Inorganica Chimica Acta, 143 (1988) 13–14

Mono and Bisacetylacetonato But-2-yne Complexes of Tungsten(II)

ELAINE M. ARMSTRONG and PAUL K. BAKER*

Department of Chemistry, University College of North Wales, Bangor, Gwynedd LL57 2UW, U.K.

(Received September 29, 1987)

An abundance of mono and bisalkyne complexes of molybdenum(II) and tungsten(II) containing anionic bidentate sulphur donor ligands such as $[M(CO)(\eta^2\text{-}RC_2R')(S_2CNR_2'')_2]$ and $[M(\eta^2\text{-}RC_2R')_2(S_2CNR_2'')_2]$ (M = Mo or W; R,R′ = H, alkyl, aryl etc.; R″ = Me, Et, ^{i}Pr etc.) are known [1–6]. These complexes are generally prepared by reacting $[M(CO)_n(S_2CNR_2'')_2]$ (M = Mo or W; $n = 2$ or 3) with either one or two equivalents of RC_2R'. Hitherto only one bidentate anionic oxygen alkyne complex of molybdenum(II) or tungsten(II) has been reported [7], mainly due to the lack of availability of the precursors $[M(CO)_n(\widehat{OO})_2]$ (M = Mo or W; $\widehat{OO}$ = bidentate anionic oxygen donor ligand). The complex $[WCl(CO)_2(acac)(\eta^2\text{-}PhC_2OH)]$ was prepared [7] from photolysis of $[WCl(CO)_4(\eta^1\text{-}CC_6H_4Me\text{-}p)]$ with acetylacetone (Hacac). The hydroxy alkyne ligand in the product must result from coupling of the original carbyne ligand with a carbonyl group followed by a proton abstraction to give $[WCl(CO)_2(acac)(\eta^2\text{-}PhC_2OH)]$.

We have been investigating the chemistry of the highly versatile complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) [8]. In this communication we wish to report the reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with one equivalent of Na[acac] to give the new bisalkyne complex $[WI(CO)(acac)(\eta^2\text{-}MeC_2Me)_2]$ and an excess of Na[acac] to give the new monoalkyne complex $[W(CO)(acac)_2(\eta^2\text{-}MeC_2Me)]$.

Experimental

The compound $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ was prepared by the literature method [8]. All chemicals were purchased from commercial sources. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WH-400 MHz spectrometer at the University of Warwick (all spectra were calibrated against tetramethylsilane). Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer as $CHCl_3$ films between NaCl plates. Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas).

$[WI(CO)(acac)(\eta^2\text{-}MeC_2Me)_2]$ (1)

To a suspension of NaH (60% by weight in mineral oil) (0.034 g, 0.850 mmol) in Et_2O (5 cm^3) with continuous stirring under a stream of dry nitrogen was added $MeCOCH_2COMe$ (0.085 g, 0.850 mmol). After 5 min, the Et_2O was removed *in vacuo* and the Na[MeCOCHCOMe] resolvated in a 50% *v*/*v* MeOH/CH_2Cl_2 mixture (20 cm^3), to which was added $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (0.523 g, 0.850 mmol). Filtration and removal of solvent *in vacuo* after 17 h gave a green oil, which was recrystallized from CH_2Cl_2/Et_2O, affording a green powder. Yield 0.30 g, 65%.

Anal: $C_{14}H_{19}IO_3W$. Calc: C, 30.7; H, 3.5. Found: C, 30.8; H, 3.7%. IR: ν(C≡O) 2025(vs), ν(C=O) 1818(br, s), ν(C≡C) 1740(vw) cm^{-1}. NMR: ^{1}H{$(CD_3)_2CO$, +25 °C}: δ(ppm) = 5.53 (s, 1H, C*H*); 2.89 (s, 12H, *Me*C_2); 2.45 (s, 6H, *Me*). ^{13}C{$(CD_3)_2CO$, +25 °C}: δ(ppm) = 218.88 (s, *C*≡O); 192.61 (s, *C*=O); 189.26 (d, *C*=O); 186.02 (s, *C*≡C); 158.52 (s, *C*≡C); 103.99 (s, *C*H); 28.78 (s, Me); 28.59 (s, *Me*); 26.43 (s, *Me*C_2); 24.05 (s, C_2*Me*).

$[W(CO)(acac)_2(\eta^2\text{-}MeC_2Me)]$ (2)

To a suspension of NaH (0.095 g, 2.375 mmol) in Et_2O (5 cm^3) with continuous stirring under a stream of dry nitrogen was added $MeCOCH_2COMe$ (0.243 g, 2.375 mmol). After 5 min the Et_2O was removed *in vacuo*, and the Na[MeCOCHCOMe] resolvated in 50% *v*/*v* MeOH/CH_2Cl_2 mixture (20 cm^3) to which was added $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (0.500 g, 0.813 mmol). Filtration and removal of solvent *in vacuo* after 17 h yielded an orange–yellow powder which was recrystallised from CH_2Cl_2. Yield 0.22 g, 58%.

