Journal of Organometallic Chemistry, 233 (1982) 333—336
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF SELENOLATO- AND TELLUROLATO-BRIDGED DIMOLYBDENUM(*Mo=Mo*) COMPLEXES $[(\eta^5\text{-MeCp})\text{Mo(CO)}(\mu\text{-EPh})]_2$ (E = Se, Te)

PETER JAITNER

Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck (Austria)

(Received February 24th, 1982)

Summary

UV irradiation of the diphenylchalcogenides Ph_2Se_2 or Ph_2Te_2 in the presence of $[(\eta^5\text{-MeCp})\text{Mo(CO)}_3]_2$ induces rapid reaction to give the double μ-EPh bridged compounds $[(\eta^5\text{-MeCp})\text{Mo(CO)}_2(\mu\text{-EPh})]_2$. Subsequent decarbonylation by mild thermolysis in vacuo gives $[(\eta^5\text{-MeCp})\text{Mo(CO)}(\mu\text{-SePh})]_2$ or $[(\eta^5\text{-MeCp})\text{Mo(CO)}(\mu\text{-TePh})]_2$ in good yields. The new compounds were characterized by elemental analysis, infrared and mass spectra. The mixed Se/Te bridged complex $[(\eta^5\text{-MeCp})\text{Mo}_2(\text{CO})_4(\mu\text{-SePh})(\mu\text{-TePh})]$ was not obtained by UV irradiation of $[(\eta^5\text{-MeCp})\text{Mo(CO)}_3]_2$ in the presence of a mixture of Ph_2Se_2 and Ph_2Te_2.

Introduction

The complex $[(\eta^5\text{-MeCp})\text{Mo(CO)}_3]_2$ has a rich chemistry and has attracted much attention in the last years. Simply on heating in toluene the singly bonded $[(\eta^5\text{-Cp})\text{Mo(CO)}_3]_2$ shows a surprising ability to form the triply bonded Mo≡Mo complex $[(\eta^5\text{-Cp})\text{Mo(CO)}_2]_2$, with two semibridging carbonyls on each molybdenum, the conversion is accompanied by a very large decrease in the metal—metal distance from 3.235 to 2.448 Å [1]. The complex $[(\eta^5\text{-Cp})\text{Mo(CO)}_2]_2$ is highly reactive towards both electrophilic and nucleophilic reagents and opens the way to a rich area of organometallic molybdenum chemistry. Thus elemental sulphur induces disproportionation of the triple bond to form the tetrahedral cluster $[(\eta^5\text{-Cp})_3\text{Mo}_3(\text{CO})_6\text{S}][(\eta^5\text{-Cp})\text{Mo(CO)}_3]$ [2], while the complex reacts readily with thioketones to give the novel complexes bis(η^5-cyclopentadienyl)(thiocamphor)tetracarbonyldimolybdenum [3]. X-ray structures for these and related complexes reveal the fascinating structural possibilities in molybdenum organo-metal chemistry [4,5].

0022-328X/82/0000—0000/$02.75

Results and discussion

Knox and his colleagues reported that thiolato-bridged molybdenum complexes $[(\eta^5\text{-Cp})Mo(CO)_2(\mu\text{-SR})]_2$ also undergo decarbonylation on heating in

