A Heterobimetallic μ-SO$_2$ Complex

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Introduction

The reactions of sulfur dioxide with transition metal complexes continue to elicit attention. In addition to the inherent interest of SO$_2$ complexes and the reactions of SO$_2$ with transition metal compounds, there are more practical reasons to study SO$_2$ chemistry. Environmental consequences of SO$_2$ production from the combustion of sulfur rich fuels has led to the implementation of various catalytic methods to remove sulfur from petroleum products. This important industrial process has stimulated studies in SO$_2$ transition metal chemistry.[1]

Sulfur dioxide has many coordination modes,[2,3] and a large variety of structural motifs are found in transition metal SO$_2$ complexes. The ligand most commonly bridges the two metals in dinuclear metal species via the sulfur atom.[4−7] This coordination mode is similar to that adopted by the isolobal methylene group in μ-CH$_2$ species, and there are some closely related complexes with M(μ-X)M (X = CH$_2$ or SO$_2$) core linkages, in which either CH$_2$ or SO$_2$ groups span both metal centers.[6,8] A handful of examples of alternative bridging modes of the SO$_2$ ligand have been demonstrated.[9−11]

Most SO$_2$ bridged bimetallic complexes are homonuclear, but examples are known in which heterodinuclear complexes are bridged by SO$_2$ ligands. Among these are the species [Mo(CO)$_2$(μ-CO)(μ-SO$_2$)(μ-dppm)$_2$RhCl] (Mo−Rh),[12] [Co(CO)Cp*(μ-SO$_2$)Rh(CO)Cp*] (Co-Rh),[13] and Pd(C$_6$F$_5$)(μ-SO$_2$)(μ-dppm)$_2$PtX (X = Cl, C$_6$F$_5$).[14] The latter complex contains no Pd−Pt bond. A series of μ-dppm-bridged μ-SO$_2$ complexes have been reported recently. These include species such as [Rh(CO)(μ-SO$_2$)(μ-dppm)$_2$Mn(CO)$_3$] (Mn−Rh) and [Mo(CO)$_2$(μ-CO)(μ-SO$_2$)(μ-dppm)$_2$RhCN] (Mo−Rh) and others, none of which contain metal−metal bonds.[15−17] The structure of [Mo(CO)$_2$(μ-CO)(μ-SO$_2$)(μ-dppm)$_2$RhCl] (Mo−Rh) was determined by an X-ray diffraction study.[18]

We recently reported the synthesis and structure of [NiCp*(μ-CO)(μ-CH$_2$)W(CO)$_2$Cp] (Ni−W).[19,20] In view of the close relationship between μ-SO$_2$ and μ-CH$_2$ species and the comparative lack of structural data on heterobimetallic μ-SO$_2$ complexes, we describe the preparation of the mixed-metal SO$_2$-bridged complex [NiCp*(μ-SO$_2$)(μ-CO)W(CO)$_2$Cp$'$] (Ni−W, **2**), elucidate its structure, and compare it with that of the [NiCp*(μ-CH$_2$)(μ-CO)W(CO)$_2$Cp] (Ni−W, **4**).

Results and Discussion

(a) Isolation and Spectroscopic Characterization of 2. The pyrophoric heterobimetallic complex [NiCp*W(CO)$_3$Cp] (Ni−W) can be considered to contain a Ni−W double bond and, accordingly, behaves as a coordinatively unsaturated species.[19] A wide assortment of group 14 and group 15 two-electron donor ligands add to this compound to afford the coordinatively saturated complexes [NiCp*(μ-CO)$_2$W(CO)LCp] (Ni−W; L = PMe$_3$, PMe$_2$Ph, CO) or [NiCp*(μ-L)(μ-CO)W(CO)$_2$Cp] (Ni−W; L = Bu^{t}NC, CH$_2$).[20] More recently, we have focused our studies on the chemistry of the closely related methylcyclopentadienyl derivative [NiCp*W(CO)$_3$Cp$'$] (Ni−W, **1**), which is significantly more soluble than [NiCp*W(CO)$_3$Cp] (Ni−W). Here we discuss some chemistry of **1** with the group 16 donor ligands H$_2$O and SO$_2$.