Anal: $C_{15}H_{20}O_5W$. Calc: C, 38.8; H, 4.3. Found: C, 38.9; H, 4.7%. IR: ν(C≡O) 1880(vs), ν(C=O) 1826(br, s), ν(C≡C) 1640(vw) cm^{-1}. NMR: ^{1}H{$(CD_3)_2CO$, +25 °C}: δ(ppm) = 5.57 (s, 1H, C*H*) 5.44 (s, 1H, C*H*); 3.15 (s, 6H, *Me*C_2); 2.35 (s, 6H, *Me*); 2.15 (s, 6H, *Me*). ^{13}C{$(CD_3)_2CO$, +25 °C}: δ(ppm) = 242.87 (s, *C*≡*C*); 209.82 (s, *C*≡*O*); 194.62 (s, *C*=O); 187.60 (m, *C*=O); 100.84 (m, *C*H); 28.18 (d, *Me*); 26.47 (s, *Me*C_2).

Results and Discussion

Equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ and Na[acac] (generated *in situ* from acetylacetone and sodium hydride) react in a 50% *v*/*v* CH_2Cl_2/CH_3OH mixture at room temperature to give

---

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50

a good yield of the new monoacetylacetonato complex $[WI(CO)(acac)(\eta^2\text{-}MeC_2Me)_2]$ (**1**). Reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with an excess of Na[acac] in a 50% *v*/*v* CH_2Cl_2/CH_3OH mixture at room temperature afforded a good yield of the new bisacetylacetonato compound $[W(CO)(acac)_2(\eta^2\text{-}MeC_2Me)]$. Both complexes have been fully characterised by elemental analysis (C, H and N), IR, ^1H and ^{13}C NMR spectroscopy (see 'Experimental'). The complexes are moderately stable in the solid state for a few hours at 0 °C under nitrogen. However, they decompose rapidly in solution when exposed to air. They are soluble in $CHCl_3$ and CH_2Cl_2 and insoluble in diethylether and hydrocarbon solvents.

In view of the X-ray crystal structures determined for both the complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) [8] it is likely that the structure of $[WI(CO)(acac)(\eta^2\text{-}MeC_2Me)_2]$ (**1**) has both alkyne ligands *cis* and parallel to each other with the acac ligand occupying the sites by the acetonitrile and an iodide ligand in $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$. Hence the proposed structure for **1** is given in Fig. 1. However, further studies are in progress to attempt to grow crystals of bidentate anionic oxygen complexes of the types $[WI(CO)(\overset{\frown}{OO})(\eta^2\text{-}RC_2R)_2]$ and $[W(CO)(O\ O)_2(\eta^2\text{-}RC_2R)]$ ($\overset{\frown}{OO}$ = anionic oxygen donor ligand; R = Me or Ph).

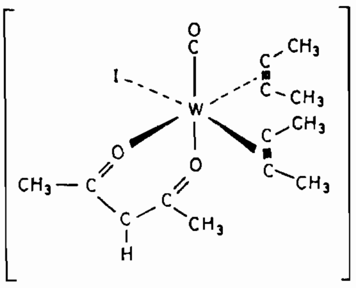

Fig. 1. Proposed structure for $[WI(CO)(acac)(\eta^2\text{-}MeC_2Me)_2]$.

The ^1H NMR spectra of **1** and **2** showed the expected features for the complexes. Ward and Templeton [9] have correlated the values of ^{13}C alkyne contact carbon (C≡C) chemical shifts with the average number of electrons donated to the metal. The ^{13}C NMR spectrum of **1** has alkyne contact carbon resonances at $\delta = 186.02$ and 158.52 ppm which indicates that both alkyne ligands in **1** are donating a total of six electrons to the tungsten. However, the but-2-yne ligand in **2** has an alkyne contact carbon resonance at $\delta = 242.87$ ppm, which suggests that the but-2-yne ligand in **2** is donating four electrons to the tungsten. The number of electrons donated by the alkyne ligands in **1** and **2** discussed above allow both complexes to obey the effective atomic number rule.

Acknowledgements

We wish to thank Dr. O. W. Howarth for running the ^1H and ^{13}C NMR spectra at the University of Warwick and we also thank the SERC for support.

References

1 J. W. McDonald, W. E. Newton, C. T. C. Creedy and J. L. Corbin, *J. Organomet. Chem., 92,* C25 (1975).

2 B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc., 102,* 1532 (1980).

3 J. L. Templeton, R. S. Herrick and J. R. Morrow, *Organometallics, 3,* 535 (1984).

4 M. A. Bennett and I. W. Boyd, *J. Organomet. Chem., 290,* 165 (1985).

5 R. S. Herrick and J. L. Templeton, *Organometallics, 1,* 842 (1982).

6 J. R. Morrow, T. L. Tonker and J. L. Templeton, *J. Am. Chem. Soc., 107,* 5004 (1985).

7 E. O. Fischer and P. Friedrich, *Angew. Chem., Int. Ed. Engl., 18,* 327 (1979).

8 E. M. Armstrong, P. K. Baker and M. G. B. Drew, *Organometallics,* 1988, in press.

9 B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc., 102,* 3288 (1980).