Preparation and Spectroscopic (UV and IR) Properties of Some Tricarbonyl(thiophene)chromium Complexes

Marino Novi, Giuseppe Guanti (1), and Carlo Dell'Erba

Istituto di Chimica Organica dell'Universitá, C.N.R. Centro di Studio sui Diariloidi e loro Applicazioni, Palazzo delle Scienze, Corso Europa, 16132 Genova, Italy

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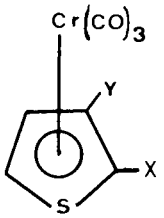
In connection with our studies on thiophene and its derivatives we became interested in the chemistry of tricarbonyl(thiophene)chromium complexes. An examination of literature data indicated that while the preparation and properties of numerous tricarbonylchromium π-complexes of benzene and its derivatives have been reported (2a-d), relatively few studies have been made in thiophene series. Recently some of these complexes have been prepared (3-10) but because of the difficulties encountered in their preparation only a limited number of compounds could be obtained (generally with alkyl groups in position 2 or 3 of the thiophene ring) in low yield.

In this paper we wish to report the synthesis and some spectroscopic properties (uv and ir) of a series of π-complexes of thiophene derivatives with tricarbonylchromium (**1a-i**).



1a-i

1a, X = OCH_3, Y = H
b, X = H, Y = OCH_3
c, X = CH_3, Y = H
d, X = H, Y = CH_3
e, X = Y = H
f, X = Br, Y = H
g, X = H, Y = Br
h, X = $COOCH_3$, Y = H
i, X = H, Y = $COOCH_3$

The method we have followed in the preparation of these compounds is based on the general procedure originally developed by Öfele (7) in 1966 to the synthesis of tricarbonyl(arene)chromium compounds from tricarbonyl(trispyridine)chromium and arenes in the presence of boron trifluoride etherate in boiling ether. We have found this method particularly facile in practice and convenient to synthetize in thiophene series both some new complexes (**1a**, **1b** and **1f-i**) and some other ones which were previously obtained *via* rather troublesome procedures (**1c-e**).

Table I lists the complexes prepared together with their analytical data. All complexes were orange-red crystalline solids moderately sensitive to light and air when pure but

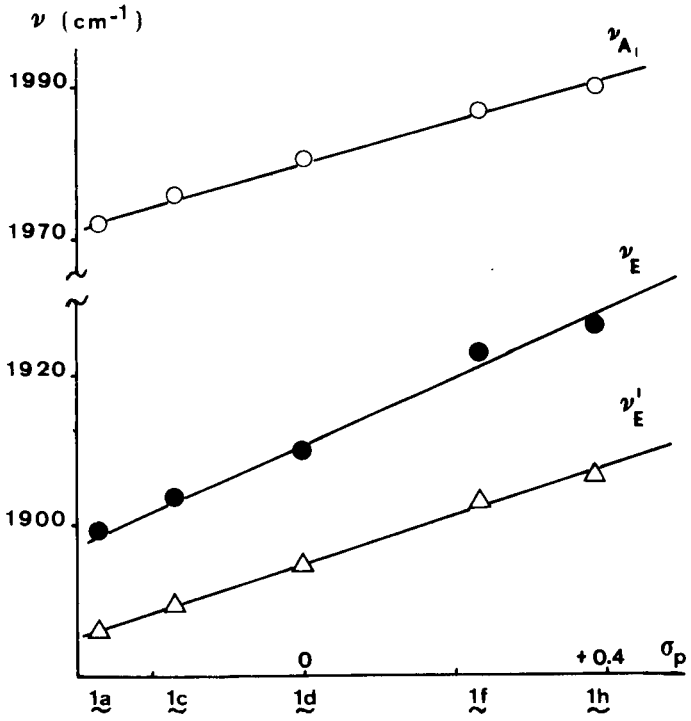


Figure 1. Plot of the carbonyl infrared frequencies (in cyclohexane) of various tricarbonyl(2-substituted thiophene)chromium complexes againts σ_p constants.

