Journal of Organometallic Chemistry, 210 (1981) 353—355
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PHOTOINDUCED SYNTHESIS OF THE NEW ORGANOSELENO MANGANESE CLUSTER $[Mn(CO)_3SeC_6H_5]_4$

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(Received November 25th, 1980)

Summary

The synthesis of the compounds $[Mn(CO)_3XC_6H_5]_4$ (X = Se, S) by UV irradiation of a mixture of $Mn_2(CO)_{10}$ with $Se_2(C_6H_5)_2$ or $S_2(C_6H_5)_2$ is described.

Introduction

W. Hieber prepared the first dimeric manganese carbonyl sulphur compound $[Mn(CO)_4SR]_2$ in 1959 by treating manganese pentacarbonyl halide with thiols [1]. Several years later the first tetrameric products $[M(CO)_3SR]_4$ (M = Mn, Re) were synthesized [2,3]. Originally they were formulated as trimeric, but later work indicated a tetrameric structure, at least for the manganese compounds in the vapour phase [4—6].

Recently, Alper and coworkers [7] reported the reaction of pentacarbonylmanganese anion with thioketones but only the well known dimeric $[Ar_2CHSMn(CO)_4]_2$ was obtained. The first photochemical reaction of a metal carbonyl, the formation of the tetranuclear cluster $[Re(CO)_3OH]_4$ upon irradiation of $Re_2(CO)_{10}$ in aqueous ether, was described by M. Herberhold et al. [8]. The photoinduced reaction of $Mn_2(CO)_{10}$ or $Fe(CO)_5$ with the diorganodiselenide $CF_3Se_2CF_3$ gave only the dimeric $[Mn(CO)_4SeCF_3]_2$ or $[Fe(CO)_3SeCF_3]_2$ [9].

Results and discussion

Both compounds $[Mn(CO)_3XC_6H_5]_4$ (X = Se, S) were prepared by such photoinduced reaction. Photolysis of $Mn_2(CO)_{10}$ produces $Mn(CO)_5$ radicals, which react with C_6H_5X radicals (X = Se, S) generated by UV irradiation also. No monomeric $Mn(CO)_5XC_6H_5$ was found after photolysis. The main products were the dimeric $[Mn(CO)_4XC_6H_5]_2$ and tetrameric $[Mn(CO)_3XC_6H_5]_4$ species.

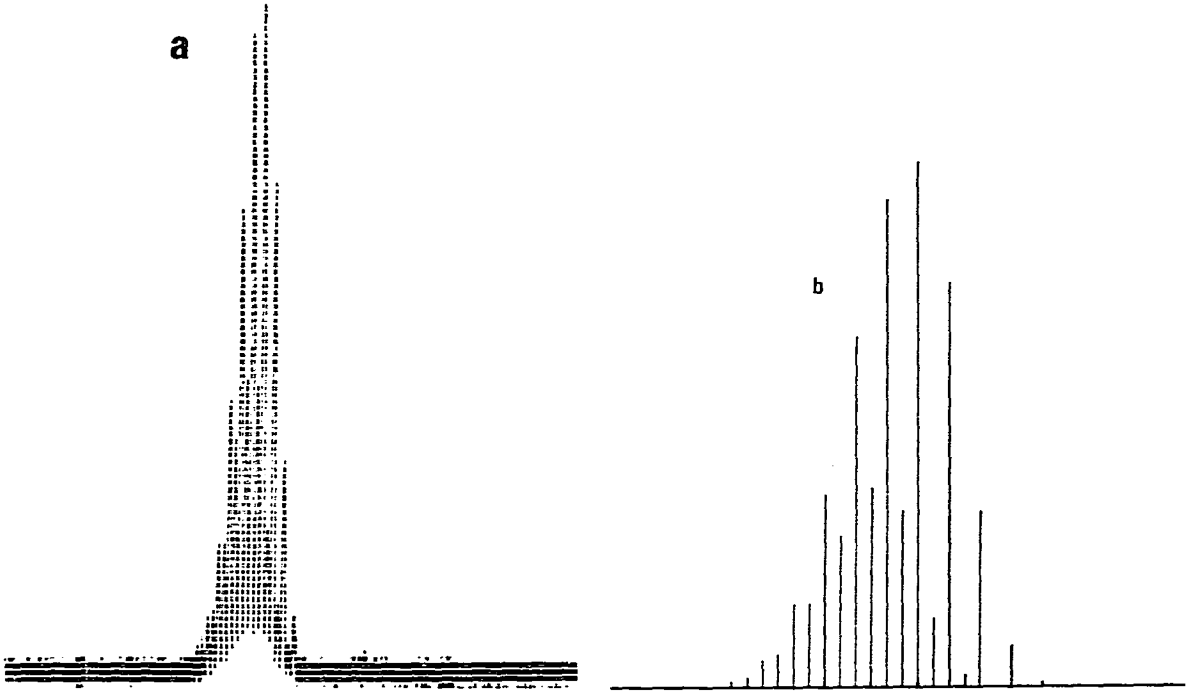

Fig. 1. Isotopic distribution patterns of $Mn_4Se_4^+$ (M = 536); a) experimental, b) calculated.

