Inorganica Chimica Acta, *218* (1994) 195–197

Note

Synthesis and characterization of molybdenum and tungsten nitrite complexes of the type $[M(NO_2)_2(CO)_2(PPh_3)_2]$

Robert D. Feltham
Department of Chemistry, University of Arizona, Tucson, AZ 85721 (USA)

Edward Rajaseelan*
Department of Chemistry, Millersville University, PO Box 1002, Millersville, PA 17551-0302 (USA)

(Received October 4, 1993; revised December 13, 1993)

Abstract

The molybdenum and tungsten complexes $[MBr_2(CO)_2(PPh_3)_2]$ (M = Mo, W) react with $NaNO_2$ in methanol to form $[M(NO_2)_2(CO)_2(PPh_3)_2]$ (M = Mo (**1**); W (**2**)). The complexes were characterized by elemental analysis, ^{15}N labeling, IR and multinuclear NMR spectroscopy. The NO_2 ligands are chelating and are magnetically equivalent. The ^{31}P and ^{13}C NMR spectra of these complexes show that the two phosphine ligands and the two carbonyl ligands are magnetically equivalent.

Key words: Tungsten complexes; Molybdenum complexes; Nitrite complexes

Introduction

The synthesis of low valent transition metal nitrite complexes is of interest because of their potential to catalyze the oxidation of various substrates by dioxygen via oxygen atom transfer reactions [1–6] and NO_2^- transfer oxygen atoms to coordinated CO with the loss of CO_2 [7–10]. Nitrite complexes have also been proposed [11] as intermediates in the catalysis of the oxidation of carbon monoxide by nitric oxide by nitrosyl complexes in solution. This reaction, which is kinetically slow in the gas phase [12], yields carbon dioxide and nitrous oxide [2, 3, 13]. Although numerous molybdenum and tungsten compounds have been characterized, few molybdenum nitrite complexes are known and there appears to be no report of any nitrite complexes of tungsten. The synthesis and characterization of new NO_2 complexes of molybdenum and tungsten are described below.

Experimental

$[M(NO_2)_2(CO)_2(PPh_3)_2]$ (M = Mo, W) complexes were prepared from the reaction of $[MX_2(CO)_2(PPh_3)_2]$ (M = Mo, W; X = Cl, Br) with sodium nitrite in methanol freshly distilled from magnesium methoxide [14]. The starting materials were synthesized using previously published procedures [15, 16].

All reactions were carried out under an atmosphere of purified nitrogen using Schlenk techniques [17, 18]. The individual preparations are described below. ^{15}N labeled (99.5%) $NaNO_2$ was purchased from MSD Isotopes, Canada. Microanalyses were carried out by Huffman Laboratories, Inc., Golden, CO. IR spectra were obtained using a Perkin-Elmer model 983 spectrophotometer. ^{31}P, ^{13}C and ^{15}N spectra were obtained using a Bruker AM 250 spectrometer.

Preparation of $[Mo(NO_2)_2(CO)_2(PPh_3)_2]$

Dibromodicarbonylbis(triphenylphosphine)molybdenum, $[MoBr_2(CO)_2(PPh_3)_2]$ (0.17 g, 0.2 mmol), was mixed with sodium nitrite (0.055 g, 0.8 mmol) in 3.0 ml of methanol. The reaction mixture was stirred for 5 h. The resultant bright yellow solid was removed by filtration, washed twice with small portions of distilled water and methanol, followed by acetone, and dried under vacuum; yield 0.098 g (64%). *Anal.* Found: C, 59.33; H, 3.94; N, 3.44; O, 12.12. Calc. for $MoC_{38}H_{30}N_2O_6P_2$: C, 59.36; H, 3.94; N, 3.65; O, 12.48%. ν(CO): 1966(s) and 1893(vs) cm^{-1} in KBr disc.

Preparation of $[Mo(^{15}NO_2)_2(CO)_2(PPh_3)_2]$

0.075 g (0.1 mmol) of $[MoCl_2(CO)_2(PPh_3)_2]$ was mixed with 0.028 g (0.2 mmol) of $Na^{15}NO_2$ in 2.0 ml of methanol. The reaction mixture was stirred for 8 h. The bright yellow product was removed by filtration, washed with small portions of distilled water and methanol, followed by acetone, and dried under vacuum; yield 0.045 g (57%).