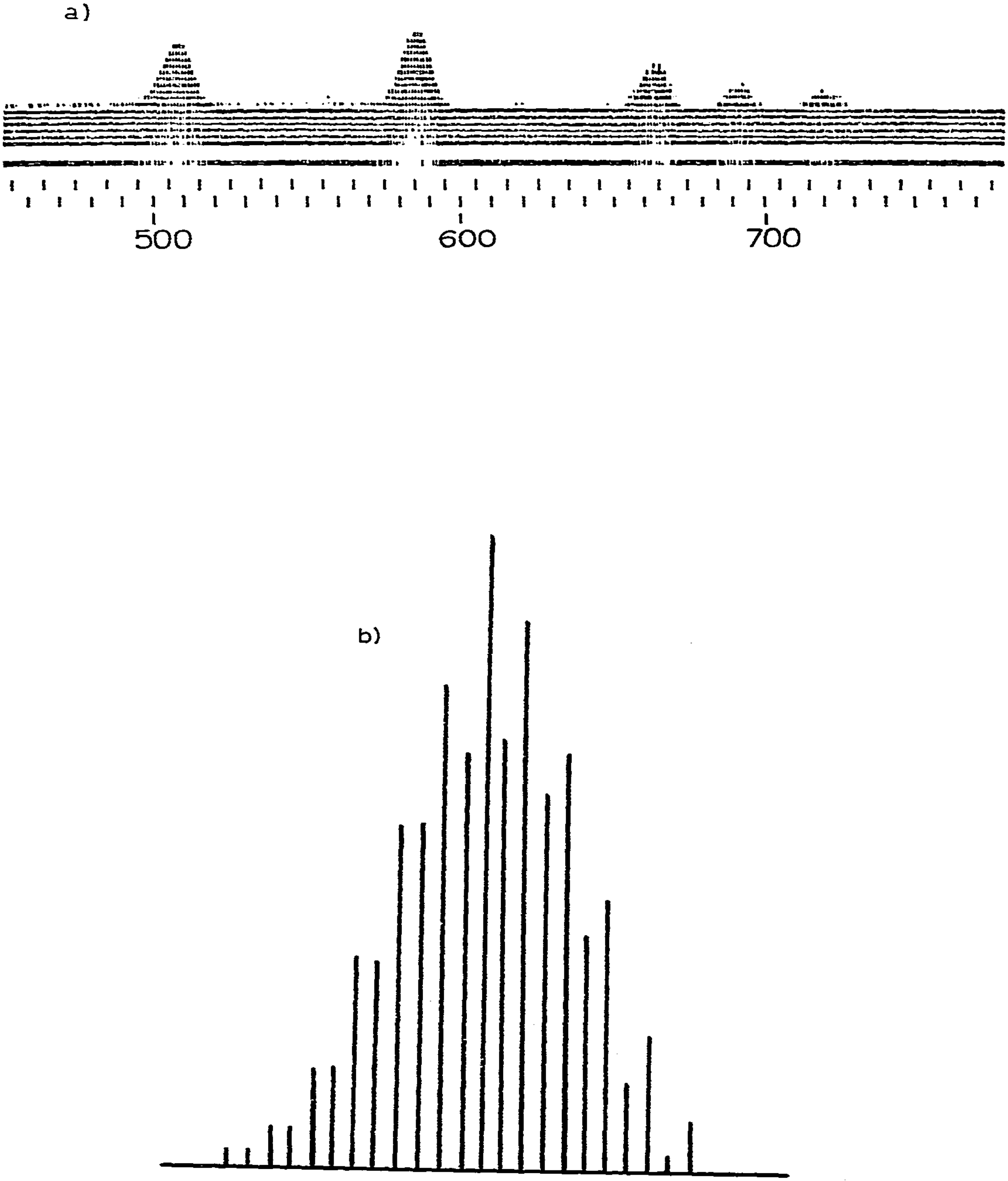


Fig. 1. Fragmentation and isotopic distribution patterns of $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-SePh})]_2$; (a) experimental, (b) calculated.

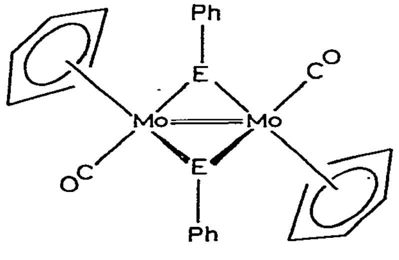
boiling heptane (yield 30—40%) to $[(\eta^5\text{-Cp})Mo(CO)(\mu\text{-SR})]_2$, with the result that two metal atoms which were initially non-bonded are brought into formal double bonding [6]. $[(\eta^5\text{-Cp})Mo(CO)_2(\mu\text{-SR})]_2$ involves a non planar Mo_2S_2 ring and a Mo···Mo distance of 3.940 Å, indicating that there is no metal—metal bonding, as predicted by the eighteen-electron rule. Distinctive features of the structure of the decarbonylated compound $[(\eta^5\text{-Cp})Mo(CO)(\mu\text{-SR})]_2$ when compared with $[(\eta^5\text{-Cp})Mo(CO)_2(\mu\text{-SR})]_2$ are that the Mo_2S_2 ring is planar and the Mo···Mo distance is shortened by ca. 1.3 to 2.616 Å, allowing the metal atoms to achieve 18-electron configuration [6].

We now report that the selenolato- and tellurolato-bridged complexes $[(\eta^5\text{-MeCp})Mo(CO)_2(\mu\text{-EPh})]_2$ (E = Se, Te), synthesized by photoinduced reaction of $[(\eta^5\text{-MeCp})Mo(CO)_3]_2$ (Hg-high pressure lamp 150 W, toluene, 3 h, room temperature) with Ph_2Se_2 or Ph_2Te_2, readily undergo decarbonylation when the solids are heated mildly in vacuo (80°C/10^{-2} mmHg) to give the dark brown $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-SePh})]_2$ or $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-TePh})]_2$. No further decarbonylation $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-EPh})]_2$ (E = Se, Te) is possible on heating, and only decomposition occurs.

