# The Preparation of Some Monodentate Coordinated Semicarbazone(O) and Thiosemicarbazone(S) Cationic But-2-yne Tungsten(II) Complexes

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Reaction of  $[WI(CO)(NCMe)(dppm)(\eta^2-MeC_2Me)][BF_4]$  {dppm = Ph<sub>2</sub>P(CH<sub>2</sub>)PPh<sub>2</sub>} with an equimolar quantity of L {L = RR'CNNHCONH<sub>2</sub> (R = R' = Me; R = H, R' = Ph)} or L {L = RR'CNNHCSNH<sub>2</sub> (R = R' = Me, Et; R = Me, R' = Et, Pr<sup>n</sup>, Bu', Ph; R = H, R' = Ph)} gives the monodentately coordinated semicarbazone or thiosemicarbazone products [WI(CO)L(dppm)(\eta^2-MeC\_2Me)][BF\_4] (1-9). <sup>13</sup>C NMR spectroscopy suggests that the but-2-yne ligand is donating four electrons to the tungsten in [WI(CO){H(Ph)CNNHCSNH<sub>2</sub>}(dppm)(\eta^2-MeC\_2Me)][BF\_4].

#### Introduction

Transition-metal ions with semicarbazones and thiosemicarbazones have been extensively studied [1-3], and generally contain the semicarbazone or thiosemicarbazone ligands attached as bidentate ligands through the oxygen or sulphur and the hydrazine nitrogen atom. Hitherto, very few lowvalent organotransition-metal complexes with semicarbazones and thiosemicarbazones have been described [4-8]. For example, the organo-iron complexes [Fe(CO)<sub>2</sub>LCp][PF<sub>6</sub>] previously reported [7]  $\{L = H_2 NNHCSNH_2 \text{ or } R'R''CNNHCSNH_2 (R' = M_2)\}$  $R'' = Me; R' = H, R'' = Ph; R' = H, R'' = p-NO_2Ph;$  $\mathbf{R}' = \mathbf{Me}, \mathbf{R}'' = p \cdot \mathbf{MePh}; \mathbf{R}'\mathbf{R}'' = C_5H_{10}$  also contain monodentately coordinated thiosemicarbazide and thiosemicarbazone ligands, which was confirmed by the X-ray crystal structure determination for R' =H, R'' = Ph[7].

In this paper we report the synthesis and spectroscopic properties of some new monodentately coordinated semicarbazone(0) and thiosemicarbazone(S) tungsten(II)-but-2-yne complexes, [WI(CO)L(dppm)( $\eta^2$ -MeC<sub>2</sub>Me)][BF<sub>4</sub>] {L = RR'CNNHCONH<sub>2</sub> (R = R' = Me; R = H, R' = Ph) or RR'CNNHCSNH<sub>2</sub> (R = R' = Me; R = H, R' = Ph) or RR'CNNHCSNH<sub>2</sub> (R = R' = Me, Et; R = Me, R' = Et, Pr<sup>n</sup>, Bu', Ph; R = H, R' = Ph)}.

### **Results and Discussion**

The starting material

 $[WI(CO)(NCMe)(dppm)(\eta^2-MeC_2Me)][BF_4]$  was prepared by reacting the neutral diiodo complex

Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen 0932-0776/93/1200-1715/\$ 01.00/0  $[WI_2(CO)(dppm)(\eta^2-MeC_2Me)]$  with one equivalent of  $Ag[BF_4]$  in acetonitrile [9]. Equimolar [WI(CO)(NCMe)(dppm)( $\eta^2$ quantities of  $MeC_2Me$ )][BF<sub>4</sub>] and L {L = RR'CNNHCONH<sub>2</sub> (R = R' = Me; R = H, R' = Ph) or RR'CNNHCSNH,  $(R = R' = Me, Et; R = Me, R' = Et, Pr^{n}, Ph; R = H,$ R' = Ph in  $CH_2Cl_2$  (or acetone for L = $Me(Bu')CNNHCSNH_{2}$  at room temperature afford the new monodentately attached semicarbazone or thiosemicarbazone products  $[WI(CO)L(dppm)(\eta^2-MeC_2Me)][BF_4]$  (1-9) in good yield. All the new complexes 1-9 have been fully characterized by elemental analysis (C, H and N) (Table I), infrared (Table II), <sup>1</sup>H and for [WI(CO){H(Ph)CNNHCSNH<sub>2</sub>}(dppm)-

 $(\eta^{2}-MeC_{2}Me)][BF_{4}]$  (9) by <sup>13</sup>C NMR spectroscopy (Tables III and IV). All the new complexes **1–9** are air-sensitive in solution, however, they can be stored under nitrogen in the solid state. The complexes are all reasonably soluble in chlorinated solvents such as CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> but more soluble in acetone, and as expected since they are ionic they are insoluble in hydrocarbon solvents and diethyl ether.