Surprisingly in view of its high reactivity, compound **1**, like its Cp congener, is inert toward water. No reaction ensues when an excess of O$_2$-free water is added to deep blue thf solutions of **1**. However, cold solutions of **1** react instantaneously with SO$_2$ to afford orange brown solutions, which deposited an orange solid that contained **2**. Orange crystals were subsequently harvested. These crystals appeared to be homogeneous as they adopted the same habit and morphology and had similar dimensions.

Spectroscopic examination of solutions of these crystals indicated that two species were present. The crystals contained a new compound **2** and, in addition, the well-known ditungsten complex [W$_2$(CO)$_6$Cp$'_2$] (W−W), **3**, which was identified by its ^{1}H NMR and IR spectra by comparison with reference samples. Furthermore, addition of a genuine sample of **3** led to an increase in intensity of those resonances attributed to **3** in NMR spectra of the orange crystals.

Large crystals of **2** could never be obtained free of **3**. However, analytically pure samples of **2** were isolated as a microcrystalline powder. The spectroscopic data of this powder were consistent with **2** being the complex [NiCp*(μ-CO)(μ-SO$_2$)W(CO)$_2$Cp$'$]. MS data for **3** did not show a parent ion, but ions corresponding to $[M - SO_2]^+$ and $[M - CO]^+$ were observed. Other μ-SO$_2$ complexes have been reported to exhibit weak or absent parent ions, indicating that loss of SO$_2$ or other ligands is facile.[18]

The NMR data for **2** indicate that an effective mirror plane exists in the molecule, as is observed for the related methylene species [NiCp*(μ-CH$_2$)(μ-CO)W(CO)$_2$Cp] (Ni−W, **4**). Presumably, a similar bridge−terminal exchange process in **2** between mutually trans CO ligands generates this effective

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(1) Shaver, A.; Plouffe, P.-Y. *Inorg. Chem.* **1992**, *31*, 1823.

(2) Schenk, W. A. *Angew. Chem.* **1987**, *99*, 101.

(3) Schenk, W. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 98.

(4) Herrmann, W. A.; Huggins, J. M.; Bauer, C.; Pfisterer, H.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *226*, C59.

(5) Herrmann, W. A.; Bauer, C.; Weichmann, J. *J. Organomet. Chem.* **1983**, *243*, C21−C26.

(6) Herrmann, W. A.; Bauer, C.; Weichmann, J. *Chem. Ber.* **1984**, *117*, 875.

(7) Schrier, P. W.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 3929−3933.

(8) Herrmann, W. A.; Bauer, C.; Schäfer, A. *J. Organomet. Chem.* **1983**, *256*, 147−168.

(9) Briant, C. E.; Theobald, B. R. C.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1981**, 963.

(10) Briant, C. E.; Hughes, G. R.; Minshall, P. C.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *224*, C21.

(11) Jarvinen, G. D.; Kubas, G. J.; Ryan, R. R. *J. Chem. Soc., Chem. Commun.* **1981**, 305.

(12) Schenk, W. A. *Z. Naturforsch.* **1986**, *41B*, 663.

(13) Hörlein, R.; Herrmann, W. A.; Barnes, C. E.; Weber, C. E.; Krüger, C.; Ziegler, M. L.; Zahn, T. *J. Organomet. Chem.* **1987**, *321*, 257−272.

(14) Forniés, J.; Martinez, F.; Navarro, R.; Redondo, A.; Tomás, M.; Welch, A. J. *J. Organomet. Chem.* **1986**, *316*, 351−366.

(15) Schenk, W. A.; Hilpert, G. H. J. *Chem. Ber.* **1989**, *122*, 1623−1627.

(16) Schenk, W. A.; Hilpert, G. H. J. *Chem. Ber.* **1991**, *124*, 433−439.

(17) Heyke, O.; Beuter, G.; Lorenz, I.-P. *Z. Naturforsch.* **1992**, *47B*, 668−674.

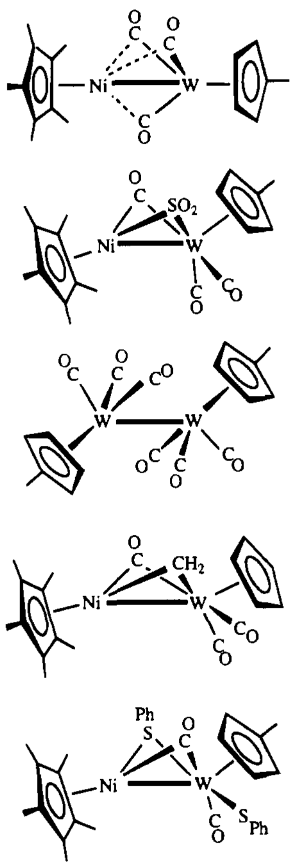
(18) Heyke, O.; Hiller, W.; Lorenz, I.-P. *Chem. Ber.* **1991**, *124*, 2217−2222.

