Inorganica Chimica Acta, 129 (1987) L45–L46

Syntheses and Characterization of the Electron-deficient Complex (TMPO)V(CO)$_3$

PETER JAITNER* and WOLFGANG HUBER

Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a, 6020 Innsbruck, Austria

(Received January 19, 1987)

Photolysis of the group VI hexacarbonyls (M = Mo, W) in the presence of the stable nitroxyl radical TMPO (2,2,6,6-tetramethylpiperidin-1-oxo) leads as we found to the highly oxidized hydroxylamido compounds (TMPO)$_2$MoO$_2$ [1] and (TMPO)$_5$W$_3$O$_5$ [2].

The hexacarbonyl V(CO)$_6$ is known to disproportionate in two ways on reaction with ligands. Calderazzo found it reacted with arenes to give [V(CO)$_4$arene$^+$][V(CO)$_6^-$], i.e. V$^+$V$^-$ [3], but in contrast Hieber found that most oxygen and nitrogen donors, including common organic solvents such as acetone, gave products of the type [VL$_x^{2+}$][V(CO)$_6^-$]$_2$, *i.e.* V^{2+}2V$^-$ [4].

In further developing our photoinduced syntheses of hydroxylamido organometallic compounds we investigated the reaction of the paramagnetic V(CO)$_6$ with the stable nitroxyl radical TMPO. We report herein the synthesis and characterization (IR, MS, CV and ^{51}V NMR) of (TMPO)V(CO)$_3$ an extremely air and moisture sensitive compound. The paramagnetic vanadium hexacarbonyl reacts spontaneously with TMPO by loss of CO forming in nearly quantitative yield (TMPO)V(CO)$_3$. The infrared spectrum exhibits three active carbonyl stretching modes characteristic for a facial V(CO)$_3$ group (2027s, 1935s, 1892s, (n-pentane)). Nearly equal intensities of the IR peaks indicate 90° angles between the CO ligands. In the mass spectra the expected molecular ion peak is observed ($M^+ = 291$). The fragmentation of the molecular ion peak occurs by successive loss of the CO ligands. The ^{51}V NMR spectrum of (TMPO)V(CO)$_3$ shows a singlet at $\delta = -430$ ppm (relative to VOCl$_3$) in n-hexane confirming a deshielded metal nucleus. A detailed comparison of metal NMR data (^{51}V, ^{55}Mn, ^{59}Co) of the related complexes (TMPO)Mn(CO)$_3$ [5], (TMPO)Co(CO)$_2$ [6] and (TMPO)V(CO)$_3$ is reported by us [7]. Cyclic voltammetry of (TMPO)V(CO)$_3$ reveals a non-reversible one electron oxidation at +570 mV in CH$_3$CN.

Very little is known about the electrochemistry of vanadium carbonyls and derivatives but comparable oxidation potentials for vanadium carbonyls were reported by Bond *et al.* [8]. In accordance with all spectroscopic data and our recently reported molecular structure of (TMPO)Mn(CO)$_3$ [5] we suggest a structure containing a penta-coordinated vanadium complex. The title compound can be described as a V(+1) centre and the anionic TMPO, comparable to the hydroxylamido ligand, acts as a four-electron donating system. Using this description (TMPO)Mn(CO)$_3$, (TMPO)Co(CO)$_2$ and (TMPO)V(CO)$_3$ are electronically unsaturated 16-electron (Mn, Co) and 14-electron complexes respectively, which explains their sensitivity and reactivity [9].

Experimental

219 mg V(CO)$_6$ (1.0 mmol) and 170 mg 2,2,6,6-tetramethylpiperidin-1-oxo (1.1 mmol) were stirred in 50 ml n-pentane at room temperature for 10 min. When CO evolution finished the solvent was removed under reduced pressure. Vacuum sublimation at 40 °C first gave unreacted TMPO (10^{-2} mm Hg, 40 °C), then sublimation of the residue at 10^{-2} mm Hg and 50 °C for some hours gave a crystalline product (melting point (m.p.): 59 °C: yield 90%). Because of the sensitivity of the probe no elemental analysis could be obtained.

IR: 2027s, 1935s, 1892s, n-pentane; Perkin-Elmer 180.

MS: Varian MAT CH 7, 70 eV, 50 °C.

^{51}V NMR: spectra were obtained on a Bruker SWL 3-100 wide-line instrument at 16.000 16 MHz as *ca.* 0.05 M n-hexane solutions contained in 14 mm diameter tubes. The solutions were prepared under Ar (300 K).

Tetrabutylammonium hexafluorophosphate (TBAH) was purified by double recrystallization from purified methanol and dried under vacuum with P$_2$O$_5$.

Electrochemical Instrumentation

All electrochemical measurements were performed with a potentiostate (Bank-Wenking LT-78), a function generator (Voltage Scan Generator VSG 72), a voltage integrator (Wenking EVI 80) and an *xy*-recorder (Hewlett Packard 7015 B). We utilized a three electrode system. This consisted of a Pt-ring working electrode (Ingold) a glassy carbon counter electrode (Metrohm) and a Ag/AgCl (3 M KCl, Metrohm) reference electrode.

---

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

Acknowledgement

Thanks are due to the Fonds zur Förderung der Wissenschaftlichen Forschung, Vienna, for generous financial support.

References

1 P. Jaitner, W. Huber, A. Gieren and H. Betz, *Z. Anorg. Allg. Chem., 538,* 53 (1986).

2 P. Jaitner and W. Huber, *Inorg. Chim. Acta, 111,* L11 (1986).

3 F. Calderazzo, *Inorg. Chem., 3,* 1207 (1964).

4 W. Hieber, E. Winter and E. Schubert, *Chem. Ber., 95,* 3070 (1962); W. Hieber, J. Peterhans and E. Winter, *Chem. Ber., 94,* 2572 (1961).

5 P. Jaitner, W. Huber, G. Huttner and O. Scheidsteger, *J. Organomet. Chem., 259,* C1 (1983).

6 P. Jaitner, W. Huber, A. Gieren and H. Betz, *J. Organomet. Chem., 311,* 379 (1986).

7 D. Rehder and P. Jaitner, *J. Organomet. Chem.*, 1987, in press.

8 A. M. Bond and R. Colton, *Inorg. Chem., 15,* 2036 (1976).

9 P. Jaitner and C. Rieker, unpublished results.