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# Group VIB Metal Pentacarbonyl Complexes of N,N′-dimethylimidazolidine-2-thione

KHALID S. JASIM and CHUNG CHIEH

*Guelph-Waterloo Center for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ont., N2L 3G1, Canada*

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## Abstract

Reactions between Group VIB metal hexacarbonyl $M(CO)_6$ (M = Cr, Mo or W) and N,N′-dimethylimidazolidine-2-thione (T), either at elevated temperature or under irradiation by ultraviolet light, produced reactive, moderately stable pentacarbonyl thione complexes, $M(CO)_5T$. The physical and chemical properties of these complexes are similar, indicating that their structures are the same. The IR bands due to the carbonyls in $CHCl_3$ solution consist of four peaks at *ca.* 2060, 1970, 1920 and 1870 $cm^{-1}$, but five bands were observed for their solids with an additional band at *ca.* 1940 $cm^{-1}$, possibly due to restricted rotation of the thione in the solid which reduces their pseudosymmetry. These thione complexes reacted with tetraethylthiuramdisulfide, $Et_4tds$, at room temperature, as opposed to higher temperature required for the reaction between metal hexacarbonyls and $Et_4tds$. With equal molar quantities of $M(CO)_5T$ and $Et_4tds$, complexes $M(CO)_4(Et_4tds)$ are formed, but with excess $Et_4tds$ the thiuramdisulfide is reduced to dithiocarbamate ($Et_2dtc$) resulting in the formation of $Cr(Et_2dtc)_3$ and $M(Et_2dtc)_4$ (M = Mo or W) as the final products, although $M(CO)_4(Et_4tds)$ might have been an intermediate.

## Introduction

Interest in complexes of sulfur-containing ligands and metal carbonyls is evident from the vast number of publications which have appeared in the recent literature. Abel and Crosse [1] surveyed the sulfur-containing metal carbonyls in considerable detail but did not list any thiourea carbonyl metal complexes, perhaps due to the small number of compounds reported at that time. Since then, many publications describing the reactions of thioureas with metal carbonyls have appeared. These include reactions of thiourea with rhenium [2] or manganese [3, 4] pentacarbonyl chloride, *o*-phenanthrolinemolybdenum tetracarbonyl [5], cycloheptatrienemolybdenum tricarbonyl [6, 7] and diiron enneacarbonyl [8]; the products were always S-bonded thiourea–metal carbonyl complexes.

These studies led to the discovery of interesting reactions and new complexes [9–12], yet only a few publications reported the studies of cyclic thiones [13–16]. In general, reactions between Group VIB metal hexacarbonyls and heterocyclic ligands (L) produce compounds of the type $M(CO)_5L$ (M = Cr, Mo, W). When L is pyridine, pyrazine, pyradazine or pyrimidine, nitrogen is the donor atom [17–19], whereas S is the donor atom when L is thiomorpholine-2-thione [14, 16], thiazolidine-2-thione [13] or imidazolidine-2-thione [15]. Some physical and chemical properties of these complexes have been reported, but the field is wide open for further exploration.

The complexes with S-containing ligands are relatively reactive, a property making these compounds suitable as intermediates for the preparation of other multinuclear metal complexes [20] or metal clusters [21]. In our study of metal complexes with S-containing ligands, we observed the formation of metal clusters from heating of $Mo_2(dtc)_6$ [22], thus the $M(CO)_5$ moiety might be a useful fragment in inorganic syntheses.

This paper reports the syntheses, characterization, and chemical and physical properties of some complexes of the form $M(CO)_5T$; where M = Cr, Mo, W; and T = N,N′-dimethylimidazolidine-2-thione (referred to as thione).

## Experimental

### *1. Measurements and Purification*

Infrared spectra were recorded at 2% KBr and CsBr disks and in chloroform solutions on the following instruments: Beckman Acculab 10 and Perkin-Elmer 457 and 180. The $^1H$ NMR spectra were recorded in acetone $d_6$ on a Bruker WP-80 NMR spectrometer. Electronic spectra were obtained in chloroform solution using Cary 80 UV/Vis spectrophotometer. Gas chromatographic analyses were performed on a Hewlett-Packard 5830 Gas Chromatograph using a 1.6 m glass column of 2 mm internal

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diameter, packed with Aue packing of 0.25 wt.% Carbowax 20 M on Chromosorb W (120 mesh). The starting temperature was 273 K raised by 8 K/min to a maximum of 573 K. The photochemical reactions were carried out in a Rayonet reactor manufactured by the Southern N.E. Ultraviolet Company. Elemental analyses were performed by Guelph Chemical Laboratories Ltd. Solvents were dried by storing them over molecular sieves 4A for several days followed by filtration and purging with nitrogen gas immediately before use.

