

Organotransition-metal complexes of multidentate ligands

IV *. Facile formation of a heat- and air-stable, 17-electron radical, $\text{Tp}'\text{Mo}(\text{CO})_3$, and a sulfur-bridged dimer, $[\text{Tp}'\text{Mo}(\text{CO})_2]_2\text{S}$ ($\text{Tp}' = \text{hydridotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$)

Kom-Bei Shiu* and Li-Yun Lee

Department of Chemistry, National Cheng Kung University, Tainan, Taiwan 70101

(Received January 5th, 1988)

Abstract

A heat- and air-stable, 17-electron (17e) radical, $\text{Tp}'\text{Mo}(\text{CO})_3$, and a sulfur-bridged dimer, $[\text{Tp}'\text{Mo}(\text{CO})_2]_2\text{S}$ ($\text{Tp}' = \text{hydridotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$), are obtained from the reaction of $\text{Tp}'\text{Mo}(\text{CO})_3^-$ with Cp_2Fe^+ and from that of $\text{Tp}'\text{Mo}(\text{CO})_3$ with sulfur, respectively. Success in obtaining the stable $\text{Tp}'\text{Mo}(\text{CO})_3$ radical supports the concept that bulky multidentate ligands help to stabilize the 17e organometallic radicals whereas the facile formation of the dimer indicates that sulfurization of the 17e compounds can provide a facile route to metal-sulfur compounds.

Introduction

Currently there is much interest in carbonyl-containing 17-electron (17e) organometallic radicals [2], but few attempts had been made at isolating such paramagnetic species for obvious reasons. Our understanding of properties of transition-metal carbonyl derivatives of multidentates with differing steric bulk [1], led us to believe that bulky multidentate ligands could play a very important role in the stabilization of 17e compounds. In order to confirm this viewpoint, we attempted to synthesize the $\text{Tp}'\text{Mo}(\text{CO})_3$ radical ($\text{Tp}' = \text{hydridotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$), which was thought to be a possible intermediate in the conversion of the anion, $\text{Tp}'\text{Mo}(\text{CO})_3^-$, into $\text{Tp}'\text{Mo}(\text{CO})_2(\eta^2\text{-COAr})$ and $\text{Tp}'\text{Mo}(\text{CO})_2(\eta^1\text{-CCl})$

* For Parts I–III, see ref. 1.

in 1983) [3] and gained success. We now wish to report the synthesis and sulfurization of this air-stable radical which was also found to have good thermal stability. Although the sulfur-bridged dimer, $[\text{Tp}'\text{Mo}(\text{CO})_2]_2\text{S}$, has been reported previously [4,5], our procedure which uses sulfur and $\text{Tp}'\text{Mo}(\text{CO})_3$ appears to be the best procedure of all. We thus think that sulfurization of the 17e organometallic radicals may provide easy access to metal-sulfur compounds which have recently attracted much attention [6*] owing to the fact that they play a major rôle in the activity of a variety of biologically important enzymes and coenzymes [7] and that they have enormous commercial value as a hydrodesulfurization catalyst [8].

Experimental

All operations were carried out under N_2 by standard Schlenk and vacuum-line techniques. Organic solvents were dried by standard procedures and distilled under N_2 before use. IR spectra, calibrated with polystyrene, were recorded on a Hitachi 260-30 model instrument. NMR spectra were obtained on a Bruker WP-100 FT NMR spectrometer using tetramethylsilane as internal standard. Elemental analysis results were obtained using the Heraeus CHN-O-RAPID analyzer.

Preparation of $\text{Tp}'\text{Mo}(\text{CO})_3$

To a solution of $\text{Et}_4\text{N}^+\text{Tp}'\text{Mo}(\text{CO})_3^-$ [9] (0.607 g, 1.00 mmol) in 25 ml of CH_3CN was added portionwise $\text{Cp}_2\text{Fe}^+\text{PF}_6^-$ [10] (0.397 g, 1.20 mmol). The solution immediately changed color from yellow to red and darkish red crystals formed. The suspension was further concentrated to 5 ml and filtered. The solid was washed twice with 3 ml of cold CH_3CN and dried under vacuum to give 0.453 g (95% yield) of $\text{Tp}'\text{Mo}(\text{CO})_3$. IR(KBr): $\nu(\text{CO})$, 1966s, 1844vs cm^{-1} . IR(CH_2Cl_2): $\nu(\text{CO})$, (s) (vs) 1998s, 1864vs cm^{-1} . Anal. Found: C, 45.05; H, 4.67; N, 17.70. $\text{C}_{18}\text{H}_{22}\text{BMoN}_6\text{O}_3$ calcd.: C, 45.31; H, 4.65; N, 17.61%. ^1H NMR (CDCl_3 , 100 MHz, r.t.): δ 1.55 (s, 3H), 18.39 (s, 9H), 35.40 (s, 9H) ppm.

