Reaction of 1,1-Dimethylallene with $NiMo(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$. Isomerization of the Product to $NiMo(\mu\text{-}CO)(CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)C(Me)CH_2\}(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$: A 1,2-Methyl Migration or a 1,4-Proton Shift?

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Summary: $NiMo(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$ (**1**) reacts with 1,1-dimethylallene affording $NiMo(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}CMe_2{=}C{=}CH_2)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$ (**2**), which isomerizes on silica gel affording the complex $NiMo(\mu\text{-}CO)(CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(Me)C(Me)CH_2\}(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$ (**3**), whose structure was determined by X-ray diffraction. The bridging ligand in this compound is best described as a metalloallyl π-coordinated to the molybdenum atom, rather than as a methyl(1-methylvinyl)alkylidene species. A deuterium-labeling study indicates that a 1,4-proton shift, and not a 1,2-methyl migration, is operative in the transformation of **2** to **3**.

Our group has been studying the reactions of heterobimetallic compounds containing nickel and a group 6 metal.[1] Allenes often bond to dinuclear transition-metal species by adopting an η^2,η^2-bridging mode by acting as four-electron donor ligands,[2] akin to alkynes in bridging alkyne species. Diverse bonding modes of allenes to dimetal centers are known,[3] and coupling reactions have also been observed in reactions of allenes with transition-metal complexes.[2i,j,4,5] Following our ongoing investigations of the reactivity of $NiMo(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$ (**1**) and its derivatives with alkynes,[1a,b,6] the chemistry of **1** toward allenes was of interest.

Green solutions of **1** and 1,1-dimethylallene[7] turn brown over a 2-day period: dark crystals of a new product (**2**) were isolated when the crude reaction mixture was concentrated and cooled to −20 °C.[8] Spectroscopic data[9] for **2** were consistent with the formulation $NiMo(CO)_2(CMe_2{=}C{=}CH_2)(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4Me)$ and indicated that isomerization of the 1,1-dimethylallene ligand to an isopropylacetylene ($HC{\equiv}CCHMe_2$) group had not taken place.

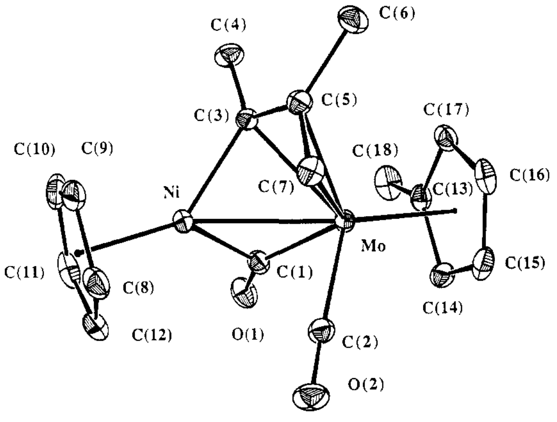

Figure 1. ORTEP diagram for **3**, showing the ellipsoids at the 50% probability level. Important bond lengths (Å) and angles (deg) for **3**: Ni–Mo = 2.577 (2); Mo–C(1) = 2.040 (4); Mo–C(2) = 1.982 (4); Mo–C(3) = 2.216 (4); Mo–C(5) = 2.304 (4); Mo–C(7) = 2.329 (5); Ni–C(1) = 1.935 (4); NiC(3) = 1.910 (4); C(3)–C(5) = 1.408 (6); C(5)–C(7) = 1.410 (6); Mo–C(Cp′, mean) = 2.333; Ni–C(Cp, mean) = 2.145; Mo–C(1)–O(1) = 150.2 (3); Mo–C(2)–O(2) = 177.2 (4); Ni–C(1)–O(1) = 129.0 (3); Mo–C(3)–C(4) = 129.2 (3); Mo–C(3)–Ni = 76.9 (1); Mo–C(3)–C(5) = 75.3 (2); Ni–C(3)–C(4) = 117.7 (3); Ni–C(3)–C(5) = 118.3 (3); C(4)–C(3)–C(5) = 122.7 (4); C(3)–C(5)–C(7) = 117.8 (4); C(3)–C(5)–C(6) = 123.1 (4); C(6)–C(5)–C(7) = 118.8 (5).

