Journal of Organometallic Chemistry, 66 (1974) 95—101

SULFUR DIOXIDE INSERTION

XIX*. SO_2 INSERTION AND CYCLOADDITION REACTIONS OF SOME h^5-$C_5H_5W(CO)_3R$ COMPLEXES

JAMES O. KROLL** and ANDREW WOJCICKI
The McPherson Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

(Received June 18th, 1973)

Summary

Reaction of h^5-$C_5H_5W(CO)_3R$ ($R = CH_3$, C_2H_5, and $CH_2C_6H_5$) with neat sulfur dioxide at 50 - 55° for 72 h affords the corresponding *S*-sulfinates, h^5-$C_5H_5W(CO)_3S(O)_2R$, as isolable, stable solids. In contrast, reaction between h^5-$C_5H_5W(CO)_3CH_2C{\equiv}CR$ ($R = CH_3$ and C_6H_5) and sulfur dioxide proceeds very readily at 25° in pentane or hexane to yield the cycloaddition products h^5-$C_5H_5W(CO)_3\overline{C{=}C(R)S(O)OC}H_2$. These sultine-ring complexes undergo desulfination to h^5-$C_5H_5W(CO)_3CH_2C{\equiv}CR$ upon contact with alumina.

Introduction

Insertion reactions into the tungsten—carbon bond of h^5-$C_5H_5W(CO)_3R$ are not common. They are limited to two examples of carbon monoxide insertion [1], and at least one of these requires rather forcing experimental conditions [2].

It has been noted earlier in this laboratory [3] that the tungsten complexes h^5-$C_5H_5W(CO)_3R$ ($R = CH_3$ and $CH_2C_6H_5$) are virtually unreactive toward neat SO_2 at reflux. A trace amount of what appears to be h^5-$C_5H_5W(CO)_3S(O)_2CH_3$ was isolated after a 6 h treatment of h^5-$C_5H_5W(CO)_3CH_3$ with SO_2, but complete characterization of this material was not possible. By contrast, the analogous molybdenum alkyls, h^5-$C_5H_5Mo(CO)_3R$ ($R = CH_3$ and $CH_2C_6H_5$), react quite readily with neat SO_2 at reflux, or even at lower temperatures. In order to obtain a better comparison of the reactivities toward SO_2 of h^5-$C_5H_5W(CO)_3R$ and h^5-$C_5H_5Mo(CO)_3R$ we have examined the insertion in the tungsten complexes under more forcing experimental conditions. Reported herein are our results. Also reported in this paper are reactions of

---

* For Part XVIII see ref. 11.

** Based on MSc thesis, The Ohio State University, 1971.

SO_2 with the analogous tungsten 2-alkynyl complexes which yield tungsten vinyl derivatives containing a sultine ring.

Experimental

General procedures

A nitrogen atmosphere was employed routinely in running all reactions, during work-up, and in making physical measurements on solutions. Ventron alumina used in chromatographic separations and purifications was deactivated with H_2O (6 - 10%). Elemental analyses were performed by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany, and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical measurements

Infrared spectra were recorded on a Perkin- Elmer Model 337 spectrophotometer. Hydrogen-1 NMR spectra were obtained on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Melting points were taken on a Thomas—Hoover capillary melting point apparatus and are uncorrected.

Materials

Anhydrous grade SO_2, from Matheson, was passed through concentrated H_2SO_4 and a column of $CaCl_2/P_4O_{10}$ before condensation. Tungsten hexacarbonyl was purchased from Pressure Chemical Co. and was sublimed in vacuum before use. 1-Bromo-2-butyne was prepared from 2-butyne-1-ol (from Farchan Research Laboratories, Willoughby, Ohio) as described in the literature [4]. 1-Phenyl-3-bromo-1-propyne was synthesized analogously from the corresponding alcohol (also from Farchan). Tetrahydrofuran was distilled from CaH_2 under a nitrogen atmosphere immediately before use. All other solvents and chemicals were reagent grade or equivalent and were used as received.