Preparation of $[\text{Tp}'\text{Mo}(\text{CO})_2]_2\text{S}$

Elemental sulfur (0.008 g, 0.25 mmol) was added to $\text{Tp}'\text{Mo}(\text{CO})_3$ (0.238 g, 0.50 mmol) in 20 ml of THF. Evolution of gas was noted and after 1.5 h, the color of the solution had changed from dark red to dark green. The solution was concentrated to 5 ml to give a green crystalline solid (0.428 g, 92%) which was identified as $[\text{Tp}'\text{Mo}(\text{CO})_2]_2\text{S}$ by comparison with IR and NMR spectral data [4,5].

Results and discussion

Synthesis and characterization of $\text{Tp}'\text{Mo}(\text{CO})_3$

One-electron removal from the anion, $\text{Tp}'\text{Mo}(\text{CO})_3^-$, by an oxidant such as Cp_2Fe^+ , gives almost quantitatively the paramagnetic radical, $\text{Tp}'\text{Mo}(\text{CO})_3$, according to eq. 1. (The radical has a magnetic moment of 1.95 μB in CDCl_3 at 294 K, $\text{Tp}'\text{Mo}(\text{CO})_3^- + \text{Ox.} \rightarrow \text{Tp}'\text{Mo}(\text{CO})_3 + \text{Red.}$ (1)

measured by Evan's method, close to that expected for a ground state doublet).

* Reference number with asterisk indicates a note in the list of references.

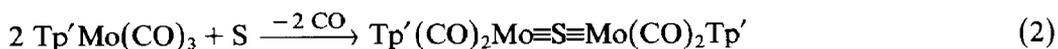
$\text{Tp}'\text{Mo}(\text{CO})_3$ is a darkish red solid which shows two carbonyl stretching bands at 1998s and 1864vs cm^{-1} in solution. The bands of strong and very strong intensity with decreasing frequencies are consistent with what is expected for *fac*- $\text{L}_3\text{M}(\text{CO})_3$ complexes where L_3 may represent one symmetrical tridentate e.g. Tp' . The frequencies are 10–20 cm^{-1} lower than the $\nu(\text{CO})$ of the analogous $\text{TpMo}(\text{CO})_3$ radical [11] indicating an increase in Mo–CO back bonding as expected from the more electron-donating methyl-substituted Tp' than Tp (Tp = hydridotris(pyrazol-1-yl)borate).

In contrast to $\text{TpMo}(\text{CO})_3$, which decomposes very rapidly in air and gradually under N_2 at 25 °C [11], the 17e radical we prepared is quite stable in air at room temperature. The stability in air of this complex can be attributed to steric effects of the bulkier Tp' ligand, which contains methyl groups at the 3-position of the ring thus increasing the size of the ligand relative to Tp and restricting access to the transition-metal atoms, but the thermal stability is probably due to fortunate combination of both steric and electronic factors of the ligand so that there is a lack of suitable decomposition routes with low activation barriers. Thus our success in obtaining the much more air-stable 17e paramagnetic radical using the bulky ligand, Tp' , supports our concept that bulky multidentate ligands help to stabilize the 17e compounds.

The ^1H NMR spectrum of the radical, $\text{Tp}'\text{Mo}(\text{CO})_3$, consists of three singlets which are shifted from their normal positions in the diamagnetic compounds [12]. In CDCl_3 , the chemical shifts of 1.55 (3H), 18.39 (9H), and 35.40 (9H) ppm for $\text{Tp}'\text{Mo}(\text{CO})_3$ indicate a downfield shift while those values for $\text{TpMo}(\text{CO})_3$ show an upfield shift. Although the EHMO calculations were performed to supplement the ^1H NMR spectrum of $\text{TpMo}(\text{CO})_3$ [11], we used the integrated intensity ratio and line widths to assign the three singlets in the ^1H NMR spectrum of $\text{Tp}'\text{Mo}(\text{CO})_3$. (The line widths of resonances can be related to the relaxation rate which has an inverse dependence on the distance between paramagnetic center and proton [13]). Thus, from the ratio, it is clear that the signal at 1.55 ppm can be assigned to the hydrogen atoms at the 4-position on the ring and the other two signals can be assigned to the methyl groups at the 3- and 5-positions on the ring of the Tp' ligand. Since the line width of 35.40 ppm signal is broader than that of 18.39 ppm resonance, the former is assigned to the methyl groups at the 3-position on the ring and the latter is assigned to the methyl groups at the 5-position on the ring.

