The aqueous washes were then combined and extracted five times with ether. The ether layers were combined and dried over magnesium sulfate. The ether was distilled through a 30-in. Vigreux column until less than 300 mL of solution remained. The remainder was fractionally distilled through a 12-in. Vigreux column. After a forerun of ether, cyclohexanone (bp 155 °C) was distilled to give 92.9 g (95.8%) of a colorless liquid which had ^1H NMR and IR spectra and VPC retention time identical with those of an authentic sample.

Oxidation of 2-Ethyl-1,3-hexanediol. 2-Ethyl-1,3-hexanediol (Eastman, 10.12 g, 0.068 mol) was dissolved in glacial acetic acid (50 mL) in a 250-mL 3-neck flask equipped with a thermometer and magnetic stirring bar. Aqueous sodium hypochlorite (49 mL of 1.48 M solution, 0.072 mol) was added dropwise over 1 h. The reaction was cooled in an ice–water bath as necessary to maintain the temperature between 20 and 25 °C. The mixture was stirred for 30 min after completion of the addition, after which a potassium iodide–starch test was negative. The reaction mixture was poured into ice-brine (300 mL), and the resulting mixture was extracted five times with ether. The combined ether extract was washed three times with saturated aqueous sodium carbonate solution and twice with aqueous sodium hydroxide solution (5% by weight). The aqueous washes were combined and extracted three times with ether. The ether extracts were then combined, dried over anhydrous magnesium sulfate, and concentrated by rotary evaporation to give a colorless oil (9.64 g). Vacuum distillation in a short-path apparatus gave 8.42 g (85%) of 2-ethyl-1-hydroxy-3-hexanone as a colorless oil:[10] ^1H NMR (200 MHz) δ 3.73 (2 H, ddd, J = 6, 11, 11 Hz, CH_2OH), 2.65 (1 H, m, O=CHEt), 2.49 (2 H, t, J = 7 Hz, $CH_2CH_2C{=}O$), 2.12 (1 H, t, J = 6 Hz, CH_2OH, exchanges with D_2O), 1.40–1.80 (4 H, m, CH_2), 0.85–1.05 (6 H, superimposed t, CH_2CH_3); ^{13}C NMR δ 215.0 (C=O), 62.9, 55.8, 45.2, 21.5, 16.8, 13.8, 11.8; IR (CCl_4) 3450 (br, OH), 2950 (s, CH), 2920 (m, CH), 2864 (m, CH), 1703 cm^{-1} (s, C=O); exact mass, m/e found 144.1146, calculated for $C_8H_{16}O_2$ 144.1151.

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Registry No. (–)-Borneol, 464-45-9; (±)-isoborneol, 24393-70-2; (–)-menthol, 2216-51-5; cyclohexanol, 108-93-0; 2,2,5-trimethylcyclohexanol, 73210-25-0; 9-cyanoisoborneol, 73210-26-1; 5α-androstane-3β,17β-diol, 571-20-0; norborneol, 1632-68-4; 2-octanol, 123-96-6; 1-decyl alcohol, 112-30-1; 2-ethyl-1,3-hexanediol, 94-96-2; (–)-camphor, 464-48-2; (±)-camphor, 21368-68-3; (–)-menthone, 14073-97-3; cyclohexanone, 108-94-1; 2,2,5-trimethylcyclohexanone, 933-36-8; 9-cyanocamphor, 56906-71-9; 5α-androstane-3,17-dione, 846-46-8; norcamphor, 497-38-1; 2-octanone, 111-13-7; decyl decanoate, 1654-86-0; 2-ethyl-1-hydroxy-3-hexanone, 27970-80-5.

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[10] I. I. Lapkin and F. G. Saitkulova, *Zh. Org. Khim.*, 6, 450, (1970).