(19) Chetcuti, M. J.; Grant, P. E.; Fanwick, P. E. *Organometallics* **1990**, *9*, 1345−1347.

(20) Chetcuti, M. J.; Deck, K. J.; Fanwick, P. E.; Gordon, J. C.; Grant, B. E. *Organometallics* **1992**, *11*, 2128−2139.

0020-1669/95/1334-0980$09.00/0

Chart 1



NiCp*WCp'(CO)$_3$, **1**

NiCp*(μ-SO$_2$)(μ-CO)W(CO)$_2$Cp', **2**

W$_2$(CO)$_6$Cp'$_2$, **3**

NiCp*(μ-CH$_2$)(μ-CO)W(CO)$_2$Cp, **4**

NiCp*(μ-SPh)(μ-CO)W(SPh)(CO)Cp', **5**

mirror plane on the NMR time scale. The ^{1}H and ^{13}C NMR data for **2** are otherwise unremarkable.

The solution IR of **2** exhibited three ν(CO) bands: one of these, observed at 1794 cm^{-1}, indicated that a bridging CO ligand was present. Solid mull absorption bands seen at 1184 and 1032 cm^{-1} can be attributed to ν(SO) stretches. The positions of absorptions and the wavenumber difference between the two stretches has been used to assign which bonding mode the SO$_2$ ligand adopts.[21] The observed IR stretching frequencies for **2** are consistent with those expected for a μ-SO$_2$ ligand that bridges the two metals. They also fall in the range of ν(SO) stretches (1188–1147 and 1070–1024 cm^{-1}, respectively, for the two sets of ν(SO) stretches) that were observed for a variety of μ-SO$_2$ heterobimetallic complexes.[15,16,18] (All these latter species are also bridged by μ-dppm or related bidentate ligands.)

(b) X-ray Structural Analysis of 2. The data obtained for **2** were compatible with the structure shown in Chart 1 for **2** but did not necessarily establish this structure. Accordingly, crystals of **2** suitable for a single crystal X-ray diffraction study were obtained. As referred to earlier, spectroscopic data indicated that these crystals should be formulated as **2**·$^1/_2$**3**. Crystals in which there are two different neutral organometallic complexes are not common but are certainly not unprecedented.[22] Data collection parameters, key atom positional parameters, key bond lengths, and key bond angles (of **2**) are collected in Tables 1–3. More detailed structural data tables for both **2** and **3** are collected in the supplementary information tables.

Table 1. Crystallographic Data and Data Collection Parameters for 2[NiCp*(μ-SO$_2$)(μ-CO)W(CO)$_2$Cp]·[W$_2$(CO)$_6$Cp'$_2$] (**2**·$^1/_2$**3**)

formula	C$_{56}$H$_{58}$Ni$_2$O$_{16}$S$_2$W$_4$	*c*	24.490(5) Å
monoclinic, space group	*P*2$_1$/*n*	*b*	90.88(1)°
fw	1904.03	*Z*	2
a	9.811(2) Å	*R*(*F*)^a	0.024
b	12.165(1) Å	*R*$_w$(*F*)^b	0.030

^{a} $R = \sum|F_o - F_c|/\sum F_o$. ^{b} $R_w = [\sum w(|F_o - F_c|)^2/\sum wF_o^2]^{1/2}$.