Tungsten alkyls and 2-alkynyls

Literature procedures were employed to synthesize h^5-$C_5H_5W(CO)_3CH_3$ [5], h^5-$C_5H_5W(CO)_3C_2H_5$ [5], and h^5-$C_5H_5W(CO)_3CH_2C_6H_5$ [3]. The 2-alkynyl h^5-$C_5H_5W(CO)_3CH_2C{\equiv}CCH_3$ (reported earlier [6] but with few experimental details) was prepared as follows.

To a 1,2-dimethoxyethane solution (ca 200 ml) of Na[h^5-$C_5H_5W(CO)_3$], prepared from 1.4 ml (17 mmol) of freshly cracked C_5H_6, 5.9 g (17 mmol) of $W(CO)_6$ and 0.39 g (17 mmol) of sodium [7], was added dropwise 4.5 g (34 mmol) of 1-bromo-2-butyne while the mixture was maintained at reflux. The reaction was followed by thin layer chromatography and reached completion in 2 h. Solvent was then removed on a rotary evaporator, the resulting amber-colored oil was extracted with several 25 ml portions of hexane, and the combined extract was filtered through Zeolite. The volume of the extract was reduced to ca. 10 ml and the resultant solution was chromatographed on alumina eluting with pentane. The yellow band which had developed was collected under nitrogen and the solvent was removed to give 2.9 g (45%) of light yellow crystals, m.p. 72.5°. Infrared spectrum: ν(CO) at 2020 s, 1940 s, 1930 s cm^{-1} (pentane soln.). ^{1}H NMR spectrum: τ8.15(m, br, CH_3), 7.70(m, br, CH_2), 4.53 ppm (s, C_5H_5)($CDCl_3$ soln.).

The complex h^5-$C_5H_5W(CO)_3CH_2C{\equiv}CC_6H_5$ [6] was obtained analogously from Na[h^5-$C_5H_5W(CO)_3$] and $C_6H_5C{\equiv}CCH_2Br$ (reaction time 1 h). Yield 50%, m.p. (dec) 69°. Infrared spectrum: ν(CO) at 2025 s, 1940 s, 1930 s cm^{-1} (pentane soln.). ^{1}H NMR spectrum: τ 7.78 (s, CH_2), 4.50 (s, C_5H_5), 2.68 ppm (s, C_6H_5)($CDCl_3$ soln.).

Preparation of h^5-$C_5H_5W(CO)_3S(O)_2R$

A 75 ml stainless steel reaction vessel (Model HDF4-75-304 equipped with a 16 DKM4-F4-A314 valve, from Whitey Research Tool Co., Emeryville, Calif.) at −78° was charged with 1.9 g (5.5 mmol) of h^5-$C_5H_5W(CO)_3CH_3$ and 20 ml of liquid SO_2. The vessel was closed tightly and then placed in an oil bath at 50 - 55°. After 72 h, excess SO_2 was removed and the residue was washed five times with 15 ml portions of hexane. The washings were combined and filtered through Zeolite; light yellow crystals of unreacted h^5-$C_5H_5W(CO)_3CH_3$ (0.31 g, 16% recovery) separated during removal of the hexane on a rotary evaporator.

The residue in the reaction vessel was next treated with five 15 ml portions of chloroform and the combined extract was filtered. To the resulting solution was added an equal volume of hexane; concentration to 10 ml on a rotary evaporator afforded 0.22 g (10%) of yellow crystals of h^5-$C_5H_5W(CO)_3S(O)_2CH_3$.

When the above reaction was conducted at 35° for ca. 24 h, the *S*-sulfinate was obtained in 1 - 2% yield. Approximately 80% tungsten alkyl was recovered.

In a similar fashion, h^5-$C_5H_5W(CO)_3S(O)_2C_2H_5$ and h^5-$C_5H_5W(CO)_3S(O)_2CH_2C_6H_5$ were obtained by reaction of h^5-$C_5H_5W(CO)_3C_2H_5$ and h^5-$C_5H_5W(CO)_3CH_2C_6H_5$, respectively, with sulfur dioxide at 50 - 55°, also for 72 h. The yields, analytical data, and physical properties of these tungsten *S*-sulfinato complexes are listed in Table 1.