The infrared spectra of complexes 1-9 all show a single carbonyl band at  $\approx 1930 \text{ cm}^{-1}$ , which as expected is in a similar position to the complexes previously described. we have namelv  $[WI(CO)L(dppm)(\eta^2-MeC_2Me)][BF_4]$ {L =  $SC(NH_2)_2$ ,  $SC(NMe_2)_2$ ,  $SC(NH_2)(NHPhMe-o)$ , SC(NHPh)<sub>2</sub>, SC(NH<sub>2</sub>)Me,  $OC(NH_2)_2$ or  $OC(NH_{2})Me$  [10]. The thiourea complex  $[WI(CO){SC(NH_2)_2}(dppm)(\eta^2-MeC_2Me)][ClO_4]$ which was crystallized as its perchlorate salt was crystallographically characterized. Since the colours and spectroscopic properties of 1-9 are similar to  $[WI(CO){SC(NH_2)_2}(dppm)(\eta^2-MeC_2Me)][ClO_4],$ 

<sup>\*</sup> Reprint requests to Dr. P. K. Baker.

Com- pound		Colour	Yield	Analytical data (Found (%) Calcd)		
No.				С	Н	Ν
1	$[WI(CO)(Me_2CNNHCONH_2)(dppm)(\eta^2-MeC_2Me)][BF_4]$	Brown	59	41.4	3.9	3.9
				(41.7)	(3.8)	(4.3)
2	$[WI(CO){H(Ph)CNNHCONH_2}(dppm)(\eta^2-MeC_2Me)][BF_4]$	Brown	59	44.2	3.7	3.7
				(44.4)	(3.6)	(4.1)
3	$[WI(CO)(Me_2CNNHCSNH_2)(dppm)(\eta^2-MeC_2Me)][BF_4]$	Pink	66	40.7	4.0	3.9
				(41.0)	(3.7)	(4.2)
4	$[WI(CO)(Et_2CNNHCSNH_2)(dppm)(\eta^2-MeC_2Me)][BF_4]$	Pink	62	42.1	4.2	3.7
				(42.2)	(4.0)	(4.1)
5	$[WI(CO){Me(Et)CNNHCSNH_2}(dppm)(\eta^2-MeC_2Me)][BF_4]$	Pink	62	41.6	3.7	3.8
				(41.7)	(3.9)	(4.2)
6	$[WI(CO){Me(Pr^{n})CNNHCSNH_{2}}(dppm)(\eta^{2}-MeC_{2}Me)][BF_{4}]$	Pink	67	42.4	4.1	3.8
				(42.3)	(4.0)	(4.1)
7	$[WI(CO){Me(Bu')CNNHCSNH_2}(dppm)(\eta^2-MeC_2Me)][BF_4]$	Pink	63	42.8	4.4	3.7
				(42.8)	(4.2)	(4.1)
8	$[WI(CO){Me(Ph)CNNHCSNH_2}(dppm)(\eta^2-MeC_2Me)][BF_4]$	Pink	65	44.2	3.7	3.9
				(44.3)	(3.8)	(4.0)
9	$[WI(CO){H(Ph)CNNHCSNH_2}(dppm)(\eta^2-MeC_2Me)][BF_4]$	Pink	67	43.5	3.6	3.7
				(43.7)	(3.6)	(4.0)

Table I. Physical and analytical data<sup>a</sup> for  $[WI(CO)(RR'CNNHCONH_2 \text{ or } RR'CNNHCSNH_2)(dppm)(\eta^2-MeC_2Me)][BF_4]$ .

<sup>a</sup> Calculated values in parantheses.

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Table II. Infrared data<sup>a</sup> for [WI(CO)(RR'CNNHCONH<sub>2</sub> or RR'CNNHCSNH<sub>2</sub>)(dppm)( $\eta^2$ -MeC<sub>2</sub>Me)][BF<sub>4</sub>].

