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Reactions of the cationic bis(but-2-yne) complex $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$ with bidentate anionic oxygen and sulphur donor ligands

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Abstract

Treatment of the complex $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$ with an equimolar quantity of M(LL){M(LL) = $Na[S_2CNMe_2] \cdot 2H_2O$, $Na[S_2CNEt_2] \cdot 3H_2O$, $Na[S_2CN(CH_2Ph)_2]$, $[NH_4][S_2CNC_4H_8]$, $K[S_2COEt]$, $Na[OC(CH_3)CHCO(CH_3)]$, $Na[OC(CF_3)CHCO(CF_3)]$ or $Na[OC(Ph)CHCO(CH_3)]$} at room temperature in CH_2Cl_2 affords good yields of the new neutral mixed-ligand complexes $[W(CO)(LL)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ (1–8). ^{13}C NMR spectroscopy indicates that the but-2-yne is acting as a four-electron donor in these complexes.

1. Introduction

Alkyne complexes of molybdenum and tungsten have received considerable attention in recent years [1–7]. Complexes containing one or two dithiocarbamates have been reported. For example, reaction of the electrophilic reagent $[Mo(CO)_2(S_2CNEt_2)_2]$ with a variety of alkynes afforded $[Mo(CO)(S_2CNEt_2)_2(\eta^2\text{-}RC_2R')]$ (R = R′ = H, Ph, CO_2Me; R = H, R′ = Me or Ph; R = Me, R′ = Ph) [8]. These complexes may also be prepared from either $[Mo(CO)(S_2CNEt_2)_2(\eta^2\text{-}HC_2H)]$ or $[Mo(CO)_2L(S_2CNEt_2)_2]$ (L = CO or PPh_3) [9] by treatment with an alkyne to give a product in which HC_2H or L has been replaced. The analogous tungsten bis(dithiocarbamate) complexes $[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}RC_2R')]$ (R = R′ = H, Me, Et or Ph; R = H, R′ = Ph) were prepared by treating $[W(CO)_2L(S_2CNEt_2)_2]$ (L = CO [10] and PPh_3 [11]) with the relevant alkyne. Bennett and Boyd [12] have reported the preparation of the cyclo-octyne complexes $[M(CO)(S_2CNR_2)_2(\eta^2\text{-}C_8H_{12})]$ (M = Mo or W; R = Me or Et). Carlton and Davidson [13] reported the reactions of the bromo-bridged dimers $[\{W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R')_2\}_2]$ with $Na[S_2PMe_2]$, $Na[S_2CNMe_2]$ or $Tl[2\text{-}SC_5H_4N]$ to yield the mono(alkyne) complexes $[W(CO)(LL')_2(\eta^2 - RC_2R')]$ (R = R′ = Me, LL′ = S_2CNMe_2 or $2\text{-}SC_5H_4N$; R = Ph, R′ = Me, LL′ = S_2CNMe_2 or S_2PMe_2; R = R′ = Ph, LL′ = S_2PMe_2) or the bis(alkyne) compound $[W(2\text{-}SC_5H_4N)_2(\eta^2\text{-}PhC_2Ph)_2]$. Davidson and Vasapollo [14] have described the preparation of $[WBr(CO)(LL)(\eta^2\text{-}MeC_2Me)_2]$ {LL = S_2CNMe_2, $S_2\text{-}PMe_2$ or acetylacetonate(acac)}.

In recent years we have been investigating the chemistry of the versatile complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) [15], which react with one or two equivalents of dithiocarbamates and related ligands to afford $[WI(CO)(S_2CX)(\eta^2\text{-}RC_2R)_2]$ {R = Ph or Me; X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt, NC_4H_8 or NC_5H_{10}} or $[W(CO)(S_2CX)_2(\eta^2\text{-}RC_2R)]$ {R = Me, X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OEt, NC_4H_8 or NC_5H_{10}; R = Ph, X = NEt_2 or OEt}, respectively [16]. We recently reported the preparation of the cationic complex $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$ and its reactions with neutral bidentate ligands [17]. In this paper we describe the reactions of the bis(but-2-yne) complex $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$ with one equivalent of the bidentate anionic ligands M(LL) {M(LL = $Na[S_2CNMe_2] \cdot 2H_2O$, $Na[S_2CNEt_2] \cdot 3H_2O$, $Na[S_2CN(CH_2Ph)_2]$, $[NH_4][S_2CNC_4H_8]$, $K[S_2COEt]$, $Na[OC(CH_3)CHCO(CH_3)]$, $Na[OC(CF_3)CHCO(CF_3)]$ or Na[OC(Ph)-