In an attempt to obtain a further crop of crystals, the mother liquor was purified by chromatography on silica gel affording one major band. Crystals obtained from this solution were of a different product (**3**).[7,10] Spectroscopic and analytical data suggest that **2** and **3** are isomers. The complexes exhibit parent ions with identical *m/e* ratios and very similar fragmentation patterns. IR data indicate that while both species contain a terminal carbonyl ligand, **2** also has a semibridging carbonyl ligand, while **3** instead contains a bridging carbonyl group.

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(8) **1** (500 mg, 1.2 mmol) and 1,1-dimethylallene (0.5 mL, ≈5.0 mmol) were dissolved in a hexanes/toluene mixture (1:1, 20 mL). The Schlenk tube was frozen in liquid nitrogen, evacuated, warmed to ≈35 °C, and stirred for 2 days. Solvents were then removed, and the residue was dissolved in hexane and filtered through a Celite pad. Crystallization at −20 °C afforded **2** (176 mg, 0.41 mmol). The mother liquor was subjected to chromatography on silica gel: elution using a hexanes/ether mixture (20:1) followed by crystallization from hexanes yielded **3** (22 mg, 0.051 mmol). Combined yields: 38%.

(9) Spectroscopic data for **2**: ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 5.14 (5 H, $C_5\mathit{H}_5$), 4.85, 4.78, 4.68, and 4.65 (m, ABCD type, 4 H, $C_5\mathit{H}_4Me$), 4.22 (1 H, CH*H*), 2.81 (1 H, CH*H*), 2.35 (3 H, Me), 2.04 (3 H, $C_5H_4\mathit{Me}$), 1.83 (3 H, *Me*); ^{13}C NMR δ 254.0 (*C*O), 238.7 (*C*O), 171.6 (=C=), 119.0 ($Me_2\mathit{C}{=}$), 107.2 [C(1), C_5H_4Me], 94.0, 93.0, 91.7, and 90.9 [C(2)–C(5), C_5H_4Me], 93.9 (C_5H_5), 54.0 ($\mathit{C}H_2{=}$), 32.9, 23.7 ($\mathit{Me}_2C{=}$), 13.4 ($C_5H_4\mathit{Me}$). IR [ν(CO), cm^{-1}]: hexane, 1928 (w), 1809 (s); Nujol, 1924 (s), 1790 (s). MS: *m/e* = 424, with the expected NiMo isotopic envelope pattern. HREIMS for ^{60}Ni, ^{100}Mo: *m/e* 427.984 ($C_{18}H_{20}MoNiO_2$ requires 427.984). Anal. Calcd for $C_{18}H_{20}MoNiO_2$: C, 51.11; H, 4.77. Found: C, 50.97; H, 4.87.

(10) Spectroscopic data for **3**: ^1H NMR (300 MHz, $CDCl_3$ ppm) δ 5.03 (5 H, $C_5\mathit{H}_5$), 4.66 (2 H, m, $C_5\mathit{H}_4Me$), 4.60 (1 H, m, $C_5\mathit{H}_4Me$), 4.51 (1 H, m, $C_5\mathit{H}_4Me$), 2.94 (d, 1 H, CH*H*, $^2J_{HH} = 1.5$ Hz), 2.76 (m, 1 H, CH*H*), 2.15 (3 H, *Me*), 2.01 (3 H, $C_5H_4\mathit{Me}$), 1.83 (3 H, *Me*); ^{13}C NMR δ 262.9 (μ-CO), 229.8 (CO), 145.9 [$Me\mathit{C}{-}C(Me){=}CH_2$], 107.7 [C(1), C_5H_4Me], 101.6 ($Me\mathit{C}{=}CH_2$), 94.4, 92.6, 92.0, and 91.8 [C(2)–C(5), C_5H_4Me], 93.1 (C_5H_5), 51.0 ($\mathit{C}H_2{=}$), 29.9 (*Me*), 20.4 (*Me*), 13.0 ($C_5H_4\mathit{Me}$). IR [ν(CO), cm^{-1}]: hexane, 1948 (s), 1784 (s); Nujol, 1936 (s), 1757 (s). MS: *m/e* = 424 with the expected NiMo isotopic envelope pattern. HREIMS for ^{60}Ni, ^{100}Mo: *m/e* 427.984 ($C_{18}H_{20}MoNiO_2$ requires 427.984). Anal. Calcd for $C_{18}H_{20}MoNiO_2$: C, 51.11; H, 4.77. Found: C, 51.14; H, 5.00.