Table 2. Positional and Equivalent Isotropic Thermal Parameters^a for Key Atoms of Complex **2** in [2NiCp*(μ-SO$_2$)(μ-CO)W(CO)$_2$Cp']·[W$_2$(CO)$_6$Cp'$_2$] (**2**·$^1/_2$**3**) with Esd's in Parentheses

atom	*x*	*y*	*z*	B_{eq} (Å^2)
W(1)	0.74327(2)	0.02495(1)	0.81286(1)	2.201(4)
Ni	0.98980(6)	−0.00622(5)	0.85598(2)	2.29(1)
S	0.8457(1)	−0.1344(1)	0.85816(5)	2.68(2)
O(1)	0.8769(4)	−0.2320(3)	0.8260(2)	3.76(8)
O(2)	0.7959(4)	−0.1591(3)	0.9130(2)	4.05(8)
C(1)	0.5453(6)	0.0279(5)	0.8654(2)	4.0(1)
C(2)	0.5522(6)	0.1246(4)	0.8324(3)	4.3(1)
C(3)	0.5449(6)	0.0955(5)	0.7769(3)	4.3(1)
C(4)	0.5345(6)	−0.0176(5)	0.7742(2)	4.1(1)
C(5)	0.5344(5)	−0.0605(5)	0.8275(2)	3.7(1)
C(6)	0.5379(7)	0.0201(7)	0.9251(3)	5.8(2)
C(7)	0.8482(5)	0.0854(4)	0.8824(2)	3.0(1)
O(7)	0.8422(4)	0.1462(3)	0.9198(2)	4.49(9)
C(8)	0.8354(6)	−0.0497(4)	0.7495(2)	3.5(1)
O(8)	0.8838(4)	−0.0923(4)	0.7132(2)	4.9(1)
C(9)	0.8356(5)	0.1593(5)	0.7828(2)	3.3(1)
O(9)	0.8837(4)	0.2366(3)	0.7667(2)	4.74(9)
C(10)	1.1596(5)	0.0443(5)	0.9016(2)	3.5(1)
C(11)	1.1648(5)	−0.0695(5)	0.8911(2)	3.5(1)
C(12)	1.1751(5)	−0.0831(5)	0.8334(2)	3.4(1)
C(13)	1.1764(5)	0.0204(5)	0.8091(2)	3.1(1)
C(14)	1.1615(5)	0.0993(4)	0.8513(2)	3.4(1)
C(15)	1.1574(7)	0.0997(7)	0.9565(3)	6.1(2)
C(16)	1.1683(7)	−0.1606(6)	0.9327(3)	6.2(2)
C(17)	1.1928(7)	−0.1919(6)	0.8044(3)	5.6(2)
C(18)	1.1852(7)	0.0449(6)	0.7492(3)	5.2(2)
C(19)	1.1636(7)	0.2229(5)	0.8441(3)	6.0(2)

^{a} *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter B_{eq} defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Complex **2**, NiCp*(μ-SO$_2$)(μ-CO)W(CO)$_2$Cp' (Ni–W), adopts the structure shown in Chart 1, as indicated by the ORTEP diagram (Figure 1). The SO$_2$ ligand bridges the two metals via its sulfur atom, which is in a distorted tetrahedral environment. The core of this structure is similar to the structures adopted by the methylene complex NiCp*(μ-CH$_2$)(μ-CO)W(CO)$_2$-Cp (**4**, Ni–W) and by the benzenethiolate-bridged complex NiCp*(μ-SPh)(μ-CO)W(SPh)(CO)Cp' (**5**, Ni–W).[20,23] The structure of **2** merits close comparison with these related compounds. A short list of related geometrical parameters are collected in Table 4. All three species contain butterfly-type NiWCS or NiWC$_2$ cores, with a carbon atom and the other carbon or sulfur atom located in the wing tip positions. The Ni–W distance is 2.6523(6) Å, indicative of a Ni–W single bond.[24]

The interplanar angle between the NiWS and NiWC planes is 109.1°, almost identical to the interplanar core NiWC$_2$ angle of 108.7° found in **4**. The two dienyl ligands in each of these three species are in a *trans* configuration. The S–O distances of 1.458(4) and 1.468(4) Å are in the range observed for the S–O bonds in the complex [Mo(CO)$_2$(μ-CO)(μ-SO$_2$)(μ-dppm)$_2$-RhCl] (Mo–Rh)[18] and are very similar to S–O distances found

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(21) Borec, H.; Dixneuf, P.; Carty, A. J.; Lang, A. K. *Inorg. Chem.* **1978**, *17*, 2568.

(22) Batchelor, R. J.; Davis, H. B.; Einstein, F. W. B.; Johnston, V. J.; Jones, R. H.; Pomeroy, R. K.; Ramos, A. F. *Organometallics* **1992**, *11*, 3555–3565.