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TABLE 1. Physical and analytical data for the compounds $[W(CO)(S_2CX)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ and $[W(CO)(O\text{-}O)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$

Complexes	Colour	Yield (%)	Analytical data (found (calc.) (%))
1 $[W(CO)(S_2CNMe_2)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$	Green	56	C: 31.0 (29.4) H: 4.0 (3.8) N: 4.8 (5.1)
2 $[W(CO)(S_2CNEt_2)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$	Green	57	C: 31.5 (32.1) H: 4.3 (4.3) N: 4.8 (5.0)
3 $[W(CO)(S_2CNC_4H_8)_2(\eta^2\text{-}MeC_2Me)]$	Green	64	C: 32.5 (32.3) H: 3.8 (4.0) N: 4.6 (5.0)
4 $[W(CO)\{S_2CN(CH_2Ph)_2\}(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$	Green	58	C: 43.9 (43.9) H: 4.3 (4.1) N: 3.7 (4.1)
5 $[W(CO)(S_2COEt)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$	Green	59	C: 29.8 (29.3) H: 4.0 (3.6) N: 2.2 (2.6)
6 $[W(CO)(CH_3COCHCOCH_3)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$	Brown	59	C: 35.3 (35.2) H: 4.0 (4.1) N: 2.6 (2.7)
7 $[W(CO)(CF_3COCHCOCF_3)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$	Orange/brown	63	C: 29.2 (29.1) H: 2.3 (2.4) N: 2.1 (2.3)
8 $[W(CO)(CH_3COCHCOPh)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$	Red	62	C: 41.6 (41.9) H: 4.4 (4.1) N: 2.2 (2.4)

$CHCO(CH_3)]\}$ to afford the first examples of mixed-ligand complexes of the type $[W(CO)(LL)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$.

2. Results and discussion

Reaction of $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$ with 1 equiv. of M(LL) {M(LL) = $Na[S_2CNMe_2] \cdot 2H_2O$, $Na[S_2CNEt_2] \cdot 3H_2O$, $[NH_4][S_2CNC_4H_8]$, $Na[S_2CN(CH_2Ph)_2]$, $K[S_2COEt]$, $Na[OC(CH_3)CHCO(CH_3)]$, $Na[OC(CF_3)CHCO(CF_3)]$ or $Na[OC(Ph)CHCO(CH_3)]$} in CH_2Cl_2 at room temperature afforded good yields of the new mixed ligand complexes $[W(CO)(LL)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ (**1**–**8**). The complexes (**1**–**8**) have been characterized by elemental analysis (C, H and N) (Table 1), IR, ^1H and in selected cases ^{13}C NMR spectroscopy (Tables 2–4). The complexes **1**–**8** are all stable for prolonged periods when stored under nitrogen in the dark; however, they slowly decompose when exposed to air in solution. Complexes **1**–**8** also show no tendency to disproportionate into $[W(CO)(LL)_2(\eta^2\text{-}MeC_2Me)]$ and $[W(CO)(S_2CNC_4H_8)_2(\eta^2\text{-}MeC_2Me)]$, which is in contrast with the results obtained from the reactions of the complexes $[WI(CO)(S_2CX)(\eta^2\text{-}MeC_2Me)_2]$ and 1 equiv. of $Na[S_2CX']$, in an attempt to synthesize the mixed ligand complexes $[W(CO)(S_2CX)(S_2CX')(\eta^2\text{-}MeC_2Me)]$, which resulted in a mixture of the symmetric bis(dithiocarbamate) complexes [18]. The non-occurrence of disproportionation of the mixed-ligand complexes formed from the cation $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$ is likely to be due to the absence of the potentially nucleophilic iodide that is liberated from the complexes $[WI(CO)(S_2CX)(\eta^2\text{-}MeC_2Me)_2]$ on treatment with a second equivalent of an anionic ligand. Also, it has been shown that treatment of $[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}MeC_2Me)]$ with NaI in the presence of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ and MeC_2Me affords $[WI(CO)(S_2CNEt_2)(\eta^2\text{-}MeC_2Me)_2]$