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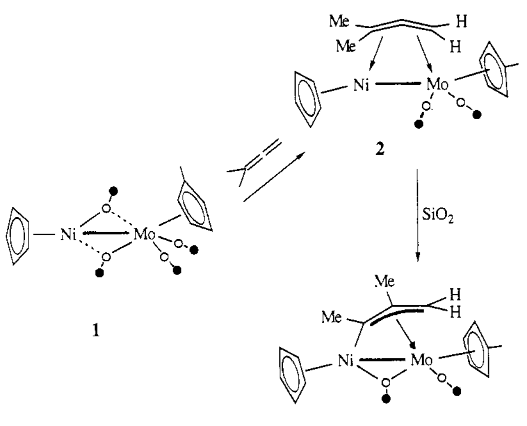
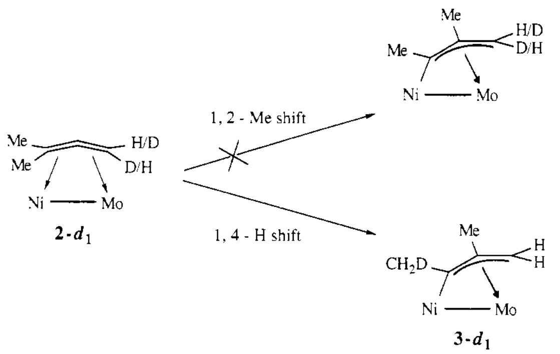
Scheme I



Scheme II



The ^{1}H and ^{13}C NMR spectra of **3** also lend credence to our belief that **2** and **3** are isomers. While the data reveal that **3** contains signals assignable to the same groups present in **2**, significant chemical shift differences are observed that clearly indicate the two molecules are not identical. The ^{1}H NMR data also show that both complexes contain no symmetry elements.[11]

IR data of the crude reaction mixture indicated that **3** was absent prior to chromatography. When a sample of **2** was passed through silica gel or when ether solutions of **2** were stirred with suspended silica, **3** was obtained. These results suggest that the reaction of 1,1-dimethylallene with **1** yielded one major product (**2**), which rearranged to give **3** when exposed to silica gel.

The structure of **3** was established by single-crystal X-ray diffraction.[12] Figure 1 shows an ORTEP plot of **3**, together with pertinent bond lengths and angles. Complex **3** contains a normal Ni–Mo single bond of 2.577 (2) Å, bridged by a C(Me)C(Me)CH$_2$ ligand and a carbonyl group; it may be formulated as NiMo(μ-CO)(CO){μ-η^1,η^3-C(Me)C(Me)CH$_2$}(η-C$_5$H$_5$)(η-C$_5$H$_4$Me). As the C(3)–C(5) and C(5)–C(7) distances are both 1.40 Å and the Ni atom and atoms C(3) to C(7) are essentially coplanar, the ligand is best described as a metalloallyl rather than as a bridging metal(1-methylvinyl)alkylidene ligand.[13,14] While the molybdenum-ligated carbon atoms in this bridging fragment exhibit substantially different Mo–C distances [Mo–C(3) = 2.216 (4), Mo–C(5) = 2.304, Mo–C(7) = 2.329 (5) Å], variations of this magnitude are not unprecedented, even in unconstrained π-allyl species.[15]