N,N′-dimethylimidazolidine-2-thione was prepared by literature method [23]. $Mo(CO)_6$ (M = Cr, Mo, W) were purified by sublimation under vacuum at 323, 323, and 353 K respectively. All reactions and manipulations were carried out in a nitrogen atmosphere.

### 2. *Preparation of $M(CO)_5T$ Thermochemically*

The preparation was carried out by heating a colorless ethanol solution of $M(CO)_6$ and thione (with molar ratios of 1:1, 1:2, 1:3 or 1:6) either at reflux temperature or at 333 K in a water bath. After *ca.* 10–30 min, the solution became noticeably yellow. The reaction was monitored by measuring the ir spectrum of the carbonyl stretching region. No further changes were observed after *ca.* one hour of refluxing, but three hours were required at 333 K. The reaction mixture was then cooled to room temperature and the solvent removed by evaporation under vacuum. Compounds $M(CO)_5T$ were purified by the following procedures: (a) the solid residue was heated to 333–353 K under vacuum to remove unreacted $M(CO)_6$; (b) the resulting yellow product was dissolved with excess hexane, separating it from the insoluble thione; (c) the yellow hexane solution was evaporated to dryness under vacuum; and (d) recrystallization was done by dissolving the solid in a minimum amount of ethanol and cooled in a dry ice/acetone bath. Regardless of the molar ratios or temperatures used, all reactions led to the same yellow product, $M(CO)_5T$ as indicated by the results of elemental and other analyses, yields being 10–30%.

### 3. *Preparation of $M(CO)_5T$ Photochemically*

An acetone solution containing equal molar quantities of $M(CO)_6$ and thione was irradiated under $N_2$ with ultraviolet light. Upon exposure, the solution turned yellow immediately. The reaction, from its monitored IR spectrum, seemed to reach completion in 5 to 8 hours. The volume of the reaction mixture was then reduced, equal volume of hexane added, and the mixture cooled in a dry ice/acetone bath for crystallization, following which the solvent was decanted. Recrystallization. from hexane/acetone solution was carried out till a pure yellow sample was obtained. Yields were considerably higher than those from the thermal method, 75 to 90%. *Anal.* Calcd. for $CrC_{10}H_{10}N_2O_5S$: C 37.27, H 3.11, N 8.70; found: C 37.76, H 3.75, N 8.69; Calcd. for $MoC_{10}H_{10}N_2O_5S$: C 32.79, H 2.73, N 7.65; found: C 33.32; H 2.99, N 7.55 and for $WC_{10}H_{10}N_2O_5S$: C 26.43, H 2.20, N 6.17; found: C 26.53, H 2.23, N 6.05.

### 4. *Reactions of $M(CO)_5T$ and Tetraethylethiuram Disulfide ($Et_4tds$)*

Various molar ratios of $M(CO)_5T$ and $Et_4tds$ were used in the following reactions.

All the carbonyl IR bands disappeared when acetone solutions with 1:2 molar ratio of the reactants were stirred at room temperature for 24 h. The solvent was then removed under vacuum and the residue washed with ethanol to remove the liberated thione. The products were identified to be $Cr(Et_2dtc)_3$, $Mo(Et_2dtc)_4$ and $W(Et_2dtc)_4$ by comparing their color, IR and UV/Vis spectra and melting points with their reported data (see results and discussion). The first two complexes were recrystallized from hot acetone solution whereas the third is a powder of very low solubility; yields ranged from 70 to 80%.

