to N-donor rearrangements.[7] Although it is difficult to assess how much of the resonance stabilization energy attributed to both NC_5H_5 and C_6H_6 (~35 Kcal/mol)[19] is lost upon coordination, σ-bonding to Ta must provide compensation. With pyridine, formation of a strong Ta-N bond may be critical, whereas η^2-bonding to two Ta centers is needed for benzene complexation. No mono-C_6H_6 adducts, η^2[1-4,6] or η^4,[1,5] have been observed in the course of these studies. Investigations of $(silox)_3Ta$ adduct formation and theoretical inquiries into the electronic natures of **1**, **2**, and **3** are ongoing.

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Supplementary Material Available: Tables of crystal data, fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles and experimental information pertaining to the X-ray crystallographic studies of **2** and **3**·$2C_6H_6$ (16 pages); tables of observed and calculated structure factors (45 pages). Ordering information is given on any current masthead page.

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Time Domain Spectroscopic Studies of Mixed-Valent Perovskites

Russell S. Drago,* Peter E. Doan, and Michael K. Kroeger

Department of Chemistry, University of Florida
Gainesville, Florida 32611

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We would like to report the measurement of rates of dielectric relaxation related to electron hopping in a set of mixed-valence strontium doped lanthanum orthoferrites $La_{1-x}Sr_xFeO_3$ by using Time Domain Spectroscopy (TDS). Introducing a Sr^{2+} defect into the lattices to balance the charge leads to an Fe(IV) site in the Fe(III) lattice. Early work by Gallagher and MacChesney[1] and Shimony and Knutson[2] using ^{57}Fe Mossbauer shows that the Fe sites have isomer shifts which suggest averaged oxidation states at room temperature and locked valence at 77 K. Further work by Takano et al.[3] show the isomer shifts vary with dopant level in a fashion that is consistent with averaged sites. Because the time scales associated with our TDS apparatus are at least 2 orders of magnitude faster than the ^{57}Fe Mossbauer experiment, we decided to investigate the dielectric relaxation in the neighborhood of room temperature.

The spectra obtained show a very strong dielectric relaxation in the doped systems that is not present in the undoped material. There is also measurable conductance in each of the doped samples. Highly conducting samples create problems in the interpretation of dielectric measurements by creating an effective relaxation time, τ, related to the magnitude of the static dielectric constant of the medium and the DC conductance,[4] σ. In general, TDS can measure the ohmic conductivity of the sample, but due to geometry and sample contact problems, the values obtained will only be relative. However, if the sample geometry remains relatively constant throughout the temperature range, the value obtained for the activation energy should be accurate.

Table I. Dielectric, Conductivity, and Relaxation Results

T (K)	τ (ps)	$\sigma \times 10^6$ (mho/cm)	dielectric loss $\epsilon_s - \epsilon_\infty$
	0.1 Sr^{2+} Doped		
334	1171 (30)	284 (32)	50.8
332	1346 (33)	211 (28)	51.4
310	1570 (36)	140 (25)	52.8
298	1801 (37)	105 (23)	52.0
283	2303 (63)	87 (22)	47.9
259	2813 (68)	52 (21)	41.3
	0.2 Sr^{2+} Doped		
335	1963 (46)	647 (45)	61.2
323	1813 (30)	574 (46)	53.6
312	2190 (44)	465 (37)	51.2
297	2028 (43)	394 (35)	44.1
283	2086 (57)	289 (29)	36.9
259	2194 (80)	202 (27)	30.6
	0.3 Sr^{2+} Doped		
340	1476 (31)	523 (35)	55.7
321	1464 (33)	484 (33)	50.1
297	1577 (35)	403 (30)	43.8
283	1634 (45)	334 (28)	37.0
259	1668 (28)	257 (26)	29.3

[a] The values in parentheses represent the standard deviations.

The dielectric relaxation times,[5] loss values for that relaxation, and DC conductivities for the sample with $X = 0.1$, 0.2, and 0.3 are shown in Table I. Other relaxation effects appear at very short times (up to 1 ns after the pulse), but our present analysis cannot adequately measure these rates because the Guggenheim plots are strongly curved, which suggests a distribution of relaxation times. In all three systems, the temperature behavior of the loss ($\epsilon_s - \epsilon_\infty$) related to this relaxation shows a strong increase in magnitude with increasing temperature. This is related to the number of mobile charges in the lattice and shows there is some type of thermal "trapping" occurring at the lower temperatures.