Ni(0) complexes display an interesting chemistry toward allenes,[16] but reactions of allene or 1,1-dimethylallene with [Ni(μ-CO)(η-C$_5$H$_5$)]$_2$ have not been documented.[17] The compounds Mo$_2$(CO)$_4$(μ-η^2,η^2-CH$_2$=C=CHR)(η-C$_5$H$_5$)$_2$ (R = H, OMe) may be isolated[2a,b,h] from the reaction of the triply bonded complex Mo$_2$(CO)$_4$(η-C$_5$H$_4$R′)$_2$ (Mo≡Mo; R′ = H or Me) with allene or methoxyallene; 1,1-dimethylallene does not react. This inertness, coupled with the existence of Mo$_2$(CO)$_4$(μ-η^2,η^2-CH$_2$=C=CH$_2$)(η-C$_5$H$_5$)$_2$, suggests that the C=CH$_2$ bond is π-coordinated to the molybdenum atom in **2**, while the bulkier C=CMe$_2$ group is bonded to the nickel. The structures of **1**–**3** and the net reaction sequences are depicted in Scheme I.[18]

Either a 1,2-methyl group migration or an effective 1,4-proton shift[19] could account for the isomerization of the Me$_2$C=C=CH$_2$ ligand to the (Me)CC(Me)CH$_2$ hydrocarbyl skeleton in **3**. The ligand CMe$_2$=C=CHD[7b] was synthesized to distinguish between these options. This hydrocarbon reacts with **1** affording **2**-d_1,[20] which consists of a mixture of isotopomers having the label statistically distributed between the two methylene positions, as expected for a μ-η^2,η^2-CMe$_2$=C=CHD ligand.

2-d_1 was isomerized to **3**-d_1 on silica gel. ^{1}H NMR spectra of **3**-d_1[21] clearly indicate that the CHD group is quantitatively converted into a CH$_2$D group, implying that a 1,4-proton migration has occurred. As demonstrated in Scheme II, a 1,2-methyl migration would not modify the labeled CHD group.

Reactions of other allenes with **1** and with nickel–tungsten complexes are in progress.

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[11] The ^{1}H NMR spectra of both complexes show ABCD-type multiplets for the aromatic C$_5$*H*$_4$Me protons, indicating the lack of an effective mirror plane.

[12] Monoclinic crystals of **3**, C$_{18}$H$_{20}$O$_2$MoNi, grown from hexane solutions at −20 °C belong to space group $P2_1/n$ (No. 14) with a = 9.104 (3) Å, b = 15.840 (16) Å, c = 11.559 (4) Å, β = 94.20°, V = 1662.3 Å^3, and Z = 4. The 5509 measured reflections were collected by using a θ–2θ scanning technique and graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structure was successfully solved by using SHELXS program [Sheldrick, G. M., prefinal release]. No absorption correction was performed [μ(Mo Kα) = 18.8 cm^{-1}]. All atoms were located and refined anisotropically, except for hydrogen atoms which were refined with isotropic thermal parameters. Refinement using the 3426 unique observed reflections with $F_o > 3\sigma(F_o)$ converted at R = 0.039 and R_w = 0.043.

[13] Dinuclear group 8 metal complexes containing this class of ligand are known. (a) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 803. (b) Davies, D. L.; Knox, S. A. R.; Mead, K. A.; Morris, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2293. (c) Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1985**, 1935.

[14] Two structurally characterized molybdenum species containing this type of bridging ligand are Mo$_2$(CO)$_4${μ-η^1,η^3-C(H)C(H)CMe$_2$}(η-C$_5$H$_5$)$_2$ and Mo$_2$O(CO)$_2${μ-η^1,η^3-C(H)C(H)CMe$_2$}(η-C$_5$H$_5$)$_2$. In both complexes, the C–C bond distances corresponding to C3–C5 and C5–C7 are essentially the same, and close to values observed in **3**. Carroll, W. E.; Green, M.; Orpen, A. G.; Schaverien, C. J.; Williams, I. D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1021.