Acetone solutions containing 1:1 and 2:1 molar ratios of the reactants were stirred at room temperature and the IR bands of the carbonyls were monitored. No further change was observed after *ca.* 8 to 12 hours of reaction time. When the molar ratio is 1:1, the new set of bands at *ca.* 2000, 1950, 1910 $cm^{-1}$ with two additional shoulders at 1850 and 1810 replaced the four bands of pentacarbonyls at *ca.* 2060, 1960, 1910, and 1870 $cm^{-1}$, whereas when the molar ratio was 2:1, the IR spectra consisted of both sets of bands (see results and discussion).

## Results and Discussion

The reactions between $M(CO)_6$ and thione at elevated temperatures proceeded slowly and were never complete; but the photochemical reactions gave clean yellow products accompanied by slight decomposition. The products may be purified by repeated crystallization. The decomposition might be due to trace amounts of oxygen or moisture or both present in the reaction vessel. Results from elemental analyses indicated that regardless of the initial molar ratio, only one carbonyl group is replaced by a thione in all three Group VIB metal carbonyls.

The physical and chemical properties of the family of compounds $M(CO)_5T$ are similar. They are soluble in polar solvents such as chloroform and acetone and sparingly soluble in hydrocarbons, acetonitrile, alco-

TABLE I. Comparison of IR bands between thione (T) and its complexes $M(CO)_5T$.

| Thione | $Cr(CO)_5T$ | $Mo(CO)_5T$ | $W(CO)_5T$ | Assignment |
|---|---|---|---|---|
| 1515vs[a] | 1540vs | 1547vs | 1569vs | $\mu$(CN) |
| 510s | 495s | 495s | 480s | $\mu$(CS) |
| – | 375w | 360w | 350w | $\mu$(MS) |

[a] vs, very strong; s, strong; w, weak.

hol and ether, but decompose in water. Their solubilities follow the general order $Cr(CO)_5T > Mo(CO)_5T > W(CO)_5T$. The complexes are unstable in air and decompose into thione and their respective oxides $Cr_2O_3$, $Mo_2O_5 \cdot 3H_2O$ and $WO_3$. Qualitative electron fluorescence analyses were used to confirm $Mo_2O_5 \cdot 3H_2O$ whereas color and IR spectra were used to identify other oxides and thione. In addition, gas chromatograms of the decomposed sample and that of thione are identical, the retention time being 14.8 minutes.

The stability of these complexes follows the order $Cr(CO)_5T > W(CO)_5T > Mo(CO)_5T$ which is identical to that of $M(CO)_5ttz$ (ttz = thiazolidine-2-thione) [13]. However, they are stable if stored under a nitrogen atmosphere in the dark at 273 K.

Fig. 1. The IR spectra in the carbonyl region for solution (A) and solid state (B) IR spectra of $M(CO)_5T$.

The infrared spectra of metal carbonyl complexes with another ligand containing nitrogen and sulfur atoms have four interesting regions. (a) The CN stretching region (1480–1550 $cm^{-1}$) gives information about the kind of donor atom of the ligand. An unshifted $\mu$(CN) indicates an N-bonding whereas an upward shift of *ca.* 25 $cm^{-1}$ is indicative of S-bonding due to the increased double C–N bond character. (b) The CS stretching region (480–515 $cm^{-1}$) gives additional evidence about the bonding modes. An S-bonding mode causes a downward shift because of decreased C=S bond order. (c) If the ligand does not have an absorption band in the 300–500 $cm^{-1}$ region, the band due to M–S or M–N stretching usually appears as a weak peak in this

TABLE II. Infrared spectra of $M(CO)_5T$, $\mu$(CO) $cm^{-1}$.

| Compound | Band position (in $CHCl_3$) | assignment | band position (of solids) | assignment |
|---|---|---|---|---|
| $Cr(CO)_5T$ | 2060m | A1 | 2065m | A1 |
| | 1965m | B1 | 1975m | B1 |
| | – | – | 1935sh | B2 |
| | 1915vs | E | 1915vs | A1 |
| | 1875sh | A1 | 1875s | A1 |
| $Mo(CO)_5T$ | 2060m | A1 | 2060m | A1 |
| | 1970m | B1 | 1975m | B1 |
| | – | – | 1935sh | B2 |
| | 1920vs | E | 1915vs | A1 |
| | 1870sh | A1 | 1873s | A1 |
| $W(CO)_5T$ | 2062m | A1 | 2063m | A1 |
| | 1965m | B1 | 1970m | B1 |
| | – | – | 1940sh | B2 |
| | 1915vs | E | 1905vs | A1 |
| | 1870sh | A1 | 1870s | A1 |

