Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Oligothiophenes III: Synthesis of Tetra-thienyl-Substituted Ethylenes Including an Abnormal McMurry Coupling Result

Harald Halvorsen [a] , Jan Skramstad [a] & Håkon Hope [b]

[a] Department of Chemistry, University of Oslo, Oslo, Norway

[b] Department of Chemistry, University of California, Davis, California, USA

Version of record first published: 13 Oct 2010.

To cite this article: Harald Halvorsen , Jan Skramstad & Håkon Hope (2007): Oligothiophenes III: Synthesis of Tetra-thienyl-Substituted Ethylenes Including an Abnormal McMurry Coupling Result, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 37:7, 1179-1187

To link to this article: http://dx.doi.org/10.1080/00397910701199037

Synthetic Communications®, 37: 1179–1187, 2007

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910701199037

Oligothiophenes III: Synthesis of Tetra-thienyl-Substituted Ethylenes Including an Abnormal McMurry Coupling Result

Harald Halvorsen and Jan Skramstad
Department of Chemistry, University of Oslo, Oslo, Norway

Håkon Hope
Department of Chemistry, University of California, Davis,
California, USA

Abstract: This article describes the synthesis of some selected tetra-thiophenyl-substituted ethenes by McMurry coupling of some selected thienyl ketones, including a surprising coupling product. The products were analyzed by MS, NMR, UV, and x-ray crystallography. Their cyclic voltagrams were recorded.

Keywords: Cyclic voltametry, McMurry coupling, oligothiophenes

INTRODUCTION

In the flourishing field of organic materials with interesting electrical and optical properties, tetra-aryl substituted methanes and silanes have recently attracted much interest. In particular, oligothiophenyl groups play an important part in such tetrahedral compounds.[2] We are interested in the planar analogues to these systems, (i.e., *tetra*-thiophenyl substituted ethenes). In our laboratories, we are exploring different routes to these systems. In the present communication,[1] we report the synthesis of selected

Received in the U.K. June 12, 2006
Address correspondence to Jan Skramstad, Department of Chemistry, University of Oslo, P. O. Box 1033 Blindern, N-0315, Oslo, Norway. E-mail: jan.skramstad@kjemi.uio.no

bithiophenyl-substituted ethenes by deoxygenative coupling of properly substituted ketones by the use of low-valent titanium, a method known as the McMurry reaction.[3,4]

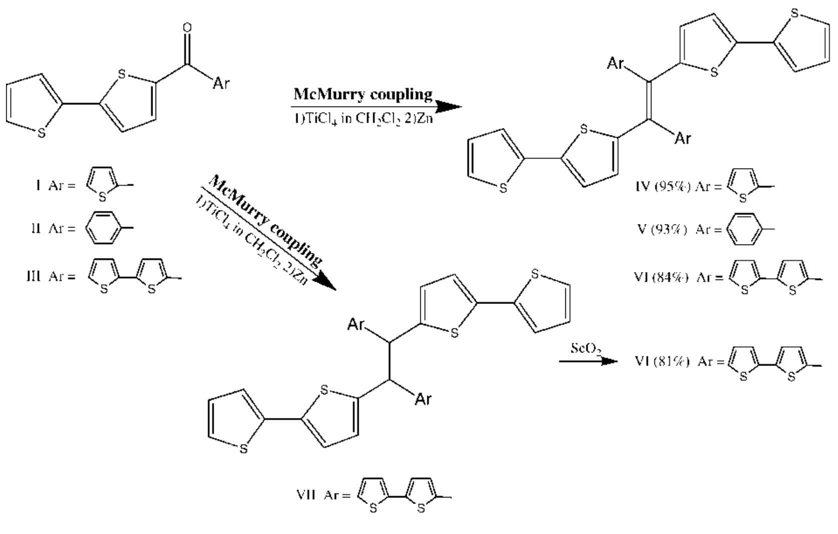
RESULTS

Our main results are depicted in Scheme 1.

The ketones I and II used as starting material for the first two coupling reactions were prepared by reacting mono-lithiated 2,2′-bithiophene with thiophene-2-carbonitrile and benzonitrile, respectively. This gave the ketones in higher yields and with better purity than the previously used Friedel–Crafts acylation of 2,2′-bithiophene with thiophene-2-carbonyl chloride or benzoyl chloride.[5] The synthesis of the symmetrical di-2,2′-bithiophen-5-ylmethanone III was achieved by reacting two equivalents of mono-lithiated 2,2′-bithiophene with carbamic chloride.