TABLE 2. Infrared data [a] for the compounds $[W(CO)(S_2CX)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ and $[W(CO)(O\text{-}O)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$

Complex	ν(C≡O) (cm^{-1})	ν(C=O) (cm^{-1})	ν(C≡C) (cm^{-1})
1	1898s	–	1680vw
2	1903s	–	1675vw
3	1902s	–	1668vw
4	1902s	–	1605vw
5	1905s	–	1645vw
6	1897s	1610s	1690vw
7	1900s	1620s	1685vw
8	1905s	1595s	1685vw

[a] Spectra recorded in $CHCl_3$ as thin films between NaCl plates s = strong, vw = very weak.

TABLE 3. ^{1}H NMR data [a] for the compounds $[W(CO)(S_2CX)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ and $[W(CO)(O\text{-}O)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$

Complex	^{1}H NMR δ (ppm)
1	3.54 (bm, 4H, $NC\mathit{H}_2$); 3.15 (s, 6H, $\equiv C\mathit{Me}$); 3.05 (s, 3H, $N\mathit{Me}$); 2.90 (s, 3H, $\equiv N\mathit{Me}$); 2.05 (bm, 4H, $C\mathit{H}_2$)
2	3.7 (bm, 8H, $NC\mathit{H}_2$); 3.25 (5, 6H, $\equiv C\mathit{Me}$); 2.0 (bm, 4H, $C\mathit{H}_2$); 1.45 (bm, 6H, $C\mathit{H}_3$)
3	3.62 (bm, 8H, $NC\mathit{H}_2$); 3.21 (s, 6H, $\equiv C\mathit{Me}$); 2.0 (bm, 8H, $C\mathit{H}_2$)
4	7.6–7.2 (bm, 10H, Ph–*H*); 4.5 (s, 4H, $NC\mathit{H}_2Ph$); 3.7 (bm, 4H, $NC\mathit{H}_2$); 3.45, 3.29 (d, 6H, $\equiv C\mathit{Me}$); 2.05 (bm, 4H, $C\mathit{H}_2$)
5	4.5 (bm, 2H, $OC\mathit{H}_2$); 3.52 (bm, 4H, $NC\mathit{H}_2$); 3.21 (s, 6H, $\equiv C\mathit{Me}$); 2.21 (bm, 4H, $C\mathit{H}_2$); 1.45 (bm, 3H, $C\mathit{H}_3$)
6	5.42 (s, 1H, $C\mathit{H}$); 3.8 (bm, 4H, $NC\mathit{H}_2$); 3.32 (s, 6H, $\equiv C\mathit{Me}$); 2.25 (s, 6H, $C\mathit{H}_3$); 2.15 (bm, 4H, $C\mathit{H}_2$)
7	6.35 (s, 1H, $C\mathit{H}$); 3.85 (bm, 4H, $NC\mathit{H}_2$); 2.95, 2.87 (d, 6H, $\equiv C\mathit{Me}$); 2.10 (bm, 4H, $C\mathit{H}_2$)
8	7.95–7.25 (bm, 5H Ph–*H*); 6.15 (s, 1H, $C\mathit{H}$); 4.85 (bm, 4H, $NC\mathit{H}_2$); 3.3 (s, 6H, $\equiv C\mathit{Me}$); 2.25 (s, 3H, $C\mathit{H}_3$); 2.05 (bm, 4H, $C\mathit{H}_2$)

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

indicating the flexibility of the dithiocarbamate ligand under these conditions [18].