TABLE III. Electronic spectra of $M(CO)_5T$ in $CHCl_3$ solution.

| $Cr(CO)_5T$ Band (kK), $\epsilon$ | $Mo(CO)_5T$ Band (kK), $\epsilon$ | $W(CO)_5T$ Band (kK), $\epsilon$ | Assignment |
|---|---|---|---|
| 22.5, 458 | 24.1, 470 | 23.2, 527 | M → S Charge transfer |
| 24.1, 430 | 26.5, 300 | 26.5, 318 | A′–E′ |
| 30.6, vw | 30.3, 30 | 29.5, 36 | Due to deviation from $C_{4v}$ |
| | | 32.3, vw | |

region. (d) The metal carbonyl region (around 2000 $cm^{-1}$) may shed light on the symmetry of the compound and the orientation of the organic ligand in the molecule with respect to the $M(CO)_5$ moiety.

Table I compares the IR absorption bands due to $\mu$(CN) and $\mu$(CS) between thione and its complexes. An increase by 25–45 $cm^{-1}$ for $\mu$(CN) and a downward shift by 15–30 $cm^{-1}$ for $\mu$(CS) suggest M–S coordination for all three compounds. The metal sulfur vibrations appeared, as expected, in the region of 350–375 $cm^{-1}$.

The IR spectra of these complexes in chloroform exhibit four bands (Fig. 1) typical of those of monosubstituted pentacarbonyls, $M(CO)_5L$ [24–26]. These bands suggest $C_{4v}$ pseudosymmetry (Table II) for the $M(CO)_5$ moiety due to free rotation of the thione in solution. In general, the MSC angle is about 105°. The Raman but not IR active B1 modes are observed, indicating an imperfect $C_{4v}$ symmetry.

Instead of four bands observed for solution, the solid state spectra exhibit five bands (Fig. 1), due to the fixed orientation of the ligand with respect to $M(CO)_5$ moiety, causing the symmetry to deviate further from $C_{4v}$, and removing the degeneracy of the E mode. Neglecting the effects of atoms not directly bonded to the metal, the $M(CO)_5$ moiety may be assumed to belong to $C_{2v}$. The bond lengths of the Cr and W complexes support the same argument [27].

Since the electronic spectra (Table III) were measured from solutions, assignments were made on the assumption of $C_{4v}$ symmetry [28, 29]. The bands at 22.5, 24.1, and 23.2 kK in the spectra of Cr, Mo and W compounds respectively may be assigned as M → S charge transfer absorptions whereas the second bands at 24.1, 26.5, and 26.5 kK are assignable to A′ → E′ transitions, as expected from diamagnetic, pseudo-octahedral $Mo(CO)_5T$ complexes [26].

The proton NMR bands of the complexes have a small downfield shift compared to those of thione, $\delta(CH_2)$ 3.9, $\delta(CH_3)$ 3.2 ppm compared to 3.6 and 3.1 ppm respectively for thione.

The complexes $M(CO)_5T$ are very reactive and they may be used as starting materials for inorganic syntheses. As a comparison, some group VIB metal compounds react with $R_2dtcNa$ and $R_4tds$ usually at reflux temperature or under irradiation by UV as follows:

$$CrCl_3{\cdot}6H_2O + 3R_2dtcNa \xrightarrow[\text{ref,4 h}]{\text{THF}} Cr(R_2dtc)_3 + 3NaCl + 6H_2O \quad [30]$$

$$Mo(CO)_6 + 2R_4tds \xrightarrow[\text{ref,5 h}]{\text{Acetone}} Mo(R_2dtc)_4 + 6CO \quad [31]$$

$$C_7H_8W(CO)_3 + 2R_4tds \xrightarrow[\text{uv,18h}]{\text{Benzene}} W(R_2dtc)_4 + 3CO + C_7H_8 \quad [32]$$

$$WX_4{\cdot}2CH_3CN + 4Et_2dtcNa \longrightarrow W(Et_2dtc)_4 + 4NaCL + 2CH_3CN \quad [33]$$

