Figure 2. Molecular structure of Fe(η^4-1)(CN'Bu)$_2$; ORTEP drawing with all non-hydrogen atoms drawn to encompass 50% of electron density. Key bond distances (Å) are Fe–C23, 1.973 (3); Fe–C28, 1.965 (3); Fe–N1, 1.927 (2); Fe–N2, 1.905 (2); Fe–N3, 1.895 (2); Fe–N4, 1.914 (2); C23–N5, 1.138 (4); C28–N6, 1.143 (4). Selected bond angles (deg): C29–N6–C28, 178.2 (3); C24–N5–C23, 176.2 (3).

(Figure 1) exhibit magnetic hyperfine interactions, indicating an integer electronic spin. Attempts to explain these data with high spin ($S = 2$) iron(IV) were unsuccessful because the fits require A values 3–4 times smaller than expected for a high spin configuration.[7] However, the data fit well to an $S = 1$ spin Hamiltonian resulting from a tetragonally or rhombically distorted t_{2g}^4 configuration (see caption of Figure 1). The Mössbauer spectra show that the magnetic hyperfine field is essentially axial. Using the model of Oosterhuis and Lang,[8] the tetragonal splitting of the t_{2g} set is $\Delta \approx 5\xi = 2000$ cm^{-1}, where $\xi = 400$ cm^{-1} is the spin–orbit coupling constant. Within this model, an axial hyperfine field can be produced even for a rhombic ligand field. Independent of the assumed symmetry, our data place the first excited state in the t_{2g} set at least 1500 cm^{-1} above the ground state.

The geometry around the iron atom of Fe(η^4-1)(CN'Bu)$_2$ is an axially distorted octahedron (Figure 2).[9] The RMS deviation from the plane of Fe and the four N donor atoms is 0.03 Å. The average Fe–C distance is 1.969 Å, while the average Fe–N distance is 1.910 Å. The average C–N length in the isocyanides is 1.14 Å, and the CNC isocyanide angles are nearly 180°. Iron–isocyanide complexes have been structurally characterized for Fe(0), Fe(I), and Fe(II).[10] Comparison with the literature data shows

that a C–N triple bond formulation is appropriate, indicating that the π-acid character of the isocyanides is not highly expressed.[11] This agrees with the observance of a nonzero spin d^4 iron center, ruling out an electronic structure in which strong π-interactions between two dπ metal orbitals and empty π* isocyanide orbitals bring about spin pairing. The existence of Fe(η^4-1)(CN'Bu)$_2$ demonstrates that the coordination chemistry of high valent iron can be expanded.

Supplementary Material Available: Tables of data collection information, atom coordinates, Gaussian amplitudes, and bond lengths and angles for Fe(η^4-1)(CN'Bu)$_2$ (7 pages); listing of structure factor amplitudes for Fe(η^4-1)(CN'Bu)$_2$ (20 pages). Ordering information is given on any current masthead page.

(10) Results of Cambridge Structural Data Base search; License of Access as given in the following: Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146. For terminal isocyanide compounds: Fe(0), 42 data points; Fe–C distances, 1.747–2.05 Å (average = 1.835 Å); C–N distances, 1.03–1.21 Å (average = 1.156 Å); CNC angles, 131.8–180° (average = 163.8°); Fe(I), 12 data points; Fe–C distances, 1.76–1.937 Å (average = 1.836 Å); C–N distances, 1.13–1.221 Å (average = 1.176 Å); CNC angles, 125.5–177° (average = 152.7°); Fe(II), 37 data points; Fe–C distances, 1.73–1.98 Å; C–N distances, 1.08–1.3 Å (average = 1.158 Å); CNC angles, 159.1–180° (average = 174.1°).
(11) A detailed analysis will appear elsewhere.

Solid-State Photochemistry. Remarkable Effects of the Packing of Molecules in Crystals on the Diastereoselectivity of the Intramolecular 2 + 2 Photocycloaddition of a 4-(3'-Butenyl)-2,5-cyclohexadien-1-one

Arthur G. Schultz,* Arthur G. Taveras, Richard E. Taylor, Fook S. Tham, and Rudolph K. Kullnig

Department of Chemistry, Rensselaer Polytechnic Institute Troy, New York 12180-3590