The infrared spectra of **1**–**8** all show a strong single carbonyl band at around 1900 cm^{-1} and a weak absorption around 1650 cm^{-1} attributed to the $\nu(C\equiv C)$ band of the ligated but-2-yne. This is at a considerably lower wavenumber compared with the band from uncoordinated but-2-yne, which is as expected since there is considerable back donation of electron density from filled metal d-type orbitals into empty π^*-orbitals on the but-2-yne. Compounds **6**–**8** also give a band around 1610 cm^{-1} attributed to the $\nu(C{=}O)$ of the bound (acac) or equivalent ligand.

The geometry of these complexes is likely to be similar to that found crystallographically for $[W(CO)(S_2CNEt_2)_2(\eta^2\text{-}HC_2H)]$ by McDonald *et al.* [11]. The two possible geometries are shown in Fig. 1(a) and (b); however, it is very difficult to distinguish between these two isomers without an X-ray structural determination. Several attempts were made to grow single crystals for X-ray crystallography of **1**–**8** without any success.

The ^{1}H NMR spectra all show the expected resonances in accord with the proposed geometry (Fig. 1) with the but-2-yne undergoing rapid propeller-like rotation at room temperature for **1**–**3**, **4**, **5** and **8**, whereas complexes **4** and **7** show two distinct methyl resonances at room temperature. Similarly, the ^{13}C NMR spectra show all the expected features consistent with the geometry (Fig. 1). The but-2-yne contact carbon resonances are all above 200 ppm, which indicates that the but-2-yne is donating four-electrons to the tungsten in these complexes [19].

3. Experimental details

The synthesis and purification of the compounds were carried out under dry nitrogen by standard Schlenk line techniques. The compound $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$ was prepared by the published method [17]. All chemicals used were purchased from commercial sources. The solvent CH_2Cl_2 was 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 a carrier gas). Infrared spectra were recorded on a Perkin–Elmer 1430 ratio recording infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 CP/MAS NMR spectrometer, with tetramethylsilane as a standard.

TABLE 4. ^{13}C NMR data [a] for selected complexes $[W(CO)(S_2CX)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ and $[W(CO)(O\text{-}O)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$

Compound	^{13}C NMR δ (ppm)
2	238.1 (s, $\mathit{C}\equiv\mathit{C}$); 212.46 (s, $\mathit{C}\equiv O$); 200.58 (s, $\mathit{C}S_2$); 197.6 (s, $\mathit{C}S_2$); 50.7 (s, $N\mathit{C}H_2$); 49.7 (s, $N\mathit{C}H_2$); 44.8 (s, $N\mathit{C}H_2$); 44.1 (s, $N\mathit{C}H_2$); 24.98 (s, $\mathit{C}H_2$); 20.36 (s, $\equiv C\mathit{Me}$); 12.77 (s, $\mathit{C}H_3$); 12.22 (s, $\mathit{C}H_3$)
3	238.1 (s, $\mathit{C}\equiv\mathit{C}$); 212.19 (s, $\mathit{C}\equiv O$); 197.6 (s, $\mathit{C}S_2$); 50.73 ($N\mathit{C}H_2$); 49.81 (s, $N\mathit{C}H_2$); 49.6 (s, $N\mathit{C}H_2$); 49.47 (s, $N\mathit{C}H_2$); 24.8 (s, $\mathit{C}H_2$); 24.87 (s, $\mathit{C}H_2$); 24.68 (s, $C\mathit{H}_2$); 24.48 (s, $\mathit{C}H_2$); 20.47 (s, $\equiv C\mathit{Me}$)
4	238.16 (s, $\mathit{C}\equiv\mathit{C}$): 237.22 (s, $\mathit{C}\equiv\mathit{C}$); 213.1 (s, $\mathit{C}\equiv O$); 203.58 (s, $\mathit{C}S_2$); 197.5 (s, $\mathit{C}S_2$); 138.47 → 127.93 (bm, Ph–*C*); 52.56 (s, $N\mathit{C}H_2$); 50.94 (s, $N\mathit{C}H_2$) 49.8 (s, $N\mathit{C}H_2$); 49.3 (s, $N\mathit{C}H_2$); 24.99 (s, $\mathit{C}H_2$); 24.67 (s, $\mathit{C}H_2$); 20.60 (s, $\equiv C\mathit{Me}$); 20.48 (s, $\equiv C\mathit{Me}$)
8	238.89 (s, $\mathit{C}\equiv\mathit{C}$); 210.1 (s, $\mathit{C}\equiv O$), 193.78 (s, $\mathit{C}S_2$); 183.3 (s, $\mathit{C}{=}O$); 181.0 (s, $\mathit{C}{=}O$); 138.3–126.9 (m, Ph–*C*); 97.32 (s, $\mathit{C}H$); 49.78 (s, $N\mathit{C}H_2$); 49.44 (s, $N\mathit{C}H_2$); 24.95 (s, $\mathit{C}H_2$); 24.30 (s, $\mathit{C}H_2$); 20.44 (s, $\equiv C\mathit{Me}$); 16.3 (s, $\mathit{C}H_3$)