The McMurry coupling reactions of these ketones were performed according to the procedure given in the literature[3,4] (see Experimental). As can be seen from Scheme 1, the yields are excellent. The products were characterized by MS, NMR, and x-ray crystallography. Ortep plots are given in Fig. 1.

An interesting observation was made during the coupling of the most sterically crowded ketone III. When III was refluxed for only 24 h (instead of the usual 72 h), an unexpected product could be isolated in 68% yield. This product turned out to be the single bond analogue, VII, of the desired



Scheme 1. Synthesis of three thiophene substituted ethenes by McMurry coupling.

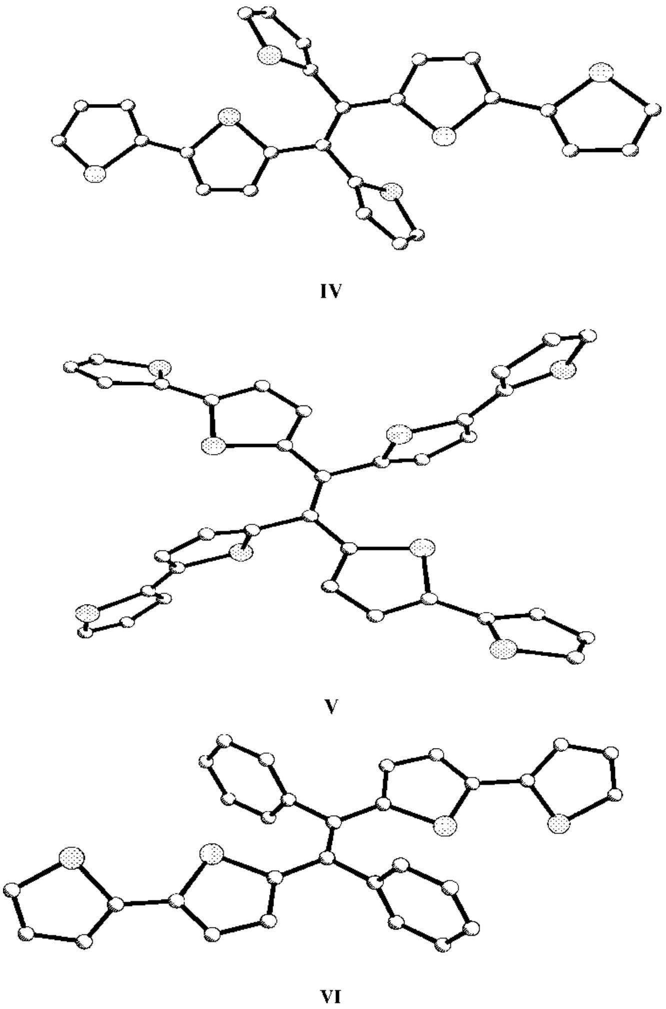


Figure 1. Ortep plots of the three target molecules, IV, V, and VI.

compound VI. By reaction with selenium dioxide, compound VII could be oxidized to VI in 81% yield (Scheme 1). As none of the other two ketones gave single bond coupling products, it is tempting to speculate that this outcome of the McMurry reaction is steric in origin. We have not been able to find precedent in the literature for this surprising result, which could throw new light on the mechanism of the McMurry reaction.

In the McMurry reaction, both E and Z isomers of the products are possible. As can be seen from the structure plots, both IV and V have the E configuration. It is also interesting to note that when phenyl groups are attached to the central double bond (V), the sulfur atoms of the dithiophenes point the same way. When the substituents are all thiophenes, the sulfurs point in opposite directions.

ELECTROCHEMICAL PROPERTIES

Cyclic voltametry (CV) was used to determine the redox potential for the target molecules. The measurements were carried out in dichloromethane/0.1 M $Bu_4N^+PF_6^-$ at a platinum disk electrode vs. ferrocene/ferrocenium couple (fc). The results are given in Fig. 2.

The CV of all the compounds exhibits reversible one-electron oxidation corresponding to the formation of a cation radical. For the phenyl-substituted compound V, a second oxidation was observed, corresponding to formation of a dication. A qualitative interpretation of this is that the removal of the second electron possibly takes place on the other side of the ethylene bridge and that is made more difficult because of conjugation with the charge through the bridge.