The intramolecular 2 + 2 photocycloadditions of 4-(3'-alkenyl)-2,5-cyclohexadien-1-ones give tricyclo[5.2.1.0^{5,10}]dec-2-en-4-ones in excellent yields.[1] Enantioselective constructions of these synthetically useful tricycles are possible[1a] because of the availability of methods for asymmetric synthesis of 2,5-cyclohexadien-1-ones[2] and the demonstration that the intramolecular 2 + 2 photocycloaddition proceeds without racemization of the photosubstrate.[3] In this paper we describe a fundamentally different kind of asymmetric control involving photochemistry of a 4-(3'-butenyl)-2,5-cyclohexadien-1-one (e.g., **1b** → **2b** or **3b**) in the solid state.[4] We show that competing and nearly isoenergetic (in the solution state) unimolecular photocycloadditions[5] can be selectively partitioned in the solid state as a result of the

(7) An $S = 2$ fit yields $A_x \approx A_y \approx -7.6$ MHz and $A_z \approx -2$ MHz. This should be compared with $A_x \approx A_y \approx A_z \approx -20$ MHz for the $S = 2$ high spin Fe(IV) complex with the same macrocycle, [Fe(η^4-1)Cl]$^-$; the latter compound yields an integer spin EPR signal at $g = 8$, which is characteristic for an $S = 2$ system, unpublished results. A values of ca. 20 MHz have also been reported for the $S = 2$ Fe(IV) sites of M$_{0.5}$La$_{1.5}$Li$_{0.5}$Fe$_{0.5}$O$_4$ (where M = Ca, Sr, Ba): Demazeau, G.; Fournes, L.; Soubeyroux, J.-L.; Takeda, Y.; Thomas, M.; Pouchard, M. *Rev. Chim. Miner.* **1983**, *20*, 155–172.
(8) Oosterhius, W. T.; Lang, G. *J. Chem. Phys.* **1973**, *58*, 4757–4765.
(9) Crystal data: Single crystals of Fe(η^4-1)(CN'Bu)$_2$ at 293 K are triclinic, space group $P\bar{1}$ with $a = 11.491$ (1) Å, $b = 10.481$ (2) Å, $c = 15.015$ (8) Å, $\alpha = 95.26$ (2)°, $\beta = 91.29$ (2)°, $\gamma = 81.58$ (1)°, $V = 1718.2$ Å^3, and $Z = 2$ [$d_{calcd} = 1.268$ g cm^{-3}, μ(Mo Kα) = 4.34 cm^{-1}]. A total of 7726 independent reflections (2° < 2θ < 55°) were collected using $\omega/2\theta$ scans with graphite-monochromated Mo Kα radiation. The structural parameters have been refined to convergence, R_1 (unweighted, based on F) = 0.058 for 6679 observed reflections [$I > 3\sigma(I)$].