The values obtained for the barriers to conductance (0.178, 0.119, and 0.067 eV for $X = 0.1$, 0.2, and 0.3 Sr(II) doping, respectively) and dielectric relaxation (0.082, 0.014, and 0.019 eV for 0.1, 0.2, and 0.3 Sr(II) doped) show the barrier to conductance is substantially higher than that for relaxation in all three systems. This corresponds to the expected trends for these systems. The mechanism for dielectric relaxation involves electron hopping near the defect; the distance between the positive and negative centers does not change. Conduction in these compounds takes place through electron diffusion between defect sites. The activation barrier would depend upon the distance between sites. The barriers fit the expected trend where $\Delta E_{(\mathrm{conductance})}$ is greater than $\Delta E_{(\mathrm{relaxation})}$.

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(4) The experimental frequency (ω) dependent dielectric constant $\epsilon\times(\omega)$ is given by

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) + [\sigma/i\omega\epsilon_0]$$

where $\epsilon'(\omega)$ is the real dielectric contribution; $i\epsilon''(\omega)$, the imaginary; the term containing σ (the DC conductivity) is the ohmic contribution, and ϵ_0 is the permittivity of free space. According to the Debye Model

$$\epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty + [(\epsilon_s - \epsilon_\infty)/(1 + i\omega\tau)]$$

where ϵ_s is the static dielectric constant and ϵ_∞ is the instantaneous dielectric constant. This lumps all relaxation effects due to conductivity ($\tau^{-1} = \sigma/\epsilon_0 t$) into dielectric loss. There is no way using dielectric measurements alone to separate these effects. See: Cole, R. H.; Windsor, P. *Fourier Transform Dielectric Spectroscopy*; Plenum Press: New York, 1982.

(5) The rate of dielectric relaxation is not the same as the rate of electron transfer. However, to correct for the difference requires knowledge of the high and low frequency dielectric constants to a degree we cannot obtain with these systems.

This is the first measurement of the rates and barriers to electron transfer in these iron perovskite mixed-valence systems. These systems are structurally similar to the high T_c superconductors, and the information about the mixed-valence metal–oxide–metal interactions may be useful in understanding the behavior of the YBaCuO systems. This research is being extended to lower dopant levels in order to decrease conductance, separate the Fe(IV) sites, and approach the electronic structure of systems more like the well understood parent compound.[6]

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Registry No. La$_{1-x}$Sr$_x$FeO$_3$ (x = 0.1), 108601-52-1; La$_{1-x}$Sr$_x$FeO$_3$ (x = 0.2), 109546-91-0; La$_{1-x}$Sr$_x$FeO$_3$ (x = 0.3), 107121-72-2.

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Preparation and Isolation of Polyenes Containing Up to 15 Double Bonds

Konrad Knoll, Steven A. Krouse, and Richard R. Schrock*

Department of Chemistry 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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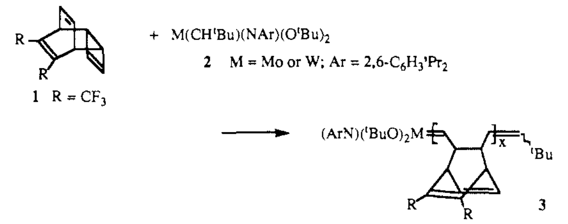
Conjugated polyene chains are important components of natural products[1] and are thought to be one of the most important features of polyacetylene.[2] Isoprenoid polyenes containing up to 19 double bonds in the backbone are known,[3] but no polyene having an unsubstituted backbone longer than a 10-ene appears to have been prepared.[4] It would be highly desirable to prepare well-characterized polyenes containing 10–20 double bonds in an unsubstituted backbone in order to address a variety of questions, inter alia those concerning excited states in polyenes[4c] and the nature of polyacetylene. Here we describe the preparation and isolation of individual polyenes containing as many as 15 double bonds by a controlled ring-opening polymerization.

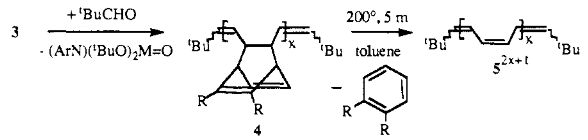
Table I. ^{13}C NMR Chemical Shifts for the Olefinic Carbon Atoms in **a** Isomers[13] of Several Di(*tert*-butyl)-Capped Polyenes (in CDCl$_3$) and One **b** Isomer[a]

5^7**a**	**5**^{9}**a**	**5**^{11}**a**	**5**^{7}**b**
147.86	148.01 (+0.15)[b]	148.05 (+0.04)	146.74
131.05	131.25 (+0.20)	131.32 (+0.07)	133.86
	130.39	130.57 (+0.18)	133.27
		130.29	132.93
129.84	129.75 (−0.09)	129.70 (−0.05)	132.37
		129.58	131.15
	129.48	129.41 (−0.07)	125.52
129.18	129.12 (−0.06)	129.05 (−0.07)	
128.27	128.21 (−0.06)	128.19 (−0.02)	
127.65	127.62 (−0.03)	127.61 (−0.01)	
120.57	120.56 (−0.01)[c]	120.55 (−0.01)	