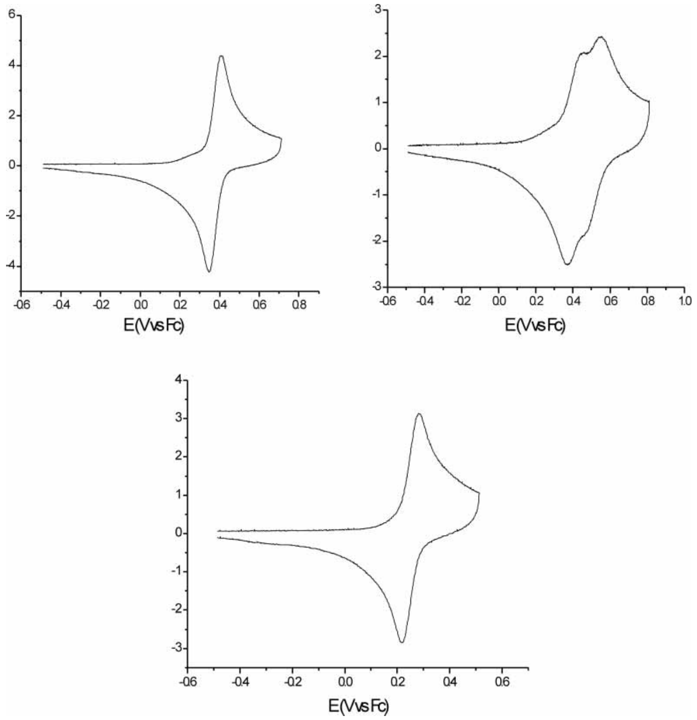


Figure 2. CV scans of target compounds IV, V, and VI. CV was measured in solution containing 0.1 M $Bu_4N^+PF_6^-$ 1.0 mM substrate ($\nu = 1.0$ V/s, 0°C, d = 0.4-mm platinum disk electrode).

Table 1. Electrochemical data extracted from the cyclic voltametric measurements of compounds IV, V, and VI

Compound	Ep(f)1 (V)	Ep(r)1 (V)	E(0)1 (V)	Delta Ep1 (mV)	Ep(f2) (V)	Ep(r)2 (V)	E(0)2 (V)	Delta Ep2 (mV)
IV	0.41	0.35	0.38	61				
V	0.46	0.37	0.42	88	0.55	0.46	0.51	90
VI	0.29	0.22	0.25	66				

Compounds IV and VI may also undergo a two-electron oxidation and here the removal of the second electron is not more difficult than removal of the first electron. (The authors acknowledge this interpretation from Professor Vernon Parker, Utah State University, USA.) Another observation is that by increasing the number of thiophene moieties in the molecule (IV → VI), the E(0) value decreases. The relevant data are given in Table 1.

EXPERIMENTAL

Melting points are uncorrected. The infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer using an attenuated total reflectance (ATR) ZnSe plate for solid samples. High-resolution NMR spectra (^{1}H and ^{13}C) were recorded on Bruker Avance DPX 300 and DRX 500 spectrometers. *J* values are given in Hertz. The mass spectra were obtained using a Fison Instrument VG Prospec Q, and the ultraviolet spectra were recorded on a Shimadzu UV-260 spectrophotometer.

2,2′-Bithiophen-5-yl(thiophen-2-yl)methanone (I)

2,2′-Bithiophene (5 g, 30 mmol) was dissolved in dry diethyl ether (50 ml) and cooled to −10°C. Then 1.6 M butyl lithium (18.8 ml, 30 mmol) in hexane was added dropwise. The reaction mixture was warmed to room temperature and stirred for 1 h. After cooling to −10 to −20°C, thiophene-2-carbonitrile (3.06 g, 28 mmol) in benzene (15 ml) was added. The mixture was then heated to reflux for 15 h, whereupon it was hydrolyzed by boiling with 30% hydrochloric acid (250 ml). Substances boiling below 100°C were then distilled off. The resulting solution was refluxed for 1 h, rendered basic with 40% sodium hydroxide, and extracted with methylene dichloride. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed. The residue was crystallized to give the title compound as a yellow solid (5.01 g, 65%), mp 104°C (pentane) (lit. 104°C).[6] δ_H (300 MHz, CD_2Cl_2) 7.08–7.11 (m, 1H), 7.21–7.23 (m, 1H), 7.27 (d, *J* 3.94, 1H), 7.37–7.39 (m, 2H), 7.73–7.75 (m, 1H), 7.83 (d, *J* 3.95, 1H), 7.90–7.92 (m, 1H). δ_C (75 MHz, CD_2Cl_2) 124.604, 126.128, 127.033, 128.427, 128.685, 133.143, 133.657, 134.442, 136.532, 141.407, 143.111, 145.771, 178.404. IR (ATR, cm^{-1}) 3102 (s), 1587 (m).