(1) (a) Schultz, A. G.; Plummer, M.; Taveras, A. G.; Kullnig, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 5547. (b) Schultz, A. G.; Geiss, W.; Kullnig, R. K. *J. Org. Chem.* **1989**, *54*, 3158. (c) Schultz, A. G.; Geiss, W. *J. Am. Chem. Soc.* **1991**, *113*, 3490.
(2) Schultz, A. G. *Acc. Chem. Res.* **1990**, *23*, 207.
(3) This result is in contrast to the type A photorearrangement of enantiomerically pure 4-carbomethoxy-3-methoxy-4-methyl-2,5-cyclohexadien-1-one, which has been shown to occur with partial racemization of the photosubstrate; see ref 1a.
(4) For the first report of a solid-state photorearrangement of a 2,5-cyclohexadien-1-one (santonin) see: Matsuura, T.; Sata, Y.; Ogura, K. *Tetrahedron Lett.* **1968**, 4627.
(5) For a review of the substantial progress that has been made in understanding crystal lattice control of unimolecular photorearrangements, see: Scheffer, J. R. *Acc. Chem. Res.* **1980**, *13*, 283.
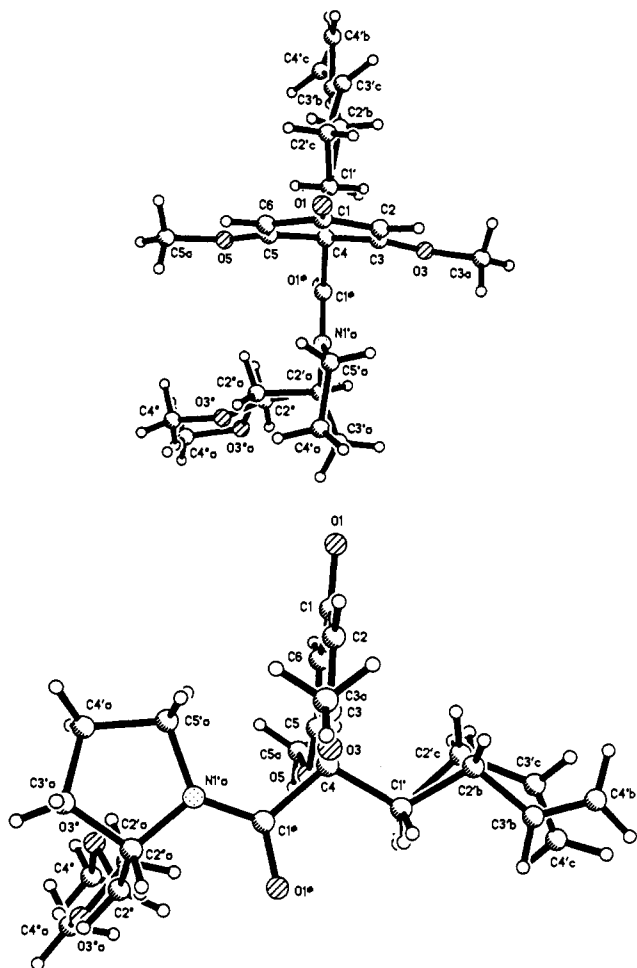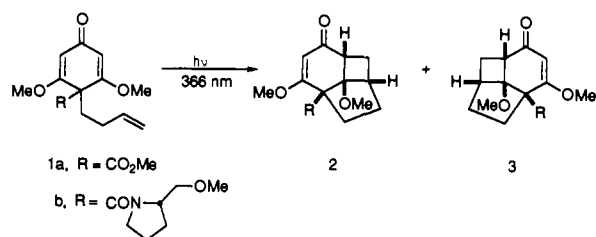
Figure 1. Molecular structure of the α-crystalline form of **1b**; composite views showing disorder with two conformations for the 4-($3'$-butenyl) and methoxymethyl side chains.

availability of effective reaction volumes.

It has been reported that 4-($3'$-butenyl)-4-carbomethoxy-2,5-cyclohexadien-1-one (**1a**) undergoes intramolecular 2 + 2 photocycloaddition in benzene solution in quantitative yield.[1a] Cy-

clohexadienone **1a** is prochiral and, therefore, gives a racemic product when the photolysis is carried out in an achiral environment. Installation of a chiral auxiliary at C(4) as shown in **1b** affords an opportunity for desymmetrization[6] of the 2,5-cyclohexadien-1-one ring. This tactic fails to provide synthetically useful diastereoselectivities via photolysis of **1b** in benzene solution (Table I).

Cyclohexadienone **1b** crystallizes from ethyl acetate–hexane in two modifications, and both have been subjected to X-ray structure determinations.[7] The α-form (mp 102–104 °C) shows

Table 1. Diastereoselectivities of Photocyclizations of **1b**

photolysis conditions[a]	product ratio[b] 2b:3b	% de	% conversion[b]
benzene solution[c]	1:1.5	20	100
α-crystal (mp 102–104 °C)[d]	1:2	33	100
	1:10	82	60
β-crystal (mp 127–128 °C)[d]	2:1	33	100
	2:1	33	13
	2.7:1	46	12
	3.4:1	55	8
	4.2:1	62	7
	7.3:1	76	5
	>20:1	>90	3