[15] In the two compounds referred to in ref 14, Mo–C(allyl) bonds range from 2.249 to 2.477 Å and 2.267 to 2.492 Å, respectively. In the unconstrained allyl complex Mo(NO)(η^3-C$_3$H$_5$)(η-C$_5$H$_5$)I, Mo–C(allyl) distances range from 2.29 to 2.44 Å. Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227.

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[17] Our experiments indicate that no reaction ensues when [Ni(μ-CO)(η-C$_5$H$_5$)]$_2$ is treated with Me$_2$C=C=CH$_2$. The parent allene does react, affording Ni$_2$(η^3,η^3-C$_6$H$_8$)(η-C$_5$H$_5$)$_2$, which contains a ligated dimerized allene. Full results will be reported elsewhere.

[18] Carbonyl carbon and oxygen atoms are shown as open or closed circles, respectively.

[19] Isomerizations of hydrocarbyl ligands have been noted on silica or alumina (ref 5 and: Eisenstadt, A.; Efraty, A. *Organometallics* **1982**, *1*, 1100).

[20] ^{1}H NMR spectra of the isotopomers that make up **2**-d_1 exhibit signals at δ 4.21 (s, 0.5 H) and 2.80 (s, 0.5 H) ppm (cf. 4.22 and 2.81 ppm for **2**). Other resonances are unchanged from those of **2**.

[21] ^{1}H NMR resonances for **3**-d_1 are the same as for **3** except for an AB-type multiplet at δ 2.137 (1 H, J_{HH} = 2.1 Hz) and 2.130 (1 H, J_{HH} = 2.1 Hz) ppm for the diastereotopic protons of a C*H*$_2$C group. J_{HD} was not resolved. These signals replace the methyl resonance observed at 2.15 ppm in **3**.

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Supplementary Material Available: Tables of crystal and data collection parameters, atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positional parameters and bond lengths and angles for 3 (8 pages); a structure factor listing (12 pages). Ordering information is given on any current masthead page.

Electrical Conductivity in a Polythiophene Induced by Complexation with $[(\eta\text{-}C_5H_5)Fe(CO)_2]^+$

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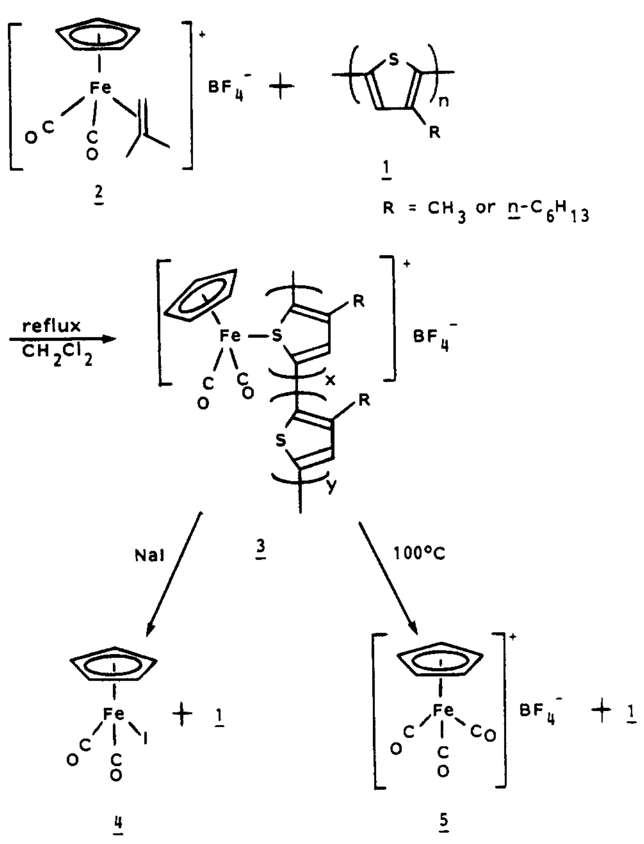
Summary: Treatment of an electrically nonconducting copolymer of 3-methyl- and 3-hexylthiophene (1) with $[CpFe(CO)_2(\text{2-methyl-1-propene})]BF_4$ gave a material (3) with greatly increased (×10^8) conductivity. The IR and NMR spectra of this material and of model complexes suggest that $[CpFe(CO)_2]^+$ residues which are attached to the sulfur atoms of less than 10% of the thiophene rings of the polymer backbone induce the improved conductivity.