Com- pound No.	Infrared $\nu(\rm NH)$	group frequencies (cm <sup>-1</sup> ) $\nu(C \equiv O) \nu(C = O) \nu(C = S)$	$\nu(\mathrm{BF})$
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1	3325 s	1935 s	1655 s	-	1020 bs
•	3150 m	1025	1650		10001
2	3450 m	1935 s	1658 s	-	1020 bs
	3350 m				
•	3300 m	1025			10001
3	3420 m	1925 s	-	1575 w	1020 bs
	3320 m				
	3220 m	1005			10001
4	3460 m	1935 s	-	1570 w	1020 bs
	3430 m				
	3330 m				
	3225 m				
5	3325 bm	1930 s	-	1575 w	1020 bs
	3175 m				
6	3425 m	1935 s	-	1570 w	1020 bs
	3325 m				
	3225 m				
7	3410 m	1920 s	-	1575 w	1020 bs
	3320 m				
8	3460 m	1920 s	-	1575 w	1020 bs
	3425 m				
	3315 m				
	3220 m				
9	3425 m	1935 s	-	1580 w	1020 bs
	3320 m				
	3250 m				

<sup>a</sup> Spectra recorded as thin films in CHCl<sub>3</sub> between NaCl plates. s = strong, m = medium, b = broad.

the proposed structure of 1-9 is shown in Fig. 1 with either the oxygen or the sulphur atoms of the semicarbazone or thiosemicarbazone ligands attached to the tungsten. This is the same type of structure as the monodentately coordinated thiosemicarbazone iron complex [Fe(CO)<sub>2</sub>(PhCHNNHCSNH<sub>2</sub>)Cp][PF<sub>6</sub>] [7], *i. e.* with an (S) bonded thiosemicarbazone.

The <sup>1</sup>H NMR spectra for **1** and **3–9** all show the expected features for the structure shown in Fig. 1. The but-2-yne ligands show two single resonances which is in accord with the two methyl groups being in different environments as shown in Fig. 1. Where-as complex **2**,



Fig. 1. Proposed structure for  $[WI(CO)(RR'CNNHCENH_2)(dppm)(\eta^2-MeC_2Me)][BF_4]$ (1-9) (E = O or S).