[a] Light source was a Hanovia 450-W medium-pressure mercury arc lamp. The lamp was placed in a water-cooled Pyrex immersion well, and Corning filters 0-25 and 7-54 provided the 366-nm light. [b] Photolysis mixtures were analyzed by gas chromatography on a 16 ft × $^1/_8$ in. stainless steel column packed with 0.5% QF-1 on Chromosorb G-HP (80–100 mesh size) and/or ^{1}H NMR spectroscopy. [c] Preparative-scale photolysis of **1b** in degassed benzene solution (0.05 M) provided a mixture of **2b** and **3b** in 97% isolated yield (oil) after flash chromatography on silica gel. [d] Solid-state photolyses were generally carried out with several milligrams of crushed crystals placed between microscope slides or in melting point capillary tubes attached to the light filters.
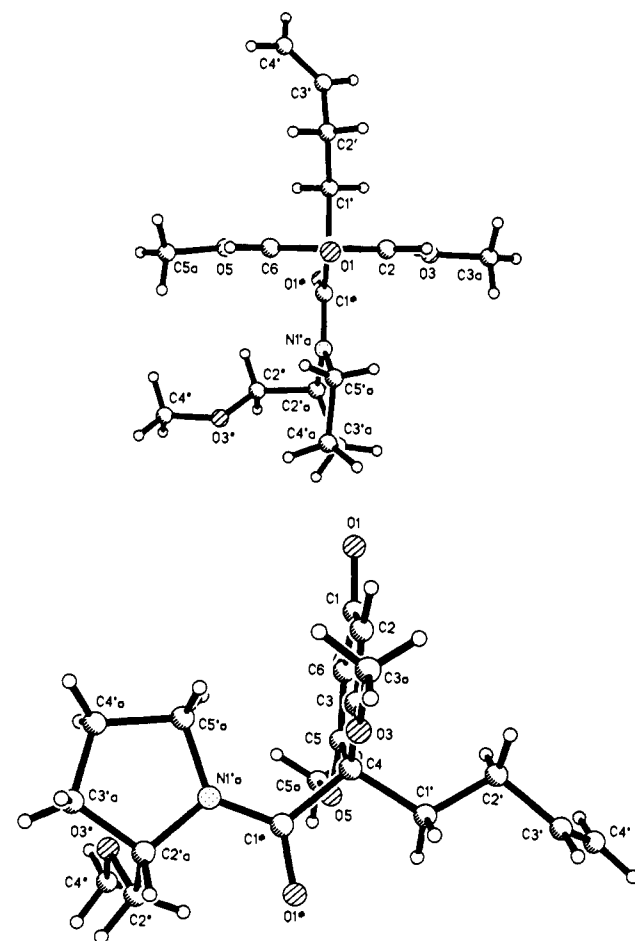

Figure 2. Molecular structure of the β-crystalline form of **1b**.

disorder, and low temperature crystallographic studies have revealed that the 4-($3'$-butenyl) side chain resides in the two conformations ($\sim$60:40 distribution) shown in Figure 1. Two

(6) For examples of chemical desymmetrization of prochiral structural units by the use of internal or external chiral auxiliaries, see: (a) Poupart, M.-A.; Paquette, L. A. *Tetrahedron Lett.* **1988**, *29*, 269. (b) Sato, Y.; Sodeoka, M.; Shibasaki, M. *J. Org. Chem.* **1989**, *54*, 4738. (c) Hart, D. J.; Huang, H.-C.; Krishnamurthy, R.; Schwartz, T. *J. Am. Chem. Soc.* **1989**, *111*, 7507. (d) Fuji, K.; Node, M.; Naniwa, Y.; Kawabata, T. *Tetrahedron Lett.* **1990**, *31*, 3175.

(7) Crystals of the α-form of **1b** are colorless prisms, orthorhombic, space group $P2_12_12_1$, $a = 8.156$ (3), $b = 12.885$ (5), and $c = 18.105$ (5) Å, $V = 1902.5$ (9) Å,[3] $z = 4$. The structure was solved by direct methods, $R = 4.29\%$ for 1454 reflections. Crystals of the β-form of **1b** are colorless prisms, orthorhombic, space group $P2_12_12_1$, $a = 8.517$ (1), $b = 12.618$ (2), and $c = 17.816$ (3) Å, $V = 1914.8$ (5) Å, $z = 4$. The structure was solved by direct methods, $R = 4.64\%$ for 1472 reflections (F > 4σF).

conformations (~80:20) also were found for the methoxymethyl side chain of the chiral auxiliary.

The molecular structure of the β-crystalline form (mp 127–128 °C) is shown in Figure 2. The most striking difference between the α- and β-form is the pronounced cant of the C(3′)–C(4′) bond of the butenyl group toward the C(5)–C(6) double bond of the cyclohexadienone ring in the β-crystal and the little deviation from a pseudosymmetric averaged positioning of the butenyl group in the α-crystal.