Oligonuclear Ruthenocene Complexes[1]

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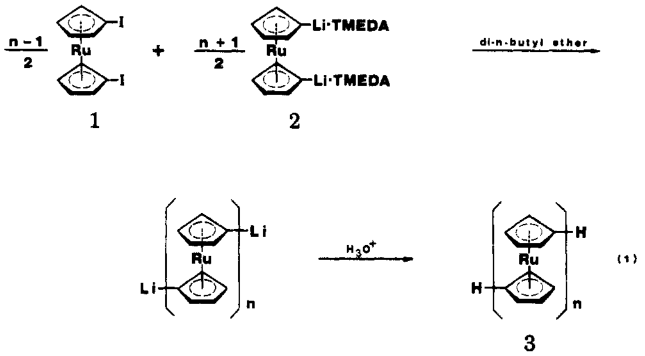
In continuation of our studies of oligo- and polynuclear metallocenes as precursors of mixed-valence systems,[1] we wished to prepare oligoruthenocenylenes of type **3** (n = 2–4). The availability of the 1,1′-diiodo derivative **1**,[2] coupled with the observed ease of lithiation of the ruthenocene complex,[2,3] suggested a ready synthetic pathway to **3** (eq 1) via coupling of **1** with the 1,1′-dilithioruthenocene **2** (chelated with TMEDA = N,N,N',N'-tetramethylethylenediamine).



The analogous reaction involving the diiodo and (TMEDA-chelated) dilithium derivatives of the iron congener, ferrocene, had previously been found to proceed smoothly in ether solvents, giving up to 85% yields of coupling products including higher polymers.[1]

In the present investigation, **1** was allowed to react with **2** in a molar ratio of 2:3 in a di-n-butyl ether medium (0.034 M in **1**) at 25–85 °C, and the hydrolyzed product mixture, after reductive elimination of any iodo groups present and removal of regenerated ruthenocene by sublimation (20% recovery), constituted crude coupling products (24% overall yield). Further workup by chromatography produced dimer (**3**, n = 2; 7.0%), trimer (**3**, n = 3; 3.5%), and tetramer (**3**, n = 4; 2.2%). In addition, a small polymeric fraction (**3**, n > 4; 5.5%) was extracted from the top of the column but was not further investigated at this time.

Other experiments conducted under a variety of conditions similar to those employed in the earlier[1,4,5] ferrocene polymerization studies, including the use of tetrahydrofuran or dimethoxyethane solvents, failed to proceed with any higher efficiency; overall yields of coupling products did not exceed 25%, although in all instances unreacted starting materials could be recovered in appreciable quantities (20–50%) after conversion to ruthenocene. Since **1** should be a more suitable substrate for nucleophilic attack than the corresponding diiodoferrocene because of reduced electron density on the rings in the ruthenium complex,[3,6] our failure to attain, or at least approach, the high coupling yields achieved in dilithioferrocene/diiodoferrocene polycondensations[1] must be traced to the low anion nucleophilicity of **2** despite the assistance given by the chelating agent. This problem requires further investigation.

Oligomers **3** (n = 2–4) possess melting points (Table I) in the same range as those of the respective oligonuclear ferrocenes but show reduced solubility relative to their ferrocene counterparts. All three homologues are colorless

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[1] Metallocene Polymers. 38. For part 37, see E. W. Neuse and L. Bednarik, *Macromolecules*, 12, 187 (1979). This work was supported by the South African Council for Scientific and Industrial Research. A generous gift of cyclopentadiene dimer from Esso Chemical Supply Co. is gratefully acknowledged.

[2] L. Bednarik and E. W. Neuse, *J. Organomet. Chem.*, 168, C8 (1979). We are grateful to one of the referees for drawing our attention to a previous, undetailed publication on halo- and lithioruthenocenes: H. Rosenberg and R. A. Ference, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, IL, Sept 1970, No INOR 158.

[3] M. D. Rausch, E. O Fischer, and H. Grubert, *J. Am. Chem. Soc.*, 82, 76 (1960).