The reactive radicals $Mn(CO)_5$ seem to aggregate to the polynuclear clusters with loss of CO. The tetranuclear clusters were characterized by elemental analysis, infrared and mass spectra. The infrared spectra of these dodecacarbonyls only exhibit two active carbonyl stretching modes, indicating highest symmetry ($[Mn(CO)_3SC_6H_5]_4$: 2028vs, 1955s cm^{-1}; $[Mn(CO)_3SeC_6H_5]_4$: 2022vs, 1951s cm^{-1}, n-pentane).

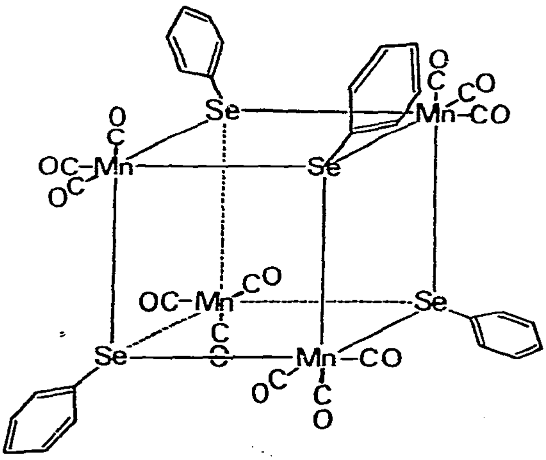

Fig. 2. Structure suggested for $[Mn(CO)_3SeC_6H_5]_4$.

In the mass spectra molecular ion peaks are observed for both compounds despite their very high molecular weights of $M = 992$ and $M = 1180$, but their relative intensities are very low compared with those of the fragment ions. The fragmentation of the molecular ion occurs first by successive lost of the 12 carbonyls and then loss of the C_6H_5 and C_6H_5X groups. The high intensities of the degraded ion peaks $Mn_4S_4^+$ and $Mn_4Se_4^+$ demonstrate the stability of the metal-chalcogen cage. The isotopic distribution patterns are as expected.

In accordance with the spectroscopic data and the known structure of $[Re(CO)_3SC_6H_5]_4$ [10] we suggest for $[Mn(CO)_3SeC_6H_5]_4$ the pseudo cubane structure illustrated in Fig. 2.

Experimental

All manipulations were carried out under dry nitrogen. Solvents were distilled from sodium wire under N_2. The C, H and O analyses were determined with a Heraeus EA 415 analyzer. Infrared spectra were recorded on a Perkin Elmer 180 and mass spectra on a Varian Mat CH 7 (70 eV). Ultraviolett irradiations were performed with a high pressure mercury lamp (Hanau 150 W) in a Schlenk tube equipped with a pressure valve.

A typical photoinduced reaction

0.5 mmol (195 mg) $Mn_2(CO)_{10}$ and 0.5 mmol $Se_2(C_6H_5)_2$ (156 mg) were dissolved in 10 ml n-pentane and irradiated for 12 hours at room temperature. During photolysis the initial yellow solution turned brown. Purification of $[Mn(CO)_3SeC_6H_5]_4$ was carried out by vacuum sublimation (130°C, 10^{-2} mmHg, yield 35—40%).

Analyses. $[Mn(CO)_3SeC_6H_5]_4$: Found: C, 37.4; H, 1.7; O, 16.4. $C_{36}H_{20}Mn_4O_{12}Se_4$ calcd.: C, 36.6; H, 1.69; O, 16.2%. $[Mn(CO)_3SC_6H_5]_4$: Found: C, 43.9; H, 2.1; O, 19.5. $C_{36}H_{20}Mn_4O_{12}S_4$ calcd.: C, 43.5; H, 2.02; O, 19.35%.

Acknowledgments

I would like to thank professors K.E. Schwarzhans and A. Engelbrecht for making this work possible and the Fonds zur Förderung der Wissenschaften, Vienna for making available certain scientific instruments.

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