Preparation of $[W(NO_2)_2(CO)_2(PPh_3)_2]$

Dibromodicarbonylbis(triphenylphosphine)tungsten, $[WBr_2(CO)_2(PPh_3)_2]$ (0.092 g, 0.1 mmol) was mixed with 0.028 g (0.4 mmol) of sodium nitrite in 2.0 ml of methanol. The reaction mixture was stirred for 5 h. The yellow product was removed by filtration, washed

---

*Author to whom correspondence should be addressed.

0020-1693/94/$07.00
SSDI 0020-1693(94)03801-T

TABLE 1. IR frequencies (cm^{-1})[a] and NMR chemical shifts (ppm)[b] of the complexes

Complex	ν_{asym}(N–O)	ν_{sym}(N–O)	δ ONO	δ^c P (2 PPh_3)	δ^d ^{15}N (2 $^{15}NO_2$)	δ^e ^{13}C (2 CO)
$[Mo(NO_2)_2(CO)_2(PPh_3)_2]$	1284m	1221s	852w	62.85s		218.65t (^2J(PC) 29.5 Hz)
$[Mo(^{15}NO_2)_2(CO)_2(PPh_3)_2]$	1261m	1201s	846w		235.33si	
$[W(NO_2)_2(CO)_2(PPh_3)_2]$	1269m	1214m	849w	35.52s (J(^{183}WP) 150.5 Hz)		238.54
$[W(^{15}NO_2)_2(CO)_2(PPh_3)_2]$	1250m	1195m	843w		250.98si	

[a]KBr disc. [b]All NMR spectra were taken at −65 °C in 10% $CDCl_3/CH_2Cl_2$. [c]Reference 85% H_3PO_4. [d]Reference nitromethane. [e]Reference TMS. Key: s = strong, m = medium, w = weak, si = singlet, t = triplet.

twice with small portions of distilled water and methanol, followed by acetone, and dried under vacuum for 12 h; yield 0.054 g (63%).

Preparation of [W($^{15}NO_2$)$_2$(CO)$_2$(PPh_3)$_2$]

The preparation was carried out as described above using 0.092 g (0.1 mmol) of $[WBr_2(CO)_2(PPh_3)_2]$ and 0.014 g (0.2 mmol) of $Na^{15}NO_2$. The reaction mixture was stirred for 8 h; yield 0.048 g (56%). *Anal.* Found: C, 57.49; H, 3.80; N, 3.31. Calc. for $WC_{38}H_{30}N_2O_6P_2$: C, 57.55; H, 3.79; N, 3.52%. ν(CO): 1955(s) and 1876(vs) cm^{-1} in KBr disc.

Results and discussion

The nitrite complexes **1** and **2** are air sensitive, soluble in dichloromethane, acetonitrile and toluene. Solutions of these complexes are very unstable at room temperature. Attempted crystallization of these complexes at low temperatures failed to produce crystals, and consequently they were not characterized by X-ray crystallography.

The elemental analysis and the IR spectra confirm the presence of two carbonyl groups, two triphenylphosphine groups, and two nitrogen atoms per metal. Conductometric measurements (no conductance observed) show these compounds are not ionic. The IR spectra of the unlabeled and ^{15}N-labelled complexes show that only one set of frequencies is associated with the nitro groups (Table 1). These frequencies are characteristic of chelating NO_2 ligands which are bonded to the metal through two oxygen atoms [13, 19–22]. Based on these observations it was concluded that the complexes are eight-coordinate. This conclusion was further confirmed by the ^{15}N NMR spectra where only a single peak appeared in the chelating NO_2 region [23]. In the ^{15}N NMR, no satellites due to coupling to the ^{183}W nucleus nor ^2J(PN) coupling were observed for the tungsten complex, indicating that the NO_2 ligands are oxygen bound. The appearance of only one sharp ^{15}N singlet shows that both NO_2 groups are equivalent. The ^{13}C NMR spectrum of complex **1** consists of one triplet (relative intensity of 1:2:1) appearing in the carbonyl region (~218 ppm). Thus the two carbonyl ligands and the two phosphine ligands are magnetically equivalent. In the tungsten complex **2** no triplet ^{13}C peaks were observed in the carbonyl region because of a poor signal to noise ratio.