Compound No.	<sup>1</sup> H NMR chemical shifts ( $\delta$ in ppm) <sup>a</sup>
1	9.97 (s, 1H, N <u>H</u> ); 8.01–6.9 (bm, 20 H, Ph– <u>H</u> , 2 H, N <u>H</u> <sub>2</sub> ); 4.63 (bm, 2 H, PC <u>H</u> <sub>2</sub> P); 3.12 (s, 3 H, $\equiv$ CMe); 2.92 (s, 3 H, $\equiv$ CMe); 2.18 (s, 6 H, CH <sub>2</sub> )
2	10.0 (s, 1H, N <u>H</u> ); 9.02 (s, 1H, N = C <u>H</u> ); 8.0–6.95 (bm, 25 H, Ph– <u>H</u> , 2H, N <u>H</u> <sub>2</sub> ); 4.73 (bm, 2H, PCH,P): 2.92 (s, 6H, = CMe)
3	9.98 (s, 1H, N <u>H</u> ); 8.1–6.95 (bm, 20H, Ph– <u>H</u> , 2H, N <u>H</u> <sub>2</sub> ); 4.95 (bm, 2H, PC <u>H</u> <sub>2</sub> P); 3.15 (s, 3H, $\equiv$ CMe); 3.10 (s, 3H, $\equiv$ CMe); 2.15 (s, 6H, CH <sub>2</sub> )
4	10.08 (s, 1H, N <u>H</u> ); 8.08–6.92 (bm, 20 H, Ph– <u>H</u> , 2 H, N <u>H</u> <sub>2</sub> ); 4.86 (bm, 2 H, PC <u>H</u> <sub>2</sub> P); 3.16 (s, 3 H, $\equiv$ CMe); 3.09 (s, 3 H, $\equiv$ CMe); 2.42 (m, 4 H, CH <sub>2</sub> ); 1.15 (m, 6 H, CH <sub>2</sub> )
5	10.23 (s, 1H, N <u>H</u> ); 8.4–6.9 (bm, 20 H, Ph– <u>H</u> , 2 H, N <u>H</u> <sub>2</sub> ); 3.15 (s, 3 H, $\equiv$ C <u>Me</u> ); 2.95 (s, 3 H, $\equiv$ C <u>Me</u> ); 2.49 (m, 2 H, CH <sub>2</sub> ); 2.05 (s, 3 H, CH <sub>2</sub> ); 1.15 (t, 3 H, CH <sub>2</sub> , $J_{H,H} = 7.3$ Hz)
6	9.98 (s, 1H, N <u>H</u> ), 8.21–6.95 (bm, 20 H, Ph– <u>H</u> , 2H, N <u>H</u> <sub>2</sub> ); 4.73 (bm, 2H, PC <u>H</u> <sub>2</sub> P); 3.10 (s, 3 H, $\equiv$ C <u>Me</u> ); 2.92 (s, 3 H, $\equiv$ C <u>Me</u> ); 2.42 (t, 2 H, C <u>H</u> <sub>2</sub> , $J_{H-H} = 6.25$ Hz); 2.14 (s, 3 H, C <u>H</u> <sub>3</sub> ); 1.65 (m, 2 H, CH <sub>2</sub> ); 0.95 (t, 3 H, CH <sub>2</sub> , $J_{H-H} = 6.25$ Hz); 2.14 (s, 3 H, C <u>H</u> <sub>3</sub> ); 1.65 (m, 2 H, CH <sub>2</sub> ); 0.95 (t, 3 H, CH <sub>2</sub> , $J_{H-H} = 6.25$ Hz)
7	$P_{1,2}(5,5)$ (1, $S_{1,2}(5,5)$ (1, $S_{1,2}(5,5$
8	10.43 (s, 1H, N <u>H</u> ); 8.15–7.0 (bm, 25 H, Ph– <u>H</u> , 2 H, N <u>H</u> <sub>2</sub> ); 4.80 (bm, 2 H, PC <u>H</u> <sub>2</sub> P); 3.16 (s, 3 H, $\equiv$ CMe); 3.04 (s, 3 H, $\equiv$ CMe); 2.25 (s, 3 H, CH <sub>2</sub> )
9	10.78 (s, 1H, N <u>H</u> ); 9.95 (s, 1H, N=C <u>H</u> ); 8.47–6.93 (bm, 25 H, Ph- <u>H</u> , 2 H, N <u>H</u> <sub>2</sub> ); 4.72 (bm, 2 H, PC <u>H</u> ,P); 3.13 (s, 3 H, =C <u>M</u> e); 2.98 (s, 3 H, =C <u>M</u> e)

Table III. <sup>1</sup>H NMR data<sup>a</sup> for [WI(CO)(RR'CNNHCONH, or RR'CNNHCSNH<sub>2</sub>)(dppm)( $\eta^2$ -MeC<sub>2</sub>Me)][BF<sub>4</sub>].

<sup>a</sup> Spectra recorded in  $CDCl_3$  (+25 °C) referenced to  $SiMe_4$ . s = singlet, d = doublet, t = triplet, m = multiplet, b = broad.

Table IV.	. <sup>13</sup> C NMR data <sup>a</sup> for
[WI(CO)	${\rm H(Ph)CNNHCSNH_2}({\rm dppm})(\eta^2-{\rm MeC_2Me})]$ -
$[BF_4]$ (9).	

this complex. This also enables complexes 1-9 to obey the effective atomic number rule.

Compound No.	<sup>13</sup> C NMR chemical shifts ( $\delta$ in ppm) <sup>a</sup>
9	228.9 (bd, $\underline{C} = \underline{C}$ ); 209.5 (s, $\underline{C} = 0$ ); 178.9 (s, $\underline{C} = S$ ); 162.5 (s, $N = \underline{C}$ ); 138.6–127.8 (m Ph-C): 29.84 (t PCH.P. $I_{ac} =$

13.2 Hz); 19.43 (s,  $\equiv$  CMe); 17.26 (s,

<sup>a</sup> Spectrum recorded in CDCl<sub>3</sub> (+ 25 °C) referenced to  $SiMe_4$ . s = singlet, t = triplet, m = multiplet, bd = broad doublet.