In contrast to the solution-state photochemistry of **1b**, irradiation (366 nm) of α- and β-crystals of **1b** provided remarkably high diastereoselectivities (Table I). At 60% conversion, the α-form gave **2b** and **3b** in a ratio of 1:10.[8] With higher conversions the crystalline structure of the sample visibly deteriorated, and at complete conversion the diastereoselectivity eroded to 1:2. Irradiation of the β-crystal gave a near complete reversal of the sense of diastereoselection for formation of **2b** and **3b** (>20:1) at very low conversions.[9]
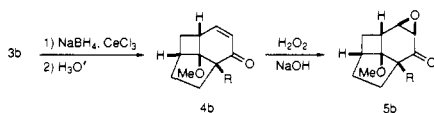
It is often assumed that reactions in crystalline solids should take place with minimum atomic and molecular movement.[10] However, local stress generated by reaction in the crystal can cause reactive intermediates to follow indirect trajectories rather than least-motion paths.[11] Considering only the molecular structure of **1b** in the β-crystal (Figure 2), it is clear that a proximity argument cannot be used to explain the preferential formation of **2b**; in fact, to generate **2b**, the 4-(3′-butenyl) group must swing toward the C(2)–C(3) rather than the more proximate C(5)–C(6) double bond.

Computer-assisted modeling of the packing arrangement of the α- and β-forms of **1b** has provided a reasonable explanation for the observed diastereoselectivities (supplementary material). It is possible to see an available reaction volume for butenyl group movement in regions that correspond to the preferred paths for 2 + 2 photocycloadditions at low conversions of the α- and β-crystals.

Fortuitous crystallizations and the erosion of diastereoselectivities with increasing degrees of photoconversion limit the synthetic utility of the solid-state photochemistry exemplified here with **1b**. Rather, the importance of this study is the demonstration that relatively subtle crystal lattice restraints can result in dramatic changes in the course of unimolecular solid-state photoreactions. It should be clear that the type of orientational control described for **1b** is very different from the distance and geometric requirements uncovered during studies of the 2 + 2 photodimerizations of cinnamic acids in the solid state.[12] We expect that these observations can be incorporated into the design of potentially more stable crystalline matrices[13] for stereocontrolled unimolecular photoreactions.

Supplementary Material Available: Experimental procedures for preparation of **1b**; tables of crystal structure data, atomic coordinates, bond lengths, bond angles, anisotropic parameters, and hydrogen atom coordinates; packing diagrams for the α-form of **1b**, the β-form of **1b**, and the epoxy ketone **5b**; and computer-generated views of the nearest neighbor interactions (39 pages). Ordering information is given on any current masthead page.

Long-Range Energy Transfer in Oligomeric Metal Complex Assemblies

Carlo Alberto Bignozzi,* Roberto Argazzi,
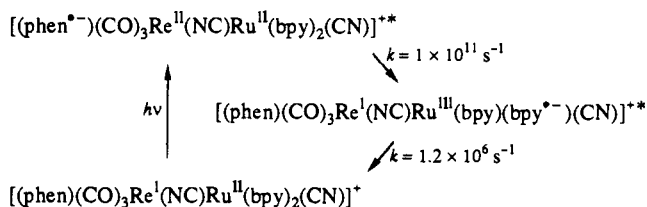Christian G. Garcia, and Franco Scandola

Dipartimento di Chimica dell' Università
Centro di Fotochimica CNR, 44100 Ferrara, Italy

Jon R. Schoonover and Thomas J. Meyer*

Chemistry Department
The University of North Carolina at Chapel Hill
*Chapel Hill, North Carolina 27599-3290*
Received June 22, 1992

Recently we demonstrated by transient infrared spectroscopy that Re^I → phen metal-to-ligand charge-transfer (MLCT) excitation of [(phen)(CO)$_3$Re^I(NC)Ru^{II}(bpy)$_2$(CN)]$^+$ (phen is 1,10-phenanthroline; bpy is 2,2′-bipyridine) in CH$_3$CN was followed by rapid (~10 ps), intramolecular energy transfer.[1] We
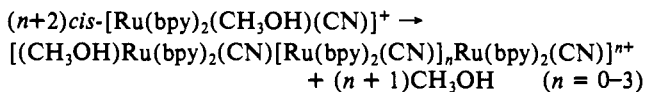
[(phen$^{\bullet-}$)(CO)$_3$Re^{II}(NC)Ru^{II}(bpy)$_2$(CN)]$^{+*}$

$k = 1 \times 10^{11}$ s^{-1}

$h\nu$ [(phen)(CO)$_3$Re^I(NC)Ru^{III}(bpy)(bpy$^{\bullet-}$)(CN)]$^{+*}$

$k = 1.2 \times 10^6$ s^{-1}

[(phen)(CO)$_3$Re^I(NC)Ru^{II}(bpy)$_2$(CN)]$^+$

have extended the cyano-bridging chemistry to the oligomers, [(phen)(CO)$_3$Re(CN)[Ru(bpy)$_2$(CN)]$_n$Ru(bpy)$_2$(CN)]$^{(n+1)+}$ (*n* = 0–3), in which every Ru^{II} center is linked to two cyanides, one by binding to carbon and one to nitrogen, and report here that they can function as molecular conduits for long-range energy transfer.