The ^{31}P NMR spectra of each complex consist of a singlet, confirming that the phosphine ligands are magnetically equivalent. In the tungsten complex, satellites due to coupling to the ^{183}W nucleus were observed. The coupling constant observed (150 Hz) is the lowest observed in this group of compounds. In six-coordinate tungsten(II) complexes the ^1J(^{183}WP) value is greater than 200 Hz [24–28] and in seven-coordinate complexes it is between 160 and 190 Hz [29]. The low value of 150 Hz in complex **2** is consistent with eight-coordination.

References

1 M.A. Andrews and K.P. Kelley, *J Am Chem Soc , 103* (1981) 2894.
2 R.D. Feltham and J.C. Kriege, *J. Am. Chem. Soc., 101* (1979) 5064.
3 J. Kriege-Simondesen, G Elbaze, M. Dartiquenave, R.D. Feltham and Y. Dartiquenave, *Inorg. Chem , 21* (1982) 230.
4 R. Ugo, S. Bhaduri, B.F.G Johnson, A. Khair and A. Pickard, *J Chem. Soc , Chem. Commun ,* (1976) 694.
5 O.A. Illeperuma and R D. Feltham, *J Am. Chem. Soc , 98* (1976) 6039.
6 B.S. Tovrog, S.E. Diamond and F Mares, *J. Am Chem. Soc , 101* (1979) 270.
7 W.L. Gladfelter, *Adv Organomet Chem., 24* (1985) 41.
8 D.R. Mantell and W.L. Gladfelter, *J. Organomet. Chem , 347* (1988) 333.
9 R.E. Stevens, D.E. Fjare and W.L. Gladfelter, *J. Organomet Chem , 347* (1988) 373.
10 M. Nakamoto, K. Tanaka and T. Tanaka, *Inorg Chim Acta, 132* (1987) 193.
11 R. Eisenberg and C.D. Meyer, *Acc Chem Res , 8* (1975) 26.
12 J.A. Connor and E. James, *J. Organomet Chem , 316* (1986) 79.

13 U. Thewalt and R.E. Marsh, *Inorg. Chem*, *9* (1970) 1604.

14 A.J. Gordon and R.A. Ford, *The Chemist's Companion, A Handbook of Practical Data, Techniques and References*, Wiley, New York, 1976.

15 R. Colton and I.B. Tomkins, *Aust. J. Chem.*, *19* (1966) 1591.

16 R. Colton and I.B. Tomkins, *Aust J. Chem.*, *19* (1966) 1143.

17 W.L. Jolly, *The Synthesis and Characterization of Inorganic Compounds*, Prentice Hall, Englewood Cliffs, NJ, 1970.

18 D.F. Shriver, *The Manipulation of Air Sensitive Compounds*, McGraw-Hill, New York, 1969.

19 K. Nakamoto, J. Fujita and H. Murata, *J Am Chem. Soc*, *80* (1958) 4817.

20 D.M.L. Goodgame and M.A. Hitchman, *Inorg. Chem*, *4* (1965) 721.

21 C.E. Strouse and B.J. Swanson, *Chem. Commun.*, (1971) 55.

22 L. El-Sayed and R.O. Ragsdale, *Inorg Chem.*, *9* (1967) 1644.

23 J. Mason, *Chem. Br*, (Aug) (1983) 654.

24 S.O. Grim, D.A. Wheatland and W. McFarlane, *J. Am Chem. Soc.*, *89* (1967) 5573.

25 S.O. Grim and J.D. Mitchell, *Inorg. Chem*, *16* (1977) 1770.

26 S.O. Grim, W.L. Briggs, R.C. Barth, C.A. Tolman and J.P. Jesson, *Inorg. Chem*, *13* (1974) 1095.

27 S.O. Grim and D.A. Wheatland, *Inorg. Chem.*, *8* (1969) 1716.

28 T.A. George and C.D. Sterner, *Inorg. Chem.*, *15* (1976) 165.

29 B.J. Brisdon, *J Organomet Chem*, *125* (1977) 225.