[a] Spectra recorded in $CDCl_3$ (+25°C) referenced to $SiMe_4$. s = singlet, m = multiplet.

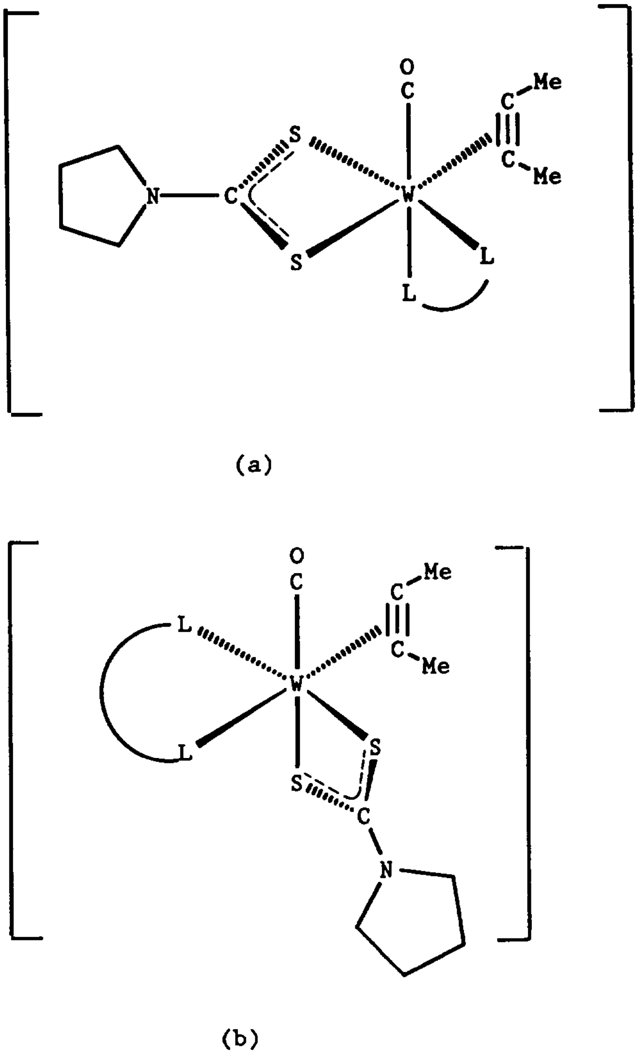

Fig. 1. Possible geometries for $[W(CO)(LL)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ (**1**–**8**).

3.1. $[W(CO)(S_2CNMe_2)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ (1)

To a stirred solution of $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$ (0.5 g, 0.841 mmol) in CH_2Cl_2 (20 cm^3) under a stream of dry dinitrogen was added $Na[S_2CNMe_2]\cdot 2H_2O$ (0.1506 g, 0.841 mmol). After 20 h stirring, the solution was filtered and the solvent volume reduced to 0.5 cm^3 *in vacuo*. Addition of diethyl ether and cooling yielded analytically pure green crystals of $[W(CO)(S_2CNMe_2)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ (**1**) (0.25 g, 69%).