[4] E. W. Neuse and L. Bednarik, *Transition Met. Chem.*, 4, 87 (1979).

[5] E. W. Neuse and L. Bednarik, *Transition Met. Chem.*, 4, 104 (1979).

[6] S. P. Gubin and A. A. Lubovich, *J. Organomet. Chem.*, 22, 183 (1970).

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Table I. Spectroscopic and Analytical Data for Oligonuclear Ruthenocenes

						UV/vis spectra[d]					
						band system V		band system IV		band system II	
			anal. found[c]								
compd	mp, °C[a]	P^+,[b] *m/e*	C	H		λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	λ_{max} nm	ϵ, M^{-1} cm^{-1}
biruthenocene (**3**, *n* = 2)	238–239	462	51.98	4.04	a	249	6400	261	5300	322	670
					b	247	6300	262	4500	320	620
1,1′-terruthenocene (**3**, *n* = 3)	276	692	52.11	3.99	a	252	9400	265	8600	322	1050
					b	250	*e*	266	*e*	322	*e*
1,1′-quaterruthenocene (**3**, *n* = 4)	269–271	922	52.07	3.80	a	253	9400	265	8500	323	1300
					b[e]						

[a] Capillary sealed under N_2. [b] Mass spectral parent ion peak for ^{102}Ru (70 eV; 200–400 °C inlet temp). [c] Anal. Calcd for **3** (*n* = 2): C, 52.16; H, 3.94. Calcd for **3** (*n* = 3): C, 52.24; H, 3.80. Calcd for **3** (*n* = 4): C, 52.28; H, 3.73. [d] Band-system designation in Gray's notation.[7] Line a was determined in 1,2-dichloroethane and line b in hexane. The molar extinction coefficient, ϵ, was calculated per metallocene unit. For comparison, λ_{max}, nm (ϵ, M^{-1} cm^{-1}), of ruthenocene is given for band systems V, IV, and II in hexane solution as 218 (4800), 238 (2300), and 320 (230) and for band systems IV and II in 1,2-dichloroethane solution as 237 (3800) and 322 (235). [e] Not determined in hexane because of insufficient solubility.

crystalline compounds. The electronic absorption spectra, taken on hexane and 1,2-dichloroethane solutions, show significant batho- and hyperchromic shifts of the characteristic charge-transfer bands in the UV region (band systems IV and V in Gray's notation;[7] Table I) as one goes from ruthenocene to the dimer. In the latter, one may expect an essentially parallel alignment of the two directly interconnected cyclopentadienyl rings and, hence, a moderate extent of conjugation between the two metallocene units. Only minor further shifts are apparent in the trimer spectrum, and the differences between the spectra of the trimer and the tetramer are negligible. This trend, reflecting the lack of substantial electronic charge delocalization across the metal center in the ruthenium complex, is comparable to the situation in the analogous oligoferrocene series, where both λ_{max} and ϵ were found to reach their highest values in the trimer/tetramer region, with no additional shifts occurring on further chain extension.[4]

It is of interest to note that, contrasting with the UV band systems IV and V, the ligand-field absorption maximum near 320 nm (band system II;[7] Table I) remains invariant with the degree of polymerization. This invariance, however, is a fortuitous result of the interplay of the two transitions[7] contributing to this composite band. Careful inspection of the dichloroethane solution spectra reveals the existence of two submaxima, viz., a predominant one near 310 nm in ruthenocene (315–322 nm in the dimer and trimer) and a second somewhat less intense maximum at about 335 nm in ruthenocene (345–350 nm in the dimer and trimer).[8] As a consequence of vibrational distortion in the oligomers,[9] both component bands increase in intensity in the sequence ruthenocene, biruthenocene, terruthenocene, quaterruthenocene, the greatest enhancement being noticeable in the dimer relative to the monomer. Our spectra indicate the 310-nm component band to be enhanced in intensity more rapidly with growing degree of polymerization than that near 335 nm, which explains the observed failure of the composite maximum (Table I) to follow the bathochromic shift trend shown by the band systems IV and V.