Both compounds were characterized by elemental analysis, infrared, and mass spectra. The infrared spectra of solutions of these bridged complexes exhibit two carbonyl stretching modes revealing the presence of the isomers, based on *cis-* or *trans*-arrangements of the methylcyclopentadienyl ligands (with respect to the Mo_2Se_2 or Mo_2Te_2 ring: 1878s and 1850m cm^{-1}; 1881s and 1865m cm^{-1}, n-pentane, respectively).

In the mass spectra the expected molecular ion peaks are observed for both compounds. The fragmentation of the molecular ions occurs first by successive loss of the two carbonyls and then loss of the methylcyclopentadienyl groups. The isotopic distribution patterns for both compounds are as expected (Fig. 1).

In accordance with all spectroscopic data and the recently reported molecular structure of $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-SBu}^t)]_2$ [6] we suggest for $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-EPh})]_2$ (E = Se, Te) the structure illustrated in Fig. 2, containing a formally double bonded molybdenum (Mo=Mo)-selenium or -tellurium ring. No mixed Se/Te compound $[(\eta^5\text{-MeCp})_2Mo_2(CO)_4(\mu\text{-SePh})(\mu\text{-TePh})]$ could be obtained by analogous photoreactions of a mixture of Ph_2Se_2, Ph_2Te_2 and $[(\eta^5\text{-MeCp})Mo(CO)_3]_2$. Presumably the strain in such a "MoSeMoTe ring" rules out the presence of two different chalcogens.



(E = Se,Te)

Fig. 2. Structure suggested for $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-EPh})]_2$.

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). Ultraviolet irradiations were performed with a mercury high pressure lamp (Hanau 150 W) in a Schlenk tube equipped with a pressure valve under a slow N_2 stream.

Photoinduced reactions

Synthesis of $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-SePh})]_2$. 0.25 mmol (129.5 mg) $[(\eta^5\text{-MeCp})Mo(CO)_3]_2$ and 0.25 mmol (78 mg) Ph_2Se_2 were dissolved in toluene (9 ml) and irradiated for 3 h at room temperature under a slow N_2 stream. During photolysis the solution turned dark brown. IR and mass spectral examination of the product showed it to be $[(\eta^5\text{-MeCp})Mo(CO)_2(\mu\text{-SePh})]_2$. Mild thermolysis of this solid in vacuo (10^{-2} Torr, 80°C, 4 h) yielded the decarbonylated grey brown $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-SePh})]_2$ (m.p. 140°C (decomp.), yield >50%). The elemental analyses (C, H, O) agreed with the calculated values.

Synthesis of $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-TePh})]_2$. A solution of 0.25 mmol (129.5 mg) $[(\eta^5\text{-MeCp})Mo(CO)_3]_2$ and 0.25 mmol (102.3 mg) Ph_2Te_2 in toluene (10 ml) was irradiated for 2.5 h at room temperature under a slow N_2 stream. The solid product $[(\eta^5\text{-MeCp})Mo(CO)_2(\mu\text{-TePh})]_2$ was subjected to mild thermolysis in vacuo (10^{-2} Torr, 80°C, 12 h) to give the dark brown $[(\eta^5\text{-MeCp})Mo(CO)(\mu\text{-TePh})]_2$ (m.p. 125°C, 148°C (decomp.), yield >60%). The elemental analyses (C, H, O) agreed with the calculated values.

Acknowledgments

Thanks are due to the Fonds zur Förderung der Wissenschaften, Wien for allowing access to instruments, to E. Gehrer for helpful assistance, and to Mag. H. Schottenberger for recording the mass spectra.

References

1 R.J. Klingler, W.M. Butler and M.D. Curtis, J. Am. Chem. Soc., 100 (1978) 5034.
2 M.D. Curtis and W.M. Butler, J. Chem. Soc. Chem. Soc., (1980) 998.
3 H. Alper, N.D. Silavwe, G.I. Birnbaum and F.R. Ahmed, J. Am. Chem. Soc., 101 (1979) 6582.
4 M.H. Chisholm, F.A. Cotton, M.W. Extine and L.A. Rankel, J. Am. Chem. Soc., 100 (1978) 807.
5 D. Mohr, H. Wienand and M.L. Ziegler, J. Organometal. Chem., 134 (1977) 281.
6 I.B. Benson, S.D. Killops, S.A.R. Knox and A. Welch, J. Chem. Soc. Chem. Comm., (1980) 1137.