ν_{A_1} line: slope = 25.4 (r = 0.996; s = 0.7)
ν_E line: slope = 42.7 (r = 0.993; s = 1.6)
ν'_E line: slope = 32.0 (r = 0.998; s = 0.7)

TABLE I

Compound Number	Reaction Time (minutes)	Yield (%)	Recrystallization Solvent (a)	M.p. (°C)	Formula	Analysis Calcd. (Found)
1a	30	76	A-B (1:3)	81	$C_8H_6CrO_4S$	C, 38.40 H, 2.40 (C, 38.61 H, 2.45)
1b	30	75	A-B (1:3)	110	$C_8H_6CrO_4S$	C, 38.40 H, 2.40 (C, 38.52 H, 2.47)
1c	15	80	A-B (1:2)	124 (b)	$C_8H_6CrO_3S$	C, 41.03 H, 2.56 (C, 41.20 H, 2.58)
1d	15	81	A-B (1:2)	114 (c)	$C_8H_6CrO_3S$	C, 41.03 H, 2.56 (C, 41.10 H, 2.59)
1e	15	86	A-B (1:1)	160 dec.	$C_7H_4CrO_3S$	C, 38.18 H, 1.82 (C, 38.28 H, 1.80)
1f	60	50	C	109	$C_7H_3BrCrO_3S$	C, 28.09 H, 1.00 (C, 28.15 H, 1.01)
1g	60	52	C	95	$C_7H_3BrCrO_3S$	C, 28.09 H, 1.00 (C, 28.18 H, 1.03)
1h	60	72	A-B (1:2)	107	$C_9H_6CrO_5S$	C, 38.85 H, 2.16 (C, 38.87 H, 2.20)
1i	60	75	A-B (1:2)	120	$C_9H_6CrO_5S$	C, 38.85 H, 2.16 (C, 38.80 H, 2.18)

(a) A = Ethyl ether, B = light petroleum, C = *n*-hexane. (b) See reference (10) m.p. 125°. (c) *Ibid.*, m.p. 122°.

slowly attacked under these conditions when dissolved and were best handled and stored under nitrogen.

The ultraviolet and infrared spectra of these compounds were then registered. The λ max and log ε of the uv spectra in cyclohexane and the ir absorption frequencies in the C-O stretching region in various solvents of the **1a-i** complexes are reported in Table II. For comparison the spectral data of tricarbonyl(benzene)chromium (**2**) and hexacarbonylchromium (**3**) are also reported. The examination of uv data reveals that complexing thiophene or substituted thiophenes with tricarbonylchromium group results in a perturbation of the electronic structure properties of both moieties. The spectra exhibit in the region of 210-365 nm three bands similar in intensity and position to those observed for other tricarbonyl(arene)chromium derivatives (7, 12a-c). The other two bands (the former always more intense than the latter) which appear in the region of 400-550 nm are typical of tricarbonyl(thiophene)chromium complexes. Moreover a bathochromic shift in both these bands is observed on passing from the 3-substituted to the 2-substituted thiophene complex.

More specific observations and more useful informations are possible with the help of infrared spectra. By examination of the ir data the following points emerge: i) All the compounds have three bands: a sharp band (ν_{A_1}) resulting from the symmetric vibration of the three carbonyl groups and two other bands (ν_E and ν'_E) of lower energy and intensity resulting from the asymmetric vibrations. ii) The position of the C-O bands appears to be sensitive to the type of substituent present in the thiophene ring. The

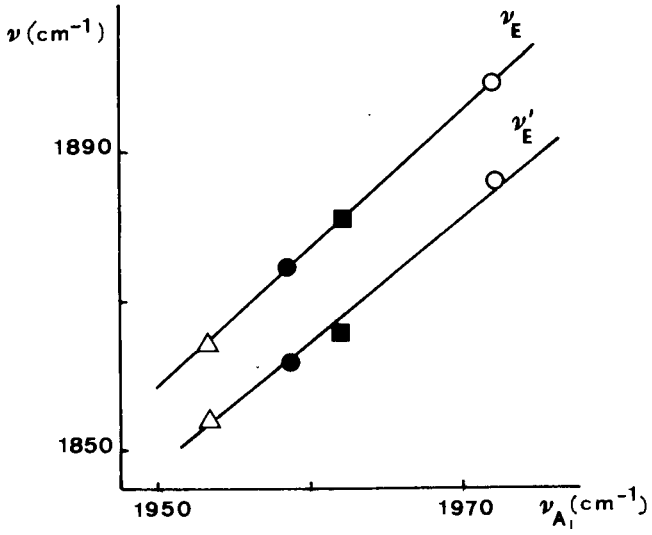


Figure 2. Plot of the carbonyl asymmetric vibrations (ν_E and ν'_E) against the symmetric vibration (ν_{A_1}) for the **1a** complex in different solvents (○, cyclohexane; ■, chloroform; ●, dichloromethane; △, nitromethane).