2,2′-Bithiophen-5-yl(phenyl)methanone (II)

2,2′-Bithiophene (5 g, 30 mmol) was dissolved in dry diethyl ether (50 ml) and cooled to −10°C. Then 1.6 M butyl lithium (18.8 ml, 30 mmol) in hexane was added dropwise. The reaction was warmed to room temperature and stirred for 1 h. After adjusting the temperature to −10 to 20°C, benzonitrile (2.9 g, 28 mmol) in benzene (15 ml) was added. The mixture was refluxed for 15 h and then hydrolyzed by boiling with 30% hydrochloric acid (250 ml), whereupon substances boiling below 100°C were removed by distillation. The resulting solution was refluxed for 1 h, rendered basic with 40% NaOH, and then extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and filtered and the solvent was removed. The residue was crystallized to give a yellow solid (4.8 g, 63%), mp 74–76°C (pentane) (lit. 74–76°C).[7] δ_H (300 MHz, CD_2Cl_2) 7.14 (dd, *J1* 1.43, *J2* 3.6, 1H), 7.36 (d, *J* 4.0, 1H), 7.51 (dd, *J1* 1.86, *J2* 4.0, 1H), 7.55–7.65 (m, 5H), 7.87 (dd, *J1* 1.67, *J2* 7.96, 2H). δ_C (75 MHz, CD_2Cl_2) 124.58, 125.33, 126.89, 127.98, 128.81, 129.38, 129.64, 133.05, 136.84, 138.79, 142.44, 146.43, 187.68. IR (ATR, cm^{-1}) 3069 (m), 1623 (m).

Di-2,2′-bithiophen-5-ylmethanone (III)

2,2′-Bithiophene (5 g, 30 mmol) was dissolved in THF (50 ml) and cooled to −78° Butyl lithium (1.6 M, 18.8 ml, 30 mmol) in hexane was added dropwise. After 30 min, carbamic chloride (1.2 g, 15 mmol) was added. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was then quenched with water. The phases were separated, and the organic phase was dried ($MgSO_4$) and filtered. The solvent was evaporated, affording a crude reaction product, which was dissolved in ether. The title compound crystallized to give a yellow solid (3.77 g, 70%), mp 154–155°C (diethyl ether). δ_H (300 MHz, CD_2Cl_2) 7.82 (d, *J* 4.04, 2H), 7.38–7.39 (m, 4H), 7.28 (d, *J* 4.04, 2H), 7.09–7.12 (dd, *J1* 3.74, *J2* 1.29). δ_C (75 MHz, CD_2Cl_2) 177.829, 145.660, 141.263, 136.563, 134.117, 128.708, 127.050, 126.146, 124.634. IR (ATR, cm^{-1}) 3083 (b w), 1571 (s), 1442 (s). M/z: 358 (100), 330 (7.5), 193 (40). High-resolution MS: 357.961369; calculated for $C_{17}H_{10}OS_4$: 357.961452.

(E)-1,2-Di(2,2′-bithiophen-5-yl)-1,2-di(thiophen-2-yl)ethene (IV)