Preparation of h^5-$C_5H_5W(CO)_3\overline{C{=}C(R)S(O)OCH_2}$

Gaseous SO_2 was passed into a solution of h^5-$C_5H_5W(CO)_3CH_2C{\equiv}CCH_3$ (2.25 g, 5.8 mmol) in 150 ml of hexane at 25°. Immediate formation of a yellow precipitate was noted, and the reaction appeared to reach completion within 30 min. The precipitate was collected by filtration and dissolved in chloroform. The resultant solution was filtered through Zeolite, treated with an equal volume of hexane, and then concentrated on a rotary evaporator to afford yellow crystalline h^5-$C_5H_5W(CO)_3\overline{C{=}C(CH_3)S(O)OCH_2}$ (1.80 g, 69%).

h^5-$C_5H_5W(CO)_3\overline{C{=}C(C_6H_5)S(O)OCH_2}$ was obtained in an analogous manner from h^5-$C_5H_5W(CO)_3CH_2C{\equiv}CC_6H_5$ and SO_2 in pentane. The yields, analytical data, and physical properties of these tungsten vinyl complexes containing a sultine ring are given in Table 1.

Results and discussion

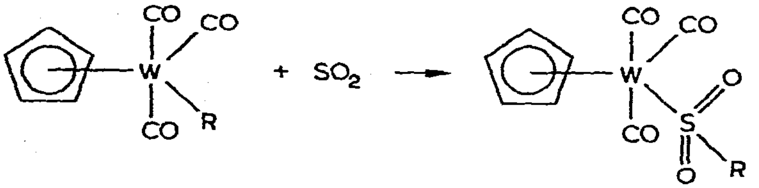
Treatment of the tungsten alkyls h^5-$C_5H_5W(CO)_3R$ (R = CH_3, C_2H_5, and

TABLE 1

YIELDS, ANALYTICAL DATA, AND PHYSICAL PROPERTIES OF $h^5\text{-}C_5H_5W(CO)_3S(O)_2R$ AND $h^5\text{-}C_5H_5W(CO)_3\overline{C{=}C(R)S(O)OC}H_2$

Compound	Yield (%)	Analysis found (calcd.)(%)		M.p. (dec) (°C)	Color
		C	H		
$h^5\text{-}C_5H_5W(CO)_3S(O)_2CH_3$	10	26.18 (26.30)	1.92 (1.96)	176 - 179	Yellow
$h^5\text{-}C_5H_5W(CO)_3S(O)_2C_2H_5$	27	28.21 (28.25)	2.38 (2.37)	167	Golden-brown
$h^5\text{-}C_5H_5W(CO)_3S(O)_2CH_2C_6H_5$	25	37.24 (36.98)	2.39 (2.48)	167	Orange
$h^5\text{-}C_5H_5W(CO)_3\overline{C{=}C(CH_3)S(O)OC}H_2$	69	32.64 (32.09)	2.39 (2.24)	139 - 143	Yellow
$h^5\text{-}C_5H_5W(CO)_3\overline{C{=}C(C_6H_5)S(O)OC}H_2$	50	39.14 (39.94)	2.27 (2.37)	124 - 126	Light yellow

$CH_2C_6H_5$) with neat SO_2 at 50 - 55° for 72 h leads to the isolation of the appropriate *S*-sulfinates [eqn. (1), (I)] as yellow to orange crystalline solids.

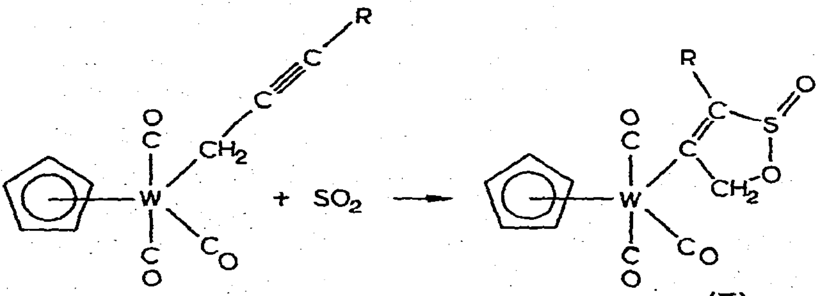


(I)

(1)

The yields are relatively low — from 10 to 27% — and some unreacted alkyl (16 to 30%) may be recovered. These *S*-sulfinates exhibit high thermal and oxidative stability. They melt with decomposition at 167 - 179°, and their solutions in organic solvents show no signs of deterioration over a period of 1 - 2 days.