Sulfurization of $\text{Tp}'\text{Mo}(\text{CO})_3$

Comparison of the IR and NMR spectral data, led us to believe that elemental sulfur converts $\text{Tp}'\text{Mo}(\text{CO})_3$ into a sulfur-bridged dinuclear compound, $[\text{Tp}'\text{Mo}(\text{CO})_2]_2\text{S}$ (eq. 2), which was previously reported to have been prepared from either $\text{Tp}'\text{Mo}(\text{CO})_3^-$ and $(\text{NSCl})_3$ in tetrahydrofuran at 0 °C [4] or from



$\text{Tp}'\text{Mo}(\text{CO})_3^-$ and sulfur by refluxing in $\text{C}_2\text{H}_4\text{Cl}_2$ for 24 h [5]. Although the anion readily reacts with $(\text{NSCl})_3$, the product is a mixture of the dimer (15%) and $\text{Tp}'\text{Mo}(\text{CO})_2(\text{NS})$ (24%). Sulfurization of the neutral radical is apparently better than that of the anion, because a 92% yield is obtained when the radical is used, whereas a 50% yield results when the anion is used. Furthermore, in the final

work-up, column chromatography, adopted for the anionic and the $(\text{NSCl})_3$ method, was not required to separate the pure dimer if the radical route was used. Thus sulfurization of 17e organometallic radicals can provide a quick and new approach to metal-sulfur compounds.

Acknowledgement

We thank the National Science Council of the Republic of China for financial support of this research.

References

- 1 (a) Part 1, K.-B. Shiu and W.-J. Vong, *J. Chinese Chem. Soc.*, 34 (1987) 195; (b) Part 2, K.-B. Shiu and C.-J. Chang, *ibid.*, 34 (1987) 297; and (c) Part 3, K.-B. Shiu and K.-S. Liou, *ibid.*, in press.
- 2 M.J. Therien and W.C. Trogler, *J. Am. Chem. Soc.*, 109 (1987) 5127 and ref. therein.
- 3 (a) T. Desmond, F.J. Lalor, G. Fergusson, B. Ruhl, and M. Parvez, *J. Chem. Soc., Chem. Comm.*, (1983) 55; (b) T. Desmond, F.J. Lalor, G. Fergusson and M. Parvez, *ibid.*, (1983) 457.
- 4 D.L. Lichtenberger and J.L. Hubbard, *Inorg. Chem.*, 23 (1984) 2718.
- 5 S. Lincoln, S.-L. Soong, S.A. Koch, M. Sato, and J.H. Enemark, *Inorg. Chem.*, 24 (1985) 1355.
- 6 E.g. (a) R.A. Fischer and W.A. Hermann, *J. Organomet. Chem.*, 330 (1987) 377; (b) D.E. Coons, J.C.V. Laurie, R.C. Haltiwanger, and M.R. DuBois, *J. Am. Chem. Soc.*, 109 (1987) 283; (c) M.W. Droegge and H. Taube, *Inorg. Chem.*, 26 (1987) 3316.
- 7 (a) M.P. Coughlin (Ed.), *Molybdenum and Molybdenum Containing Enzymes*; Pergamon, Oxford, 1980; (b) W. Lovenberg (Ed.), *Iron Sulfur Proteins*; Academic, New York, 1976.
- 8 S.C. Schuman and H. Shalit, *Catal. Rev.*, 4 (1970) 245.
- 9 S. Trofimenko, *J. Am. Chem. Soc.*, 88 (1966) 1842.
- 10 J.C. Smart and B.L. Dinsky, *J. Am. Chem. Soc.*, 102 (1980) 1009.
- 11 (a) K.-B. Shiu and M.D. Curtis, *Organometallics*, 2 (1983) 936; (b) M.D. Curtis, K.-B. Shiu, W.M. Butler, and J.C. Huffman, *J. Am. Chem. Soc.*, 108 (1986) 3335.
- 12 S. Trofimenko, *J. Am. Chem. Soc.*, 91 (1969) 588.
- 13 G.N. LaMar, W. DeW. Horrocks, Jr., and R.H. Holm, (Eds.) *NMR of Paramagnetic Molecules*, Academic, New York, 1973.