The oligomers were prepared by warming solutions of a reactive solvento intermediate generated by the reaction[2]

cis-[Ru(bpy)$_2$(NO)(CN)]$^{2+}$ + N$_3^-$ + CH$_3$OH →
    cis-[Ru(bpy)$_2$(CH$_3$OH)(CN)]$^+$ + N$_2$ + N$_2$O
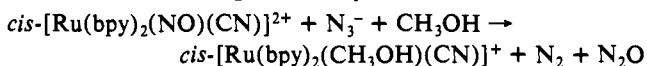
The oligomers which formed were end-capped with Re(phen)(CO)$_3$(CN) in a second step and separated by chromatography.[3]

(*n*+2)*cis*-[Ru(bpy)$_2$(CH$_3$OH)(CN)]$^+$ →
[(CH$_3$OH)Ru(bpy)$_2$(CN)[Ru(bpy)$_2$(CN)]$_n$Ru(bpy)$_2$(CN)]$^{n+}$
    + (*n* + 1)CH$_3$OH   (*n* = 0–3)

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(8) Assignments of relative configuration to **2b** and **3b** could not be made directly but were deduced by an X-ray crystallographic analysis of epoxy ketone **5b**, prepared from **3b** by the sequence of reactions shown below.

(9) For rare examples of reactivity differences between two polymorphic modifications in a unimolecular photoreaction, see: (a) Evans, S. V.; Omkaram, N.; Scheffer, J. R.; Trotter, J. *Tetrahedron Lett.* **1986,** *27*, 1419. (b) Lewis, T. J.; Rettig, S. J.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1991,** *113*, 8180.

(10) Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1975,** *14*, 386.

(11) McBride, J. M. *Acc. Chem. Res.* **1983,** *16*, 304.

(12) Schmidt, G. M. J. *Pure Appl. Chem.* **1971,** *27*, 647.

(13) For progress in the design of cocrystals and other aggregate structures, see: Etter, M. C.; Frankenbach, G. M. *Chemistry of Materials* **1989,** *1*, 10 and references cited therein.

(1) Gordon, K. C.; Dyer, R. B.; Schoonover, J. R.; Meyer, T. J.; Bignozzi, C. A.; Argazzi, R. *J. Phys. Chem.*, in press.

(2) (a) Adeyemi, S. A.; Miller, F. J.; Meyer, T. J. *Inorg. Chem.* **1972,** *11*, 994. (b) Bignozzi, C. A.; Roffia, S.; Chiorboli, C.; Davila, J.; Indelli, M. T.; Scandola, F. *Inorg. Chem.* **1989,** *28*, 4350.

(3) To a 0.60-g sample of [Ru(bpy)$_2$(NO)(CN)](PF$_6$)$_2$ (0.79 mmol)^{2b} suspended in 60 mL of CH$_3$OH was added 0.051 g of NaN$_3$ (0.79 mmol). The resulting purple-brown solution was heated at reflux for 2 h, and 0.7 g of Re(phen)(CO)$_3$(CN) (1.57 mmol)^4 was added. The mixture was heated at reflux for 9 h, and the solvent was removed by evaporation. The solid was redissolved in CH$_3$CN and filtered to remove Re(phen)(CO)$_3$(CN), and the CH$_3$CN solution was eluted on a 1.5 × 5 cm silica gel column with CH$_2$Cl$_2$ to remove Re(phen)(CO)$_3$(CN), with methanol to collect the Re–Ru complex, and with a NaCl-saturated methanol solution containing 5–15% water to collect the Re–Ru–Ru oligomer followed by Re–Ru–Ru–Ru and Re–Ru–Ru–Ru–Ru. Higher oligomers were irreversibly retained on the column. The eluted bands were concentrated, NaCl was filtered off, PF$_6^-$ salts were precipitated by the addition of (NH$_4$)(PF$_6$), and excess Cl$^-$ was removed by reprecipitation with added (NH$_4$)(PF$_6$). The reprecipitation cycle was repeated three times.