In contrast to the above insertion, reaction between the tungsten 2-alkynyls $h^5\text{-}C_5H_5W(CO)_3CH_2C{\equiv}CR$ ($R = CH_3$ and C_6H_5) and SO_2 proceeds readily at room temperature in pentane or hexane and is complete within 30 min [eqn. (2)]. The resultant tungsten vinyl complexes with a sultine ring



(II)

(2)

(II) are also thermally and oxidatively stable. They melt with decomposition at 124 - 143° and are not affected by air at room temperature. However, chromatography on alumina results in loss of SO_2 and formation of the parent 2-alkynyl complex. Such desulfination on chromatography has been noted earlier for h^5-$C_5H_5Fe(CO)_2\overline{C{=}C(CH_3)S(O)OC}H_2$ [8].

The new *S*-sulfinato and sultine-ring complexes have been characterized with the aid of infrared and ^1H NMR spectroscopy. Their spectra are summarized in Table 2.

The CO stretching frequencies of the *S*-sulfinates are 25 - 40 cm^{-1} higher than those of the parent alkyl complexes [3,5]. The magnitude of this shift is comparable to that observed for the corresponding complexes of h^5-$C_5H_5Mo(CO)_3$ [3,5], but somewhat lower than that for the complexes of h^5-$C_5H_5Fe(CO)_2$ [9]. For the sultine-ring complexes, the CO stretching frequencies are not more than 15 cm^{-1} higher than those of their 2-alkynyl precursors. Similar changes in $\nu(CO)$ have been reported earlier for analogous complexes of molybdenum and iron [8].

The values of $\nu(SO)$ for the tungsten *S*-sulfinato products fall in the ranges 1190 - 1171 and 1051 - 1038 cm^{-1}. They are virtually identical with the corresponding absorptions for other transition metal *S*-sulfinato carbonyl complexes [10] and thus provide strong support for the proposed structure of the W—SO_2R moiety. The sulfur—oxygen stretching modes for the sultine-ring complexes also absorb at frequencies which are very similar to those for previously reported analogous compounds [8].

The ^1H NMR spectra of the SO_2-containing complexes of tungsten reveal striking similarities with those of their molybdenum counterparts [5,8]. A salient feature in the spectra of the sultine-ring compounds is the magnetic nonequivalence of the CH_2 protons. The internal chemical shift (τ0.33 - 0.54 ppm) and the geminal coupling constant (14 Hz) of the methylene protons are essentially identical with the reported values for similar compounds [8]. Thus they lend strong support to the assigned structure.

It is of interest to compare and contrast the relative reactivities toward SO_2 of the alkyl and 2-alkynyl complexes of tungsten with those of molybdenum. The insertion of SO_2 into a transition metal—carbon bond is thought to proceed by electrophilic attack of SO_2 on the α-carbon of R [11,12]. Since M=CO π-bonding appears to be more extensive for tungsten than for molybdenum [13], the electrons at the α-carbon in h^5-$C_5H_5W(CO)_3R$ should experience a greater attraction by the metal than those in the corresponding h^5-$C_5H_5Mo(CO)_3R$. This is expected to lead to a stronger M—R bond with tungsten than with molybdenum. Moreover, the reduced electron density on the α-carbon in h^5-$C_5H_5W(CO)_3R$ compared to h^5-$C_5H_5Mo(CO)_3R$ should render it less susceptible to electrophilic attack by SO_2. As a consequence, the W—R bond would be more inert to the insertion than the Mo—R bond, in agreement with the observation.