Similar reactions of $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$ with an equimolar quantity of $Na[S_2CNEt_2]\cdot 3H_2O$, $[NH_4][S_2CNC_4H_8]$, $Na[S_2CN(CH_2Ph)_2]$ or $K[S_2COEt]$ in CH_2Cl_2 at room temperature afforded the analogous compounds $[W(CO)(S_2CX)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ (**2**–**5**) (see Table 1 for physical and analytical data).

3.2. $[W(CO)(CH_3COCHCOCH_3)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ (6)

To a stirred solution of $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$ (0.5 g, 0.841 mmol) in CH_2Cl_2 (20 cm^3) under a stream of dry dinitrogen was added Na[acac] (generated by the action of NaH on acac in thf) (0.1027 g, 0.841 mmol). After 20 h stirring, the solution was filtered to remove $Na[BF_4]$ and the solvent volume reduced to 0.5 cm^3. Addition of diethyl ether and cooling yielded analytically pure brown crystals of $[W(CO)(CH_3COCHCOCH_3)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ (**6**) (0.254 g, 59%).

Similar reactions of $[W(CO)(NCMe)(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)_2][BF_4]$ with an equimolar quantity $Na[CF_3COCHCOCF_3]$ and $Na[C_6H_5COCHCOCH_3]$ in CH_2Cl_2 at room temperature afforded the analogous neutral compounds $[W(CO)(\overset{\frown}{O\ O})(S_2CNC_4H_8)(\eta^2\text{-}MeC_2Me)]$ (**7**, **8**) (see Table 1 for physical and analytical data).

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References

1 J. L. Templeton, *Adv. Organomet. Chem.,*, *29* (1989) 1 and refs therein.
2 M. Green, *J. Organomet. Chem.*, , *300* (1986) 93 and refs. therein.
3 P. L. Watson and R. G. Bergman, *J. Am. Chem. Soc.*, *102* (1980) 2698.
4 J. L. Davidson and G. Vasapollo, *J. Chem. Soc., Dalton Trans.*, (1985) 2239.
5 P. B. Winston, S. J. N. Burgmayer, T. L. Tonker and J. L. Templeton, *Organometallics*, *5* (1986) 1707.
6 P. Umland and H. Vahrenkamp, *Chem. Ber.*, *115* (1982) 3580.
7 E. M. Armstrong, P. K. Baker and M. G. B. Drew, *J. Organomet. Chem.*, *336* (1987) 377.
8 J. W. McDonald, W. E. Newton, C. T. C. Creedy and J. L. Corbin, *J. Organomet. Chem.*, *92* (1975) C25.
9 J. L. Templeton, R. S. Herrick and J. R. Morrow, *Organometallics*, *3* (1984) 535.
10 B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc.*, *102* (1980) 1532.
11 L. Ricard, R. Weiss, W. E. Newton, G. J.-J. Chen and J. W. McDonald, *J. Am. Chem. Soc.*, *100* (1978) 1318.
12 M. A. Bennett and I. W. Boyd, *J. Organomet. Chem.*, *290* (1985) 165.
13 L. Carlton and J. L. Davidson, *J. Chem. Soc., Dalton Trans.*, (1988) 2071.
14 J. L. Davidson and G. Vasapollo, *J. Chem. Soc., Dalton Trans.*, (1988) 2855.
15 E. M. Armstrong, P. K. Baker and M. G. B. Drew, *Organometallics*, *7* (1988) 319.
16 E. M. Armstrong, P. K. Baker, K. R. Flower and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, (1990) 2535.
17 P. K. Baker, K. R. Flower, M. E. Harman and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1990) 3169.
18 E. M. Armstrong and P. K. Baker, unpublished results.
19 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, *102* (1980) 3288.