### [WI(CO){H(Ph)CNNHCONH<sub>2</sub>}(dppm)-

 $\equiv$ CMe)

 $(\eta^2 - MeC_2Me)$  [BF<sub>4</sub>] shows a single resonance at  $\delta = 2.92$  ppm which suggests the but-2-yne is undergoing rapid propeller like rotation, fast on the NMR timescale at room temperature. The <sup>13</sup>C NMR spectrum for [WI(CO){H(Ph)CNNHCSNH<sub>2</sub>}(dppm)- $(\eta^2 - MeC_2Me)$  [BF<sub>4</sub>] (9) shows a broad resonance at 228.9 ppm for the alkyne contact carbons. From Templeton and Ward's [11] correlation of the number of electrons donated to the metal and the <sup>13</sup>C NMR alkyne contact carbon chemical shift, resonances above 200 ppm suggest that the but-2-yne ligand is donating four electrons to the tungsten in

It may be that the semicarbazone and thiosemicarbazone ligands in 1-9 are not monodentately coordinated but in a bidentate manner as in  $[W(CO)(dppm)(O^N \text{ or } S^N)(\eta^2-MeC_2Me)][BF_4]I$ with the iodide displaced by the imine nitrogen atom. This is very unlikely since the reactions of [WI(CO)(Me<sub>2</sub>CNNHCONH<sub>2</sub>)(dppm)-

 $(\eta^2$ -MeC<sub>2</sub>Me)][BF<sub>4</sub>] (1) with two equivalents of Na[BPh<sub>4</sub>] in acetonitrile did not give the bis(tetraphenylborate) exchanged product:

[W(CO)(dppm)(Me<sub>2</sub>CNNHCONH<sub>2</sub>)- $(\eta^2 - MeC_2Me)][BPh_4]_2.$ 

#### Experimental

All manipulations were carried out under dry nitrogen using standard Schlenk line techniques.  $[WI(CO)(NCMe)(dppm)(\eta^2 -$ The complex  $MeC_{2}Me$ )][BF<sub>4</sub>] was prepared by the published method [9]. The semicarbazone and thiosemicarbazone ligands were prepared by the method of Sah and Daniels [12]. All solvents and chemicals used were of reagent grade quality, and the solvents were dried and distilled before use.

Elemental analyses (C, H and N) were determined by using a Carlo Erba Elemental Analyser MOD 1106 (using helium as the carrier gas). Infrared spectra were obtained as CHCl<sub>3</sub> films between NaCl plates and recorded on a Perkin-Elmer 1430 ratio recording IR spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Bruker AC 250 CP/MAS NMR spectrometer and <sup>13</sup>C NMR spectra were recorded on a Bruker WH 400 NMR spectrometer with tetramethylsilane as a standard.

## Preparation of $[WI(CO)(Me_2CNNHCSNH_2)(dppm)-(\eta^2-MeC_2Me)][BF_4]$ (3)

To [WI(CO)(NCMe)(dppm)( $\eta^2$ -MeC<sub>2</sub>Me)][BF<sub>4</sub>] (0.5 g, 0.552 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>) with continuous stirring under a stream of dry nitrogen was added Me<sub>2</sub>CNNHCSNH<sub>2</sub> (0.0724 g, 0.552 mmol). After 3 h the solution was filtered and the solvent volume reduced to 2 cm<sup>3</sup> *in vacuo*. Dropwise addition of diethyl ether precipitated the pink cationic complex [WI(CO)(Me<sub>2</sub>CNNHCSNH<sub>2</sub>)-(dppm)( $\eta^2$ -MeC<sub>2</sub>Me)][BF<sub>4</sub>] (**3**) which on recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether gave 0.36 g, 66% of pure product.

Similar reactions of equimolar quantities of  $[WI(CO)(NCMe)(dppm)(\eta^2-MeC_2Me)][BF_4]$  and L {L = RR'CNNHCONH<sub>2</sub> (R = R' = Me; R = H, R' = Ph) or RR'CNNHCSNH<sub>2</sub> (R = R' = Et; R = Me, R' = Et, Pr<sup>n</sup>, Ph; R = H, R' = Ph} in CH<sub>2</sub>Cl<sub>2</sub> {or acetone for Me(Bu')CNNHCSNH<sub>2</sub>} at room temperature gave [WI(CO)L(dppm)(\eta^2-MeC\_2Me)]-[BF<sub>4</sub>] (**1**, **2**, **4**-**9**). For physical and analytical data see Table I.

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