Experimental Section

The preparative procedure was as follows. 1,1′-Dilithioruthenocene (chelated with TMEDA, **2**, 16.0 mmol), prepared from ruthenocene (20 mmol), *n*-butyllithium (40 mmol, 1.5 M in hexane), and TMEDA (40 mmol) in hexane medium and isolated in the solid state[10] as described,[2] was suspended in di-*n*-butyl ether (DBE; 100 mL) at 25 °C under Ar. To the stirred suspension was slowly added a solution of **1** (10.3 mmol) in DBE (200 mL), and stirring of the mixture was continued for 7 h at about 25 °C and for 35 h at 65 °C. The glassware used was flamed and argon purged, and all solvents and reagents were dried and deoxygenated as in previous work.[1-5] The solid reaction products obtained after hydrolysis (1 M aqueous HCl, 40 mL; 0 °C) from the organic phase were dried at 50 °C in vacuo (24 h) and treated with $NiCl_2$ (10 mmol) and $LiAlH_4$ (10 mmol) in THF as described by Ashby and Lin.[11] Admixed ruthenocene (20%) was removed from the recovered product mixture by sublimation (50 °C, 0.1 torr), and the sublimation residue (24%, based on total **1** and **2** employed) was chromatographed on alumina (activity grade II). Benzene/hexane (1:4) eluted traces of ruthenocene, followed by a band containing biruthenocene (crude yield 7%). Further elution with benzene/hexane (1:1) and neat benzene produced a trimer-containing (3.5%) band and a zone containing tetramer (2.2%). The three crude oligomers were recrystallized several times from heptane, heptane/benzene, and toluene, respectively. The material remaining on the column was extracted with boiling toluene, and from the strongly concentrated extracts a grayish polymeric fraction of **3** (5.5%) was obtained by precipitation with excess hexane.

Registry No. 1, 70210-63-8; **2**, 70210-60-5; **3** (*n* = 2), 67126-04-9; **3** (*n* = 3), 73178-90-2; **3** (*n* = 4), 73178-91-3.

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[7] Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 3603 (1971).

[8] The two maxima, associated with the $a_{1g} \rightarrow e_{1g}$ and $e_{2g} \rightarrow e_{1g}$ one-electron d–d transitions (in D_{5d} symmetry), were first observed[7] at 339 and 308 nm in a frozen EPA solution of ruthenocene at 77 K.

[9] Ring tilt, known to contribute to the relaxation of the selection rules in tilted ferocenes [T. H. Barr and W. E. Watts, *J. Organomet. Chem.*, **15**, 177 (1968); H. L. Lentzner and W. E. Watts, *Chem. Commun.*, 26 (1970)], does not appear to be a contributing factor in the present oligoruthenocene case, no unusual splitting or shifts of the characteristic absorptions in the CC stretching (1350–1420 cm^{-1}) and CH out-of-plane deformation (800–850 cm^{-1}) regions manifesting themselves in the IR spectra of the oligomeric compounds. A more detailed presentation of spectral data (including NMR) will be given in a future paper.

[10] This isolation, brought about by removing the lithiation mother liquor through filtration and washing the residual, insoluble **2** with hexane, ensured that contamination with monolithioruthenocene (chelated with TMEDA), more soluble than **2**, was minimized.

[11] E. C. Ashby and J. J. Lin, *J. Org. Chem.*, **43**, 1263 (1978).

Thermal Cis–Trans Isomerization in 1,2-Dibenzoyl-1,2-dihydroacenaphthylene[1]

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Considerable interest has recently been shown in the properties of biradicaloid intermediates based on 1,8-

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[1] Part of this work was done at The Weizmann Institute of Science, Rehovot, Israel, while F.G. was on sabbatical leave.

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