ν_E line: slope = 1.9 (r = 0.999; s = 0.23)
ν'_E line: slope = 1.7 (r = 0.991; s = 2.20)

frequencies are found to decrease (13) as the electron-donating power of the substituent in the thiophene ring increases. This fact indicates that in these complexes the electronic effect of a substituent on the thiophene moiety can be transmitted to the C-O bond of the terminal carbonyl

TABLE II

Ultraviolet (in Cyclohexane) and Infrared (C-O Stretching Frequencies in Cyclohexane, Chloroform, Methylene Chloride and Nitromethane) Spectra of some Tricarbonyl(arene)chromium Complexes and of Hexacarbonylchromium.

Compound Number	UV		IR (cm^{-1})			
	λ max (nm)	log ε	Cyclohexane	Chloroform	Dichloromethane	Nitromethane
1a	215	4.46	1972.0	1962.1	1958.6	1953.2
	284 (a)	3.55	1899.3	1880.7	1874.5	1864.0
	331	3.48	1886.0	1865.3	1862.0	1854.0
	418	3.50				
	505 (a)	2.75				
1b	206	4.54	1974.1	1964.5	1961.0	1955.3
			1903.3	1887.6	1880.3	1870.7
	334	3.49	1886.2	1863.0	1859.7	1851.6
	408	3.58				
	494 (a)	2.72				
1c	213	4.52	1974.0	1964.0	1961.1	1955.1
	284 (a)	3.62	1903.9	1884.3	1877.6	1869.4
	322	3.52	1889.4	1866.5	1864.7	1857.4
	414	3.59				
	495 (a)	2.82				
1d	215	4.48	1975.0	1963.9	1961.6	1955.2
			1907.0	1887.5	1880.8	1870.2
	319	3.56	1886.4	1864.1	1861.8	1853.9
	407	3.59				
	490 (a)	2.77				
1e	210	4.49	1979.1	1969.3	1965.2	1958.4
	260 (a)	3.82	1909.9	1891.3	1884.6	1872.6
	319	3.56	1894.5	1871.8	1868.3	1863.6
	410	3.58				
	493 (a)	2.79				
1f	214	4.40	1985.5	1977.1	1972.7	1967.1
	276 (a)	3.76	1923.0	1905.5	1898.8	1886.0
	324 (a)	3.56	1903.1	1884.2	1879.5	1874.0
	415	3.55				
	500 (a)	2.81				
1g	216	4.43	1895.5	1976.5	1972.5	1965.8
	262 (a)	3.89	1920.5	1902.8	1895.6	1884.0
	363	3.61	1907.4	1887.3	1882.8	1871.6
	403 (a)	3.50				
	494 (a)	2.77				
1h	213	4.40	1987.9	1982.7	1979.4	1973.9
	248 (a)	4.00	1926.0	1915.3	1910.2	1899.2
	296	3.68	1906.4	1889.3	1886.0	1879.5
	432	3.75				
	546	2.68				
1i	214	4.46	1987.1	1980.4	1977.1	1971.9
	253 (a)	3.95	1924.2	1911.8	1902.5	1892.4
	330	3.77	1910.9	1893.9	1890.0	1880.1
	414	3.52				
	501 (a)	2.83				
2	217	4.32	1981.8 (b)	1974.3 (b)	1971.4 (b)	1963.6
	263	3.89	1915.1 (b)	1898.3 (b)	1891.6 (b)	1881.5
	315	3.99				
3	230	4.77	1987.0	1982.2	1980.0	1978.1
	281	4.16				
	318 (a)	3.48				

ligands through the metal atom. In terms of the simple resonance theory the observed trend can be explained considering that the electronic structures (A) and (B) represent the canonical forms in resonance of these complexes and that an electron-donating group X will favour (B) in preference to (A). This donation will increase the

$$\ddot{X}\text{-M-C}\equiv\text{O} \longleftrightarrow {}^{+}\text{X=M=C=O}^{-}$$
(A) (B)

