman, L. *J. Phys. Chem.* **1973**, *77*, 1002.

[15] The free-energy changes in I and II are based on reduction potentials of model compounds reported in the literature: Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Dekker, New York, 1970. Klemm, L. H.; Lind, C. D.; Spence, J. T. *J. Org. Chem.* **1960**, *25*, 611. The value 0.05 ± 0.01 eV in III was obtained from the equilibrium measured in this work.

[16] $MTHF^+ = RH^+$ undergoes rapid proton transfer $RH^+ + RH \rightarrow R\cdot + RH_2^+$.

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[18] For a review of ET theory with references see: Schmitt, P. P. In "Specialist Periodical Reports, Electrochemistry–Volume 6"; The Chemical Society: London, 1978; Chapter 4. Extensive reference lists may also be found in ref 12 and 13.

[19] λ_v and λ_s were found to be 0.4 and 0.8 eV in rigid MTHF.[13]

[20] This distance is defined as the distance between the center of the biphenyl moiety and the center of the vinylic double bond in the cinnamoyl chromophore.

Highly Reduced Organometallics. 10.[1] Synthesis and Chemistry of the Pentacarbonylmetallate(3−) Ions of Niobium and Tantalum, $M(CO)_5^{3-}$

Garry F. P. Warnock, Julian Sprague, Kristi L. Fjare, and John E. Ellis*

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

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In this paper we report on the syntheses and characterizations of the pentacarbonylmetallate trianions of niobium and tantalum, which are the first compounds to contain these elements in a formal oxidation state of −3. Although metal carbonyl trianions of other second- and third-row transition elements have been claimed,[2] these are also the first examples to have been isolated as analytically pure substances.

Substantial differences in the carbonyl chemistry of first-row transition metals and that of second and third row homologues are often observed. For example, while $Cr(CO)_6$ readily reacts with Na–NH_3 to provide high yields of $Na_2Cr(CO)_5$, corresponding reductions of $M(CO)_6$ (M = Mo, W) give only very low yields of thermally unstable $Na_2M(CO)_5$.[3,4] For these reasons it was by no means obvious whether reductions of the isoelectronic $M(CO)_6^-$ (M = Nb, Ta) would provide species analogous to the previously reported $V(CO)_5^{3-}$.[5]

Unlike the Na–NH_3 reductions of $Mo(CO)_6$ and $W(CO)_6$, however, $[Na(diglyme)_2][M(CO)_6]$[6] are smoothly reduced by 3 equiv of sodium in liquid ammonia at −78° C to provide deep red solutions containing thermally unstable $Na_3[M(CO)_5]$, according to eq 1. After filtration and cation exchange, deep red (M = Nb) or deep brown-red (M = Ta), slightly soluble, and apparently amorphous solids are obtained in 40–50% yields, which provide satisfactory analyses for unsolvated $Cs_3[M(CO)_5]$.[7] These materials have infrared spectra that are nearly superimposable on those of $Cs_3[V(CO)_5]$.[5] Although they appear to be only slightly less thermally stable than the vanadium analogue, as dry solids they are much more *shock sensitive*. One sample of $Cs_3[Ta(CO)_5]$ *exploded* on standing at room temperature under an inert atmosphere. In this respect they resemble the unstable $K_3[V(CO)_5]$.[5] For these reasons, their chemical studies have been largely limited to the reactions of $M(CO)_5^{3-}$ formed in situ in liquid ammonia.

$$Na[M(CO)_6] + 3Na \rightarrow Na_3[M(CO)_5] + {}^1/{}_2[Na_2C_2O_2]\downarrow \quad (1)$$

Treatment of liquid ammonia solutions of $Na_3[M(CO)_5]$ dropwise with 1 equiv of Ph_3SnCl in THF provides, after metathesis, 70–80% yields of orange to orange-red, crystalline $[Et_4N]_2[Ph_3SnM(CO)_5]$.[8] These oxygen-sensitive materials have infrared spectra in the ν(CO) region that are consistent with the presence of a substituted dianion of C_{4v} symmetry.[8] Also, nearly quantitative yields of the previously unknown $Na[M(CO)_5NH_3]$ are obtained from the reaction of $Na_3[M(CO)_5]$ with ammonium chloride in liquid ammonia. Although the sodium salts are thermally unstable, 40–45% yields of red violet (M = Nb) to deep violet (M = Ta) crystalline $[Ph_4As][M(CO)_5NH_3]$ may be obtained by metathesis.[9] These ammine complexes, like their vanadium analogue,[10] are very labile in solution and readily react at −20 to 0 °C with a variety of π-acceptor ligands such as PR_3, $P(OR)_3$, and RNC to provide 50–80% isolated yields of the corresponding $M(CO)_5L^-$. For example, the first isocyanide derivatives of tantalum and niobium carbonyls were obtained by treating ammonia solutions of $Na[M(CO)_5NH_3]$ with *t*-BuNC followed by cation exchange and crystallization. Orange $[Et_4N][M(CO)_5CN\text{-}t\text{-}Bu]$ were thereby obtained in 50–60% yields.[11] The chemistry of $M(CO)_5^{3-}$ reported herein is summarized in eq 2 and 3.