[a] Estimated error ±0.005 ppm. The value in parentheses is the change in chemical shift relative to the shorter **a**-type polyene, and the boldface figures are the two chemical shifts for the four additional carbon atoms in the longer **a**-type polyene. Correlation of the 130.39 and 129.48 resonances in **5**^{9}**a** with the 130.57 and 129.41 resonances in **5**^{11}**a** (respectively) should be regarded as tentative. [b] J_{CH} = 153 Hz. [c] J_{CH} = 154 Hz.



(1)



(2)

Feast[5] has discovered that tricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes (e.g., the 7,8-bis(trifluoromethyl) derivative **1**; eq 1) and related molecules can be ring-opened by classical olefin metathesis catalysts[6] to give a polymer from which an arene is ejected upon heating to give polyacetylene. We have developed catalysts of the type M(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$(M = Mo or W; Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$) that will ring-open polymerize norbornenes in a controlled manner[7a,b] and now find that they can be used to ring-open polymerize (more accurately oligomerize) **1** in a controlled manner (eq 1).[8] Treating **3** with pivaldehyde gives the metal-free oligomer **4** via a Wittig-type reaction (eq 2).[9] Heating **4** to 200 °C for 5 m in toluene in a glass bomb yields a deep red solution, 90–95% of the contents of which is soluble in pentane. The most abundant polyenes[10] ($\mathbf{5}^{2x+1}$; x = 3–7) having $2x + 1$ double bonds capped at each end by a *tert*-butyl group ($\mathbf{5}^7$–$\mathbf{5}^{15}$) can be isolated by chromatography on silica gel at −40 °C under dinitrogen in high yields[8] relative to theory.[10] The polyenes become increasingly unstable to air (a solution of $\mathbf{5}^{15}$ is rapidly decolorized) and thermally unstable in concentrated solution or in the solid state (after several days in the absence of air in the solid state

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(3) β-Carotene, one of the longest and most important of the naturally occurring polyenes, is an 11-ene isoprenoid.[1] The longest synthetic isoprenoid is "Dodecapreno-β-carotene", a 19-ene, obtained by derivatizing natural isoprenoids, see: Karrer, P.; Eugstler, C. H. *Helv. Chim. Acta* **1951**, *34*, 1805.

(4) A number of reviews are available.[4a–c] The longest well-characterized polyenes containing an unsubstituted backbone are 10-enes.[4d,c] Longer polyenes (e.g., the diphenyl-capped 15-ene[4a]) have been claimed,[4a,f] but no conclusive data were provided. Di(*tert*-butyl)-capped polyenynes containing up to 30 carbon atoms have been reported.[4g] (a) Kuhn, R. *Angew. Chem.* **1937**, *34*, 703. (b) Yanovskaya, L. A. *Russ. Chem. Rev.* **1967**, *36*, 400. (c) Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982. (d) Bohlmann, F.; Mannhardt, H.-J. *Chem. Ber.* **1956**, *89*, 1307. (e) Sondheimer, F.; Ben-Efraim, D. A.; Wolovsky, R. *J. Am. Chem. Soc.* **1961**, *83*, 1675. (f) Nayler, P.; Whiting, M. C. *J. Chem. Soc.* **1955**, 3037. (g) Wudl, F.; Bitler, S. P. *J. Am. Chem. Soc.* **1986**, *108*, 4685.

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(8) Full details are available as Supplementary Material.

(9) The fact that the retro Diels–Alder reaction is occurring at 25° prevents accurate characterization of 4 by GPC methods. GPC studies at −17° of polyacetylene precursor polymers prepared with classical catalysts showed polydispersities to be between 2 and 3, see: Harper, K.; James, P. G. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 55.

(10) If we assume that initiation is the same rate or faster than propagation, the yields predicted by the Poisson equation (assuming a pyrolysis yield of 100%) are 3.4% ($\mathbf{5}^5$), 8.4% ($\mathbf{5}^7$), 14% ($\mathbf{5}^9$), 18% ($\mathbf{5}^{11}$), 18% ($\mathbf{5}^{13}$), 15% ($\mathbf{5}^{15}$), 11% ($\mathbf{5}^{17}$), 6.5% ($\mathbf{5}^{19}$), and 3.6% ($\mathbf{5}^{21}$).

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