metal-carbon bond order and lower the carbon-oxygen bond order and thus decrease the carbonyl stretching frequency. The comparison of the C-O stretching frequencies of the 2- and 3-substituted thiophene complexes indicates that there is practically no influence due to the position of the substituents within the ring. This fact indicates that the over-all increase in the π-electron density on the whole aromatic ring rather than in a particular position is responsible for the shift of carbonyl bands. A correlation between the vibration frequencies and the σ constant of the substituent was also attempted. In Fig. 1 the three carbonyl frequencies registered in cyclohexane for each 2-substituted thiophene complex are plotted against σ_p of the corresponding substituent (14). The good correlation found and the values of the slopes indicate that as found in similar cases (2a) the σ_p constants well represent the effect of the substituent in these complexes and that the two asymmetric vibrations are more sensitive to the change of the substituent in the thiophene ring than it is the symmetric vibration. It is also interesting to note that the splitting between the two asymmetric vibrations increases with increasing the electron-attracting power of the substituent.

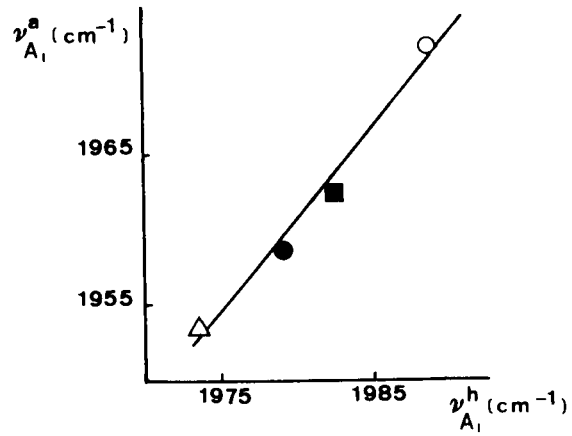


Figure 3. Plot of the symmetric carbonyl vibration of **1a** complex ($\nu^a_{A_1}$) against the symmetric carbonyl vibration of **1h** complex ($\nu^h_{A_1}$) in different solvents (○, cyclohexane, ■, chloroform; ●, dichloromethane; △, nitromethane). Slope = 1.3 (r = 0.983; s = 1.79).

The effect of solvent upon the carbonyl stretching frequencies was also examined. The infrared spectra of the complexes were registered in solvents with increasing polarity (cyclohexane, chloroform, methylene chloride and nitromethane). The examination of Table II reveals the following points: i) by increasing the polarity of the medium the vibration frequency decreases (13). ii) The frequency shift is greater for the asymmetric modes than for the totally symmetric mode. This effect is well evidenced in Fig. 2 for the **1a** complex. Similar plots, with slopes in all cases greater than unity can be obtained for the other complexes. iii) Generally by increasing the back-donation to a carbonyl group increases the solvent effect. This effect is well evidenced in Fig. 3 where the symmetric carbonyl vibration of the **1a** complex is plotted against the same vibration of the **1h** complex in different solvents.

This behaviour is in line with the theoretical description of the structure of these compounds and with the theory on the transmission of substituent effect in these complexes and is probably due to a dipole-dipole type of interaction between the π-complex and the solvent (15a,b).

EXPERIMENTAL

The ultraviolet spectra were registered on a Perkin-Elmer Model 402 spectrophotometer or on a Zeiss PM Q II. The former recording instrument was used to determine spectral shapes and the latter for the accurate determination of optical densities.

The infrared spectra were measured on a Perkin-Elmer Model 257 spectrophotometer. All bands in the spectra of samples were measured by reference to the spectrum of polystyrene; 0.1 mm. cells with sodium chloride windows were used for all solvents. The accuracy of the results is between ± 1 and ± 2 cm^{-1}. Each spectrum was obtained at least four times and the average value taken, the maximum deviation from this being 0.7 cm^{-1} for the A_1 mode vibration and 1.5 cm^{-1} for the E mode vibrations.

The solutions of the complexes were prepared just before recording the spectra in order to avoid decomposition.

All the solvents purified by standard procedure (16), were deoxygenated by heating under reflux in a nitrogen stream, distilled through a 75 cm Vigreux column and stored under nitrogen. Light petroleum had b.p. 30-50°.

2-Methyl and 3-methylthiophene were commercial specimens (Fluka). 2-Methoxythiophene (17), 3-methoxythiophene (18), 2-bromothiophene (19), 3-bromothiophene (20), 2-carbomethoxythiophene (21) and 3-carbomethoxythiophene (22) were prepared by literature methods and distilled just prior to use.

All melting points were determined in a sealed capillary.

General Procedure to Prepare Tricarbonyl(thiophene)chromium Complexes (**1a-i**).