The reactions of $M(CO)_5T$ with $Et_4tds$ yielded the above three dithiocarbamates (the violet $Cr(Et_2dtc)_3$, the purple $Mo(Et_2dtc)_4$ and the mustard $W(Et_2dtc)_4$) by stirring at only room temperature, when the molar ratio of reactants is 1:2. The last three compounds were characterized by comparing their IR and electronic spectra with published data [30–33] (see Table IV). For $Cr(Et_2dtc)_3$, three bands at 15.6, 20.4, and 31.7 kK are comparable to those of [34]; bands at 17.7, 19.0, 22.0, and 25.3 kK for $Mo(Et_2dtc)_4$ are similar to those of [31, 35]; and of the five bands at 19.4, 21.3, 24.3, 25.1, and 27.8 kK, the first three were reported in [36] for $W(Et_2dtc)_4$. However, during the reactions of $M(CO)_5T$ (M = Mo, W) with $Et_4tds$ we observed dramatic changes in the carbonyl region of the IR spectra, suggesting that these reactions proceed via metal carbonyl intermediates. All attempts of their isolation were unsuccessful; they lost their carbonyl groups on conversion to solid state giving a mixture. Separation of the molybdenum intermediate by column chromatography resulted in the formation of the well known $Mo_2O_3(Et_2dtc)_4$ as identified

TABLE IV. Infrared data for the products from $M(CO)_5T$ and $Et_4tds$.

a) Compounds without carbonyl groups

| Compound | ref. | $\mu$(CN) | $\mu$(NC2) | $\mu$(CS) | $\mu$(MS) |
|---|---|---|---|---|---|
| $Cr(Et_2dtc)_3$ | [a] | 1490vs | 1142vs | 992s | 370m |
| | [30] | 1488vs | 1140vs | 990s | 376m |
| $Mo(Et_2dtc)_4$ | [a] | 1500vs | 1150vs | 1000s | 352m |
| | [31] | 1500vs | – | 1002s | 355m |
| $W(Et_2dtc)_4$ | [a] | 1522vs | 1158vs | 982s | 360m |
| | [33] | 1525vs | 1155vs | 993s | 365m |

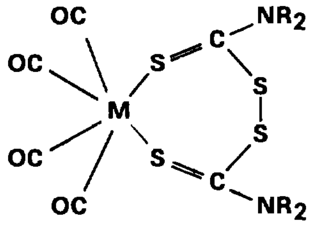
b) Band positions of the carbonyl group

| | |
|---|---|
| $Mo(CO)_4Et_4tds$ | 2000m, 1955m, 1910s, 1855sh, 1810sh |
| $W(CO)_4Et_4tds$ | 1995m, 1950m, 1905s, 1845sh, 1805sh |

[a] This work.

from its IR spectra [37] and elemental analysis. The source of oxygen is likely from air contamination in the column.

In order to identify the intermediate products, we resorted to reactions using less $Et_4dts$. When the molar ratios were 2:1, unreacted compounds $M(CO)_5T$ were left even after prolonged reflux. The newly formed compounds had another set of IR bands at about 2000 $cm^{-1}$ indicating the formation of yet another type of carbonyl complexes. Experiments with a 1:1 molar ratio seem to give a complete conversion as seen from the monitored IR bands. Bands due to the pentacarbonyl were replaced by a new set of bands similar to those of *cis*-tetracarbonyl metal complexes [38]. The above results suggest the formation of tetraethylthiuram disulfide complexes, not those of dithiocarbamate. An additional piece of evidence is the recovery of $Et_4tds$ when the complexes decomposed. Therefore the following compounds may have been formed.



Further reactions of these compounds with $Et_4dts$ result not only in the depletion of all carbonyls, but also the reduction of the disulfide to dithiocarbamate, thus leading to the formation of their respective metal dithiocarbamates.