Certain organic polymers such as polyacetylene, polypyrrole, and polythiophene become electrically conducting[1] when doped with strong oxidizing agents such as I_2 or H_2SO_4 or with strong reducing agents such as sodium or potassium metal.[2] The technological promise of such materials has encouraged the development of additional doping techniques and reagents. However, most of the systems reported are unstable in the long term due to the reactive nature of the dopants. This has led to difficulties in processing these materials and in investigating their physical properties and internal structure. Our interest in organometallic complexes embedded in polymers[3] led us to consider them as possible dopants for polythiophene. The ability of a complex to modify the electronic structure of a conjugated polymer should be a function of the metal, the organic ligands present, and the mode of bonding to the polymer (for example, σ or π). Complexes might prove to be tunable probes to study the mechanisms of conduction in such materials. We report the first example to our knowledge of the induction of improved electrical conductivity in a conjugated polymer via covalent attachment of an organometallic "dopant". Treatment of the soluble thiophene copolymer (1) with $[CpFe(CO)_2(Me_2CCH_2)]BF_4$ (2), where Cp = η-C_5H_5, gave a material whose conductivity is 8 orders of magnitude greater than that of the starting copolymer.

Scheme I



A 1:1 copolymer of 3-methyl- and 3-hexylthiophene was chosen for study because it was soluble in CH_2Cl_2 and also because it possessed good mechanical properties. In our hands poly(3-methylthiophene) was too insoluble and poly(3-hexylthiophene) was too soft and rubbery. Copolymer 1 was prepared by the nickel-catalyzed Grignard coupling of 2,5-dibromo-3-methylthiophene and 2,5-dibromo-3-hexylthiophene in the ratio 1:1 following a procedure similar to that reported for the synthesis of polythiophene.[2b,4] The molecular weight of this copolymer is estimated[5] to be about 2000 (i.e., 15 rings) on the basis of elemental analysis of the residual bromo terminal groups. The material is dark red and is soluble at room temperature in common organic solvents such as tetrahydrofuran, $CHCl_3$, and CH_2Cl_2. It was pressed into a thin disk at room temperature which exhibited low conductivity.[6,7] Exposure of the disk to I_2 vapor increased the conductivity to σ = 5–10 Ω^{-1} cm^{-1} which then decreased steadily upon standing consistent with the reported behavior of other polythiophenes.[7] Copolymer 1 was treated with 2 (3:1 ratio) under N_2 atmosphere in refluxing CH_2Cl_2 for 80 min following a procedure similar to that reported[8] to give thiophene complexes. The residue upon evaporation of the CH_2Cl_2 was washed with methanol and dried under vacuum to give brown-black 3. The conductivity of disks

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(6) The conductivity of samples pressed into thin disks was measured via the four-probe method using a Harrison 6516A DC power supply and a Keithley 169 multimeter. The instrumentation was sensitive to conductivity values as low as 10^{-6} Ω^{-1} cm^{-1} which sets an upper limit for the value for 1. However, poly(2,5-thiophene) prepared in the same manner is reported[7] to have conductivity values in the range 10^{-10}–10^{-11} Ω^{-1} cm^{-1}.

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