THF (50 ml) was cooled to 0°C under argon atmosphere. $TiCl_4$ (1.0 M, 8.0 ml, 8 mmol) in dichloromethane was added dropwise, and then zinc (1.1 g, 16.8 mmol) was added. The reaction mixture was warmed to room temperature with stirring. After 6 h, the mixture was cooled to 0°C and pyridine (2.5 ml) and I (1.55 g, 5.6 mmol) in THF (30 ml) were added. The reaction mixture was allowed to reach room temperature. Finally, the reaction mixture was refluxed for 72 h. After cooling, CH_2Cl_2 (250 ml) was added, and the mixture was washed with 0.1 M HCl. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated, affording the crude reaction product, which was chromatographed on silica gel with chloroform–hexane (10:1). The product was crystallized to give a yellow solid (1.37 g, 95%), mp 207–208°C (toluene). δ_H (300 MHz, CD_2Cl_2) 6.67 (d, *J* 3.99, 2H), 6.95–7.00 (m, 4H), 7.05–7.08 (m, 6H), 7.22 (dd, *J1* 1.11, *J2* 5.13, 2H), 7.46 (dd, *J1* 1.96, *J2* 4.42, 2H). δ_C (75 MHz, CD_2Cl_2) 125.057, 125.073, 127.796, 127.805, 128.165, 128.253, 128.274, 128.352, 130.582, 130.690, 131.357, 143.200, 143.427. M/z: 520 (100), 260 (10). High-resolution MS: 519.956961; calculated for $C_{26}H_{16}S_6$: 519.957631. UV (CCl_4), log e (λ_{max}): 4.34 (230), 4.38 (330), 4.41 (424). Crystal data for $C_{26}H_{16}S_6$: Monoclinic, space group P21/a; a = 12.302(3) Å, b = 7.2878(15) Å, c = 14.012(4) Å, $\beta = 115.26(2)°$, V = 1136.1(5) $Å^3$, T = 120(1) K, λ(Cu Kα) = 1.54178 Å, Z = 2. Yellow prism, 0.26 × 0.16 × 0.13 mm. Data were collected with Siemens P4 diffractometer. Ni-filtered Cu(Kα) radiation from a rotating anode. Empirical absorption correction was done with Xabs2.[8] Solution was created with SHELXS96[9] and Fourier techinques. Full-matrix refinement with SHELX197[10] gave R = 0.0582 for 1331 reflections with Io > 2σ(Io), of 1502 independent.

(E)-1,2-Di(2,2′-bithiophen-5-yl)-1,2-diphenylethene (V)

From II (1.55 g, 5.6 mmol) in THF (30 ml), following the procedure given previously for the synthesis of IV, the title compound was prepared as a yellow solid (1.32 g, 93%), mp 193–194°C (toluene). δ_H (300 MHz, CD_2Cl_2) 7.44–7.47 (m, 10H), 7.15–7.17 (m, 2H), 6.80–6.94 (m, 4H), 6.80 (d, *J* 3.91, 2H), 6.25 (d, *J* 3.91, 2H). δ_C (75 MHz, CD_2Cl_2) 145.257, 142.004, 138.613, 137.574, 133.423, 131.373, 131.052, 129.448, 128.717, 128.160, 124.789, 123.737, 122.969. M/z: 508 (100), 254 (10). High-resolution MS: 508.042788; calculated for $C_{30}H_{20}S_4$: 508.044788. UV (CCl_4), log e (λ_{max}): 4.35 (229), 4.35 (332), 4.39 (406). Crystal data for $C_{30}H_{20}S_4$: Monoclinic, space group P21/a; a = 7.604(2) Å, b = 11.103 (3) Å, c = 13.952(3) Å, $\beta = 95.25(2)°$. V = 1173.10(5) $Å^3$, T = 90(1) K, λ(Mo Kα) = 0.71073 Å, Z = 2. Yellow needle, 0.37 × 0.16 × 0.12 mm. Data collected with Siemens (Bruker) SMART CCD diffractometer. Solution and refinement were done as for (IV) which gave R = 0.041 for 2826 reflections with Io > 2σ(Io), of 3645 independent.

1,1,2,2-Tetra(2,2′-bithiophen-5-yl)ethene (VI)