(23) Bartlone, A. F.; Chetcuti, M. J.; Fanwick, P. E.; Haller, K. A. *Inorg. Chem.* **1993**, *32*, 1435–1441.

(24) Chetcuti, M. J.; Gordon, J. C.; Green, K. A.; Fanwick, P. E.; Morgenstern, D. *Organometallics* **1989**, *8*, 1790–1799.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Key Atoms of Complex **2** in $[NiCp^*(\mu\text{-}SO_2)(\mu\text{-}CO)W(CO)_2Cp']\cdot{}^1/{}_2[W_2(CO)_6Cp'_2]$ ($\mathbf{2}\cdot{}^1/{}_2\mathbf{3}$) with Esd's in Parentheses

	(a) Distances		
W(1)−Ni	2.6523(6)	C(1)−C(2)	1.428(8)
W(1)−S	2.441(1)	C(1)−C(5)	1.422(8)
W(1)−C(1)	2.347(6)	C(1)−C(6)	1.469(9)
W(1)−C(2)	2.288(6)	C(2)−C(3)	1.404(9)
W(1)−C(3)	2.291(6)	C(3)−C(4)	1.380(9)
W(1)−C(4)	2.303(6)	C(4)−C(5)	1.407(8)
W(1)−C(5)	2.330(5)	C(7)−O(7)	1.179(6)
W(1)−C(7)	2.108(5)	C(8)−O(8)	1.139(7)
W(1)−C(8)	2.022(5)	C(9)−O(9)	1.125(7)
W(1)−C(9)	2.012(5)	C(10)−C(11)	1.408(8)
Ni−S	2.105(1)	C(10)−C(14)	1.403(8)
Ni−C(7)	1.901(5)	C(10)−C(15)	1.505(9)
Ni−C(10)	2.085(5)	C(11)−C(12)	1.428(8)
Ni−C(11)	2.058(5)	C(11)−C(16)	1.506(9)
Ni−C(12)	2.125(5)	C(12)−C(13)	1.391(8)
Ni−C(13)	2.200(5)	C(12)−C(17)	1.513(9)
Ni−C(14)	2.122(5)	C(13)−C(14)	1.418(8)
S−O(1)	1.458(4)	C(13)−C(18)	1.502(8)
S−O(2)	1.468(4)	C(14)−C(19)	1.512(8)
	(b) Angles		
S−W(1)−C(7)	73.6(1)	S−W(1)−C(8)	78.9(2)
S−W(1)−C(9)	128.7(2)	C(7)−W(1)−C(8)	123.9(2)
C(7)−W(1)−C(9)	78.2(2)	C(8)−W(1)−C(9)	82.7(2)
S−Ni−C(7)	86.0(2)	W(1)−S−Ni	70.94(4)
W(1)−S−O(1)	119.2(2)	W(1)−S−O(2)	115.2(2)
Ni−S−O(1)	116.2(2)	Ni−S−O(2)	114.0(2)
O(1)−S−O(2)	113.9(2)	W(1)−C(7)−Ni	82.7(2)
W(1)−C(8)−O(8)	178.1(5)	W(1)−C(9)−O(9)	177.6(5)

in the terminal $Ni-SO_2$ complexes $Ni(SO_2)(PPh_3)_3$ [S−O = 1.445(7), 1.450(6) Å][25] and $Ni(SO_2)(PMe_2Ph)_3$ [S−O = 1.451(8), 1.450(6) Å].[26] The Ni−S distances in the latter two complexes [2.038(4) and 2.001(3) Å, respectively][25,26] are significantly shorter than the Ni−S distances found in both **2** or **5** (Table 4).

The O−S−O angle of 113.9(2)° in **2** is almost the same as the value of 113.4(4)° found[25] in $Ni(SO_2)(PPh_3)_3$ but quite different from the angle present in $Ni(SO_2)(PMe_2Ph)_3$ [92.6(4)°].[26] The average W−S−O and Ni−S−O angles of 117 and 115°, respectively, in **2** indicate a more symmetric SO_2 bridge is present than is found in the Mo−Rh complex, where the average Mo−S−O and Rh−S−O angles are respectively 121 and 112°.[18] Other geometrical features of **2** are unremarkable.