$$Ph_3SnM(CO)_5^{2-} \xleftarrow{Ph_3SnCl} M(CO)_5^{3-} \xrightarrow{2NH_4^+} M(CO)_5NH_3^- + H_2 \quad (2)$$

$$(M = Nb, Ta)$$

$$M(CO)_5NH_3^- + L \xrightarrow{-20\ \mathrm{to}\ 0\ ^\circ C} M(CO)_5L^- + NH_3 \quad (3)$$

$$(L = PR_3, P(OR)_3, RNC)$$

It is anticipated that the carbonyl trianions of niobium and tantalum will be especially important as precursors to new metal clusters containing these elements. Studies in this latter area are in progress.

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(7) Anal. Calcd for $C_5Cs_3NbO_5$: C, 9.61; Cs, 63.12; H, 0.00. Found, C, 9.47; Cs, 63.35; H, 0.07. IR Nujol, (ν(CO) region) 1810 w (sharp), 1566 vs. (br) cm^{-1}. Anal. Calcd for $C_5Cs_3O_5Ta$: C, 8.34; Cs, 55.40; Ta, 25.14; H, 0.00. Found: C, 8.23; Cs, 55.68; Ta, 25.03; H, 0.12. IR Nujol, (ν(CO) region) 1813 w (sharp), 1562 vs (br) cm^{-1}.

(8) Anal. Calcd for $C_{39}H_{55}N_2O_5SnTa$: C, 50.29; H, 5.95; N, 3.01. Found: C, 49.95; H, 5.83; N, 3.03. IR (ν(CO), in CH_3CN) 1942 m, 1785 vs, 1755 sh cm^{-1}. Anal. Calcd for $C_{39}H_{55}N_2O_5NbSn$: C, 55.54; H, 6.57; N, 3.32. Found: C, 55.42; H, 6.48; N, 3.45. IR (ν(CO), CH_3CN) 1948 m, 1790 vs, 1750 sh cm^{-1}. ^1H NMR spectra in CD_3CN show integrations of phenyl and ethyl protons that are consistent with these formulations.

(9) Anal. Calcd for $C_{29}H_{23}O_5AsNNb$: C, 55.26; H, 3.20; N, 2.22. Found: C, 55.13; H, 3.26; N, 2.34. IR (ν(CO), Nujol) 1963 m, 1781 vs (br), 1759 vs (br) cm^{-1}. Anal. Calcd for $C_{29}H_{23}O_5AsNTa$: C, 48.49, H, 2.81; N, 1.95. Found: C, 48.03; H, 2.91; N, 1.90. IR (ν(CO), Nujol) 1960 m, 1775 s (br), 1755 vs (br) cm^{-1}.

(10) (a) Ellis, J. E.; Fjare, K. L. *Organometallics* **1982**, *1*, 898. (b) Fjare, K. L.; Ellis, J. E. *Ibid.* **1982**, *1*, 1373.

(11) Anal. Calcd for $C_{18}H_{29}N_2NbO_5$: C, 48.44; H, 6.55; N, 6.28. Found: C, 48.21; H, 6.75; N, 6.23. IR (CH_3CN) (ν(CN)) 2090 w, ν(CO): 1966 m, 1830 s cm^{-1}; ^1H NMR (CD_3CN) δ 1.46 s (9 H) (Et_4N^+ signals omitted). Anal. Calcd for $C_{18}H_{29}N_2O_5Ta$: C, 40.46; H, 5.47. Found: C, 40.79; H, 5.53. IR (CH_3CN) (ν(CN)) 2090 w, (ν(CO)) 1960 m, 1828 s cm^{-1}; ^1H NMR (CD_3CN) δ 1.48 s (9 H) (Et_4N^+ signals omitted).

Olefinic Cyclizations Promoted by Beckmann Rearrangement of Oxime Sulfonate

Soichi Sakane, Yasushi Matsumura, Yoshihiro Yamamura, Yasuko Ishida, Keiji Maruoka, and Hisashi Yamamoto*

Department of Applied Chemistry, Nagoya University
Chikusa, Nagoya 464, Japan

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The title reaction, if successful, would result in the direct formation of a wide variety of ring systems.[1-3]

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(2) The present rearrangement-cyclization process may proceed via nitrilium ions as intermediates, which can also be generated by the Ritter reaction. For an excellent review of the Ritter reaction, see: Meyers, A. I.; Sircar, J. C. In "The Chemistry of Cyano Group"; Rappoport, Z. Ed.; Interscience: New York, 1970; p 341. See also: Johnson, F.; Madronero, R. In "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1966; Vol. 6, p 95. Krimen, L. I.; Cota, D. J. *Org. React.* (*N.Y.*) **1969**, *17*, 213. Meyers, A. I.; Singh, H. *J. Org. Chem.* **1968**, *33*, 2365. Shome, M.; Smith, P. W.; Southam, R. M.; Oxford, A. W. *Tetrahedron Lett.* **1980**, *21*, 2927.

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