The formation of metal vinyl complexes containing a sultine ring from the appropriate metal 2-alkynyls and SO_2 is thought to proceed via initial electrophilic attack of SO_2 on the carbon≡carbon triple bond [14]. Since the site of attack by SO_2 is now considerably removed from the metal, the dependence of the rate on the nature of the metal might be expected to be less pronounced than in the insertion. This is borne out by the observation that the h^5-$C_5H_5W(CO)_3CH_2C{\equiv}CR$ complexes react at the rates which, qualitatively, are not

TABLE 2

INFRARED AND ^{1}H NMR SPECTRA OF h^5-$C_5H_5W(CO)_3S(O)_2R$ AND h^5-$C_5H_5W(CO)_3\overline{C{=}C(R)S(O)OC}H_2$

Compound	Infrared (cm^{-1})^a		^{1}H NMR (τ)^d	
	ν(CO)^b	ν(SO)^c	C_5H_5	Other protons
h^5-$C_5H_5W(CO)_3S(O)_2CH_3$	2050s, 1960vs(br)	1183s, 1050s	4.05s	6.73s (CH_3)
h^5-$C_5H_5W(CO)_3S(O)_2C_2H_5$	2048s, 1960vs(br)	1179s, 1050s	4.03s	8.76t, J 7 Hz (CH_3); 6.76q, J 7 Hz (CH_2)
h^5-$C_5H_5W(CO)_3S(O)_2CH_2C_2H_5$	2053s, 1975s, 1955s	1201s, 1051s	4.25s	5.63s (CH_2); 2.58s (C_6H_5)
h^5-$C_5H_5W(CO)_3\overline{C{=}C(CH_3)S(O)OC}H_2$	2035s, 1955s, 1930s	1118s, 908s	4.27s	7.88t, J 2Hz (CH_3); 4.93, 4.60 AB part of ABX_3, J_{AX}, J_{BX} 2Hz, J_{AB} 14Hz (CH_2)
h^5-$C_5H_5W(CO)_3\overline{C{=}C(C_6H_5)S(O)OC}H_2$	2035s, 1955s, 1935s	1115s, 890s	4.67s	4.77, 4.23 AB, J_{AB} 14Hz (CH_2); 2.50s (C_6H_5)

[a] Abbreviations: vs, very strong; s, strong; br, broad. [b] $CHCl_3$ soln. [c] Nujol mull. [d] $CDCl_3$ soln. Abbreviations: s, singlet, t, triplet; q, quartet; AB, AB pattern.

noticeably different from those of the h^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CR$ and h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ complexes [8]. However, we expect that a more quantitative study will reveal some dependence of the rate of these cycloaddition reactions on the nature of the metal; such an investigation is planned in our laboratory.

Acknowledgement

We thank the National Science Foundation for support.

References

1 A. Wojcicki, Advan. Organometal. Chem., 11 (1973) 87.
2 T. Kruck, M. Höfler and L. Liebig, Chem. Ber., 105 (1972) 1174.
3 M. Graziani, J.P. Bibler, R.M. Montesano and A. Wojcicki, J. Organometal. Chem., 16 (1969) 507.
4 P.J. Ashworth, G.H. Whitman and M.E. Whiting, J. Chem. Soc., (1957) 4633.
5 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.
6 J.-L. Roustan and C. Charrier, C.R. Acad. Sc. Paris, Ser. C, 268 (1969) 2113.
7 R.B. King and M.B. Bisnette, J. Organometal. Chem., 2 (1964) 15.
8 J.E. Thomasson, P.W. Robinson, D.A. Ross and A. Wojcicki, Inorg. Chem., 10 (1971) 2130.
9 J.P. Bibler and A. Wojcicki, J. Amer. Chem. Soc., 88 (1966) 4862.
10 A. Wojcicki, Accounts Chem. Res., 4 (1971) 344.
11 S.E. Jacobson and A. Wojcicki, J. Amer. Chem. Soc., 95 (1973) 6962.
12 G.M. Whitesides and D.J. Boschetto, J. Amer. Chem. Soc., 93 (1971) 1529.
13 R.B. King, Inorg. Nucl. Chem. Lett., 5 (1969) 905.
14 Y. Yamamoto and A. Wojcicki, Inorg. Chem., 12 (1973) 1779.