Tricarbonyl(trispyridine)chromium (500 mg., 1.34 mmoles) was added to a solution of the appropriate thiophene compound (30 mmoles) in dry ether (6 ml.). Freshly distilled boron trifluoride diethyl etherate (600 mg., 4.22 mmoles) was added and the mixture was allowed to stand under magnetic stirring. (The reaction times are reported in Table I). Ether (10 ml.) was added, the mixture cooled to 0° and diluted with air-free water (8 ml.). The

mixture was extracted repeatedly with ether until the extracts were virtually colourless. The combined extracts were washed with water and dried (sodium sulfate). Removal, under reduced pressure, of solvent and thiophene substrate used in excess yielded a residue which was immediately filtered, washed with light petroleum and recrystallized. Evaporation of light petroleum gave yellow crystals of pentacarbonyl(pyridine)chromium m.p. 94-95° [lit. (23), 95.5-96.5°] (The yields, solvents of crystallization, melting points and analytical data of the various complexes are reported in Table I).

Tricarbonyl(trispyridine)chromium was prepared as described in literature (24) from tricarbonyl(*N,N*-dimethylaniline)chromium (25) and pyridine and used immediately.

REFERENCES

(1) To whom correspondence should be addressed.

(2a) G. Klopman and K. Noack, *Inorg. Chem.*, 7, 579 (1968); (b) A. Mangini and F. Taddei, *Inorg. Chim. Acta*, 2, 8 (1968); (c) W. R. Jackson and W. B. Jennings, *J. Chem. Soc.*, (B), 1221 (1969); (d) M. D. Rausch, *J. Org. Chem.*, 39, 1787 (1974) and references reported therein.

(3) E. O. Fischer and K. Öfele, *Chem. Ber.*, 91, 2395 (1958).

(4) E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, and W. Semmlinger, *Z. Naturforsch.*, 13b, 458 (1958).

(5) R. D. Fischer, *Chem. Ber.*, 93, 165 (1960).

(6) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 4, 1306 (1965).

(7) K. Öfele, *Chem. Ber.*, 99, 1732 (1966).

(8) A. Mangini and F. Taddei, *Inorg. Chim. Acta*, 2, 12 (1968).

(9) C. Segard, B. Roques, and C. Pommier, *C. R. Acad. Sci., Ser. C*, 272, 2179 (1971); *Chem. Abstr.*, 75, 88741z (1971).

(10) R. Guilard, J. Tirouflet, and P. Fournari, *J. Organometal. Chem.*, 33, 195 (1971).

(11) D. A. Brown and F. J. Hughes, *J. Chem. Soc.*, (A), 1519 (1968).

(12a) G. Natta, R. Ercoli, and F. Calderazzo, *Chim. Ind.* (Milan), 40, 287 (1958); (b) R. Ercoli and A. Mangini, *Ricerca Sci.*, 28, 2135 (1958); (c) R. T. Lundquist and M. Cais, *J. Org. Chem.*, 27, 1167 (1962).

(13) Although the differences are sometimes within experimental error the same trend is observed for all the frequencies and supports the conclusions based on their absolute positions.

(14) J. Hine, "Physical Organic Chemistry", 2nd Ed., Mc Graw-Hill Book Company, Inc., New York, 1962, p. 87.

(15a) C. C. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2582 (1961); (b) D. A. Brown and H. Sloan, *ibid.*, 3849 (1962).

(16) Weissberger, "Techniques of Organic Chemistry", Vol. VII, Interscience Publ., Inc., New York, N.Y., 1955.

(17) J. Sicé, *J. Am. Chem. Soc.*, 75, 3697 (1953).

(18) S. Gronowitz, *Arkiv Kemi*, 12, 239 (1958).

(19) E. Krause and G. Renwanz, *Chem. Ber.*, B62, 1710 (1929).

(20) S. Gronowitz and T. Raznikiewicz, *Org. Synth. Coll. Vol. V*, 149, (1973).

(21) O. Turilli and M. Gandino, *Ann. Chim.* (Rome), 53, 1687 (1963).

(22) S. Gronowitz, *Arkiv Kemi*, 16, 515 (1960).

(23) H. Behrens and W. Kleck, *Z. Anorg. Chem.*, 292, 151 (1957).

(24) D. E. F. Gracey, W. R. Jackson, W. B. Jennings, and T. R. B. Mitchell, *J. Chem. Soc.*, (B), 1204 (1969).

(25) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).