From III (2.0 g, 5.6 mmol) in THF (30 ml), following the procedure given previously for the synthesis of IV and V, the title compound was prepared as a yellow solid (1.61 g, 84%), mp 194–195°C (toluene). δ_H (300 MHz, CD_2Cl_2) 6.92 (d, *J* 3.90, 4H), 6.98–7.01 (dd, *J1* 1.09, *J2* 5.17, 4H), 7.07(d, *J* 3.90, 4H), 7.14–7.15 (dd, *J1* 1.09, *J2* 3.64, 4H), 7.23–7.24 (dd, *J1* 1.09, *J2* 5.17, 4H). δ_C (75 MHz, CD_2Cl_2) 123.76, 124.30, 125.15, 127.39, 128.30, 131.68, 137.46, 139.96, 143.17. m/z: 684 (34), 344 (100), 121 (80). High-resolution MS: 683.929774; calculated for $C_{34}H_{20}S_8$: 683.929774. UV (CCl_4), log e (λ_{max}): 4.65 (319), 4.63 (345), 4.35 (440). Crystal data for $C_{34}H_{20}S_8$: Monoclinic, space group P21/n; a = 16.0424(10) Å, b = 5.5536(3) Å, c = 17.4351(11) Å, $\beta = 105.960(2)°$. V = 1493.47(16) Å^3, T = 90(1) K, λ(Mo Kα) = 0.71073 Å, Z = 2. Yellow needle, 0.39 × 0.07 × 0.04 mm. Data collection, structure solution, and refinement were done as for (V). Terminal thiophene rings are disordered. The thiophene rings were restrained to have the same geometry. R = 0.0435 for 2540 reflections with $Io > 2\sigma$ (Io), of 4794 independent. In all structures, the terminal thiophene rings are disordered. The majority conformations range from 59% to 93%.The thiophene rings were restrained to have the same geometry.

1,1,2,2-Tetra(2,2′-bithiophen-5-yl)ethane (VII)

THF (50 ml) was cooled to 0°C under an argon atmosphere. Then, 8.0 ml of 1.0 M $TiCl_4$ (0.008 mol) in dichloromethane were added dropwise before zinc (1.1 g, 0.0168 mol) was added, and the reaction mixture was warmed to room temperature. After 1 h, the mixture was heated for 5 h before it was cooled to 0°C. Pyridine (2.5 ml) was added. Di(2,2′-bithienyl) ketone (2.0 g, 5.6 mmol) in 30 ml THF was added, and the reaction mixture was warmed to room temperature and then heated to reflux for 24 h. After cooling, the mixture was added to CH_2Cl_2 (250 ml) and washed with 0.1 M HCl. The organic layer was then dried ($MgSO_4$). After filtration and evaporation of the solvent, the crude reaction product was chromatographed on silica gel with chloroform–hexane (1:1). Yield 1.3 g (68%) of a yellow solid melting at 168–169°C. δ_H (300 MHz, CD_2Cl_2) 5.11 (2H, S), 6.82 (4H, d, *J* 3.7), 6.94 (4H, d, *J* 3.7), 6.97–7.00 (4H, dd *J* 3.6 and 5.2), 7.10–7.12 (4H, dd, *J* 1.1, and 3.6), 7.19–7.21 (4H, dd, *J* 1.1, and 5.2). δ_C (75 MHz, CD_2Cl_2) 50.208, 123.461, 123.939, 124.730, 126.972, 128.147, 136.955, 137.533, 144.810.

This compound could be converted to 1,1,2,2-tetra(2,2′-bithiophen-5-yl)ethene (VI) by the following procedure:

1,1,2,2-Tetra(2,2′-bithienyl)ethane (VII) (1.3 g, 1.89 mmol) was mixed with 0.21 g (1.89 mmol) of SeO_2 and 40 ml of xylene and heated to reflux. After 16 h of reflux, the reaction mixture was filtered through cellulose. After evaporation of the solvent, the crude reaction product was chromatographed on silica gel with chloroform–hexane (10:1). Yield was 1.0 g (81%) of a yellow solid melting at 194–195°C, and spectroscopic data (NMR and MS) are in accordance with those given above for compound VI.

REFERENCES

1. Halvorsen, H.; Hope, H.; Skramstad, J. *J. Synth. Comm.* **2007**, 1–11.
2. Brasselet, S.; Cherioux, F.; Audebert, P.; Zyss, J. *Chem. Mater.* **1999**, *11*, 1915–1920.
3. McMurry, J. E. *Chem. Rev.* **1989**, *89* (7), 1513–1524.
4. Fürstner, A.; Bogdanovic, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2442.
5. Hegedu, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., and Wilkinson, G., (eds); Oxford: Pergamon, 1995; Vol. 12, and references cited therein.
6. Lescot, E., Jr.; Buu-Hoi, N. P.; Xuong, N. D. *J. Chem. Soc.* **1959**, 3234–3237.
7. Krishnaswamy, N. R.; Kumar, C. S. S. R. *Indian J. Chem.; Sect. B* **1993**, *32B* (7), 766–71.
8. Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Cryst.* **1995**, *28*, 53–56.
9. Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467–473.
10. Sheldrick, G. M. *SHELXL97*; University of Göttingen: Germany, 1997.