(c) Brief Discussion of the Structure of 3. The geometry adopted by **3**, the other compound present in crystals of $\mathbf{2}\cdot{}^1/{}_2\mathbf{3}$, is almost identical to the structures of other closely related $[W_2(CO)_6Cp''_2]$ (W−W) species (Cp″ = Cp, Cp*, C_5H_4-COOH).[27−29] The Cp′ groups are mutually *trans*, and the W−W distance in **3** is 3.2188(3) Å. This structure will be discussed at greater length elsewhere.[30]

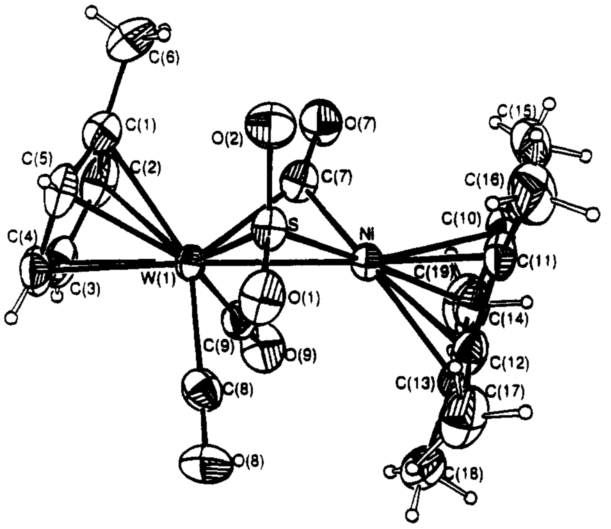

Figure 1. ORTEP diagram of $NiCp^*(\mu\text{-}SO_2)(\mu\text{-}CO)W(CO)_2Cp'$, **2**, with ellipsoids drawn at the 40% probability level. Hydrogen atoms are depicted as spheres with arbitrarily small radii.

Table 4. Comparison of Key Structural Features of Molecules **2**, **4**,[b] and **5**[c] (Esd's in Parentheses)

param	complex **2**	complex **4**	complex **5**
Ni−W (Å)	2.6523(6)	2.5689(6)	2.602(1)
$W-C_{\mu\text{-}CO}$ (Å)	2.108(5)	2.073(6)	2.01(1)
$Ni-C_{\mu\text{-}CO}$ (Å)	1.901(5)	1.916(6)	1.970(9)
$W-S_\mu$ (Å)	2.441(1)		2.469(2)
$Ni-S_\mu$ (Å)	2.105(1)		2.160(2)
dihedral angle[a] (deg)	109.1	113.2	108.7

[a] Between the $NiWC_{\mu\text{-}CO}$ plane and the $NiWC(H_2)$ or $NiWS_\mu$ planes. [b] Chetcuti, M. J.; Deck, K. J.; Fanwick, P. E.; Gordon, J. C.; Grant, B. E. *Organometallics* **1992**, *11*, 2128−2139. [c] Bartlone, A. F.; Chetcut M. J.; Fanwick, P. E.; Haller, K. A. *Inorg. Chem.* **1993**, *32*, 1435−1441.

Conclusions. The SO_2 heterobimetallic complex $[NiCp^*(\mu\text{-}CO)(\mu\text{-}SO_2)W(CO)_2Cp']$ (Ni−W, **2**) has been prepared by addition of SO_2 to the unsaturated heterodinuclear species $[NiCp^*W(CO)_3Cp']$. The complex was spectroscopically and structurally characterized. Complex **2** contains a Ni−W bond that is spanned by both an SO_2 and a CO ligand. Its structure is very similar to that of the methylene complex $NiCp^*(\mu\text{-}CH_2)(\mu\text{-}CO)W(CO)_2Cp$ (Ni−W, **4**) as expected in view of the isolobal relationship between SO_2 and CH_2 species.

Experimental Section

(a) General Techniques. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Reagent grade chemicals were used. Hexanes and diethyl ether were distilled over sodium under a nitrogen atmosphere. Methylene chloride was distilled over calcium hydride under nitrogen. Deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere and were subjected to freeze−thaw degassing cycles prior to use.

(b) Spectroscopic Measurements. IR spectra were obtained on an IBM IR-32 FT spectrometer. Mass spectra were obtained on a JEOL JMS-AX505 HA mass spectrometer. ^1H and ^{13}C NMR were recorded on a GE GN-300 instrument at 300 and 75 MHz, respectively, in chloroform-d_1; $Cr(acac)_3$ (≈0.01 M) was added to the ^{13}C NMR samples as a shiftless relaxation agent. (Spectroscopic data are only reported for **2**, even for samples in which **3** also was present.)