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## References

1 E. W. Abel and B. C. Crosse, *Organomet. Chem. Rev., 2,* 443 (1967).
2 W. Hieber and W. Rohm, *Chem. Ber., 102,* 2787 (1969).
3 W. Hieber and M. Gscheidmeier, *Chem. Ber., 99,* 2312 (1966).
4 H. C. E. Mannerkantz and G. Wilkinson, *J. Chem. Soc.,* 4454 (1962).
5 L. W. Houk and G. R. Dobson, *Inorg. Chem., 5,* 2119 (1966).
6 F. A. Cotton and F. Zingales, *Inorg. Chem., 1,* 145 (1962).
7 F. A. Cotton and F. Zingales, *Chem. Ind. (London),* 1219 (1960).
8 H. Alper and A. S. K. Chan, *Inorg. Chem., 13,* 225 (1974).
9 E. Linder and W. Nagel, *Z. Naturforsch., Teil B:, 32,* 1116 (1977).
10 H. Fischer and R. Markl, *Chem. Ber., 115,* 1349 (1982).
11 H. Alper, *J. Organomet. Chem., 61,* C62 (1973).
12 H. G. Raubenheimer, G. J. Kruger and A. Lombard, *J. Organomet. Chem., 240,* C11 (1982).
13 D. De Filippo, F. Devillanova, C. Preti, E. F. Trogu and P. Vigalino, *Inorg. Chim. Acta, 6,* 23 (1971).
14 C. Preti and D. De Filippo, *J. Chem. Soc. A:,* 1901 (1970).
15 J. Barker and E. S. Raper, *Inorg. Chim. Acta, 53,* L177 (1981).
16 M. Cannas, G. Carta, A. Cristine and G. Marongin, *Acta Crystallogr., Sect. B:, 31,* 2909 (1975).
17 M. S. Wrighton, H. A. Abrahamson and D. L. Morse, *J. Am. Chem. Soc., 98,* 4105 (1976).
18 A. Oskam and H. Daamen, *Inorg. Chim. Acta, 26,* 81 (1978).
19 G. Boxhoorn and A. Oskam, *Inorg. Chim. Acta, 29,* 1207 (1978).

20 R. L. Keiter, R. D. Borger, M. J. Madigan, S. L. Kaiser and D. L. Rowley, *Inorg. Chim. Acta, 76,* L5 (1983).

21 B. Chang, *Inorg. Chim. Acta, 65,* L189 (1982).

22 T. C. Mak, K. S. Jasim and C. Chieh, *Angew. Chem., Int. Ed. Engl., 23,* 391 (1984).

23 C. Chieh and S. K. Cheung, *Can. J. Chem., 61,* 211 (1984).

24 L. E. Orgel, *Inorg. Chem., 1,* 25 (1962).

25 F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc., 84,* 4432 (1962).

26 C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem., 2,* 533 (1963).

27 T. C. Mak, K. S. Jasim and C. Cheih, *Inorg. Chim. Acta,* 99, 00 (1985).

28 M. Wrighton, *Chem. Rev., 74,* 401 (1974).

29 K. H. Pannell, M. G. Saenz Gonzalez, H. Leano and R. Iglesias, *Inorg. Chem., 17,* 1093 (1978).

30 D. A. Brown, W. K. Glass and M. Burke, *Spectrochim. Acta, Part A:, 32,* 137 (1976).

31 K. S. Jasim, *Ph.D. Thesis,* Nat. Univ. Ire., 1982.

32 D. A. Brown, W. K. Glass, K. S. Jasim and H. J. Toma, in J. R. Dilworth and M. F. Lapport, (eds.), 'Some Recent Development in the Chemistry of Cr, Mo and W' a proceeding of a conference held at the University of Sussex by the Royal Society of Chemistry, Dalton Division, 1984, p. 29.

33 J. N. Smith and T. M. Brown, *Inorg. Nucl. Chem. Lett., 6,* 441 (1970).

34 C. K. Jorgensen, *J. Inorg. Nucl. Chem., 24,* 1571 (1962).

35 A. Nieuwpoort and J. J. Staggerda, *Rec., J. R. Netherland Chem. Soc., 95,* 294 (1976).

36 T. M. Brown and J. N. Smith, *J. Chem. Soc., Dalton Trans.,* 1614 (1972).

37 R. Colton and G. R. Scollary, *Aust. J. Chem., 21,* 1427 (1968).

38 D. A. Adams, 'Metal-Ligand and Related Vibrations', St Martin's Press, New York, 1968, p. 139.