(c) Synthesis of $NiCp^*(\mu\text{-}CO)(\mu\text{-}SO_2)W(CO)_2Cp'$. A 300 mg amount (0.55 mmol) of **1** was dissolved in 15 mL of Et_2O, and the solution was cooled to −78 °C. SO_2, obtained from the reaction of 2 M HCl and anhydrous Na_2SO_3, was bubbled through the solution under a slight N_2 flow. An orange-brown solution formed over a 15 min period. The addition of SO_2 was terminated, and the solution was maintained at −78 °C while being stirred approximately 1 h. An orange solid (**2**) precipitated from the solution: this was redissolved and recrystallized from methylene chloride/diethyl ether/hexanes (4:2:1) at −20 °C in 45% yield (150 mg). MS (*m/e*, amu): 540 $(M - SO_2)^+$, 520 $(M - 3CO)^+$, 456 $(M - SO_2 - 3CO)$. ^1H NMR (ppm): 1.81 (s, 15H, $C_5\mathit{Me}_5$), 2.158 (s, 3H, $C_5H_4\mathit{Me}$), 5.34 (m, 4H, $C_5\mathit{H}_4Me$). ^{13}C NMR

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(25) Moody, D. C.; Ryan, R. R. *Inorg. Chem.* **1979**, *18*, 223.

(26) Sieler, J.; Peters, K.; Wenschuh, E.; Hoffmann, T. *Z. Anorg. Allg. Chem.* **1987**, *549*, 171.

(27) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086−1090.

(28) Rheingold, A. L.; Harper, J. R. *Acta Crystallogr.* **1991**, *C47*, 184.

(29) Avey, A.; Tenhaeff, S. C.; Weakley, T. J. R.; Tyler, D. R. *Organometallics* **1991**, *10*, 3607−3613.

(30) Chetcuti, M. J.; Navarro, R., III; Sheng, M. *Acta Crystallogr.* in press.

(ppm): 227.0 (μ-CO), 211.8 (CO), 102.7 (C_5Me$_5$), 112.1 (C$_{ipso}$, C_5H_4-Me), 93.7, 89.5 [C(2) and C(3), C_5H_4Me], 12.4 (C_5H_4*Me*), 7.9 (C_5*Me*$_5$).

(d) X-ray Diffraction Study. Crystals for the X-ray diffraction studies were obtained from a dichloromethane/diethyl ether/hexanes (4:2:1) solution obtained after the mother liquor was evacuated to dryness and the residue redissolved. A dark orange crystal of **2**·$^1/_2$**3** was mounted on a glass fiber. Cell constants and an orientation matrix were obtained from least squares refinement of 25 reflections with $32° < \theta < 36°$. Systematic absences indicated that the space group was $P2_1/n$ (No. 14). A total of 4771 unique reflections were obtained from the entire set of 5465; the data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ-scans was applied. Only the 4398 reflections with $|F_o|^2 > 1.5\sigma|F_o|^2$ were used in the solution refinement.

The structure was solved using Patterson methods, which located the positions of the two independent tungsten atoms. Remaining atoms were located by using successive Fourier syntheses. Hydrogen atoms were located and were refined isotropically; other atoms were refined anisotropically. The center of the W−W bond of **3** lies on an inversion center while **2** lies in a general position in the unit cell. Data were corrected for anomalous dispersion. Refinement converged to $R(F) = 0.024$ and $R_w(F) = 0.036$.

Scattering factors were taken from Cromer and Waber's values.[31] Anomalous effects[32] were included in $|F_c|^2$, with values for $\Delta f'$ and $\Delta f''$ taken from Cromer.[33] All calculations were performed on a VAX Station 3200 computer using SDP/VAX.[34]

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Supplementary Material Available: Full structural data for crystals of **2**·$^1/_2$**3**, including an ORTEP diagram of **3** and tables of crystal data and data collection parameteis, positional parameters, bond lengths and bond angles for all atoms, anisotropic thermal parameters for non-hydrogen atoms, and selected least squares planes (16 pages). Ordering information is given on any current masthead page.

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(31) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(32) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(33) Cromer, D. T. In *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV; Table 2.3.1.

(34) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64−71.