Inorganica Chimica Acta, 165 (1989) 241–243

Reactions of the Cationic Monobut-2-yne Complex $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ {dppm = $Ph_2P(CH_2)PPh_2$} with Carbon Monoxide and ^{t}Butylisonitrile

PAUL K. BAKER* and KEVIN R. FLOWER

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

(Received May 23, 1989; revised July 19, 1989)

Abstract

The compound $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ reacts with carbon monoxide and ^{t}butylisonitrile in CH_2Cl_2 at room temperature to give the substituted products $[WI(CO)_2(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (1) and $[WI(CO)(CN^tBu)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (2) in good yield. The new complexes were fully characterised by elemental analysis, infrared, ^1H and ^{13}C NMR spectroscopy. ^{13}C NMR spectroscopy suggests that the but-2-yne ligand is donating four electrons to the tungsten in these complexes.

Introduction

Since the 1960s alkyne complexes of molybdenum and tungsten have received considerable attention [1–15]. In recent years we have been studying the chemistry of the bisalkyne tungsten complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me and Ph) [16]. These complexes are prepared by reacting the seven-coordinate complex $[WI_2(CO)_3(NCMe)_2]$ with RC_2R in CH_2Cl_2. The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ react with a wide range of neutral and anionic donor ligands. For example, the complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ react with 2L {L = PMe_3, PEt_3, P^nBu_3, PMe_2Ph, $PMePh_2$, PEt_2Ph, $PEtPh_2$, $PPh_2(CH_2CH{=}CH_2)$, (PPh_3 and PPh_2Cy for R = Me only); $L_2 = Ph_2P(CH_2)_nPPh_2$ (n = 1–4 and 6) or $[Fe(\eta^5\text{-}C_5H_4PPh_2)_2]$ for R = Me only} in CH_2Cl_2 at room temperature to afford the highly coloured monoalkyne complexes of the type $[WI_2(CO)L_2(\eta^2\text{-}RC_2R)]$ in good yield [17]. We have very recently reported the preparation of the cationic alkyne complexes of the type $[WI(CO)(NCMe)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)][BF_4]$ (n = 1–6; R = Me and Ph) from reaction of $[WI_2(CO)\{Ph_2P(CH_2)_nPPh_2\}(\eta^2\text{-}RC_2R)]$ with an equimolar quantity of $Ag[BF_4]$ in acetonitrile [18]. In this paper we describe the reactions of the bis(diphenylphosphino)methane cationic monobut-2-yne complex $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ {dppm = $Ph_2P(CH_2)PPh_2$} with carbon monoxide and ^{t}butylisonitrile.

Experimental

All reactions described in this paper were carried out using standard vacuum/Schlenk line techniques. The cationic monobut-2-yne complex $[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ was prepared by the published method [18]. All chemicals were purchased from commercial sources. CH_2Cl_2 was dried and distilled before use.

Microanalyses (C, H and N) were determined 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 (both spectra were run as thin films in $CHCl_3$ between NaCl plates). ^1H and ^{13}C NMR were recorded on a Bruker AC 250 CP/MAS NMR spectrometer (all spectra were calibrated against tetramethylsilane).

$[WI(CO)_2(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (1)

$[WI(CO)(NCMe)(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (0.5 g, 0.552 mmol) was dissolved in CH_2Cl_2 (20 cm^3) with continuous stirring under a stream of dry nitrogen. CO (generated by the action of conc. H_2SO_4 on formic acid) was vigorously bubbled through the solution for 6 h. Filtration, reduction of the solvent volume to 2 cm^3 *in vacuo*, followed by dropwise addition of Et_2O precipitated the brown cationic complex $[WI(CO)_2(dppm)(\eta^2\text{-}MeC_2Me)][BF_4]$ (1), which was recrystallised from CH_2Cl_2/Et_2O, yield 0.31 g, 63%. *Anal.* Calc. for $C_{31}H_{28}O_2P_2I_1W_1B_1F_4$: C, 41.7; H, 3.2. Found: C, 41.6; H, 3.3%. ^1H NMR (+25 °C, $CDCl_3$) 7.43 (bm, 20H, *Ph*); 4.25 (bm, 2H, *CH₂*); 3.30 (s, 6H, $\equiv CMe$). ^{13}C NMR (+25 °C, $CDCl_3$) 222.92 (s, $C\equiv C$); 205.58 (s, $C\equiv O$); 134.82–129.3 (m, *Ph*); 32.63 (t, CH_2, J_{PC} = 27.5 Hz); 20.36 (s, $\equiv CMe$). IR ($CHCl_3$ film): $\nu(C\equiv O)$ 1985(s), and 1975(s) cm^{-1}; $\nu(C\equiv C)$ 1635(vw) cm^{-1}.

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

[WI(CO)(CN^{t}Bu)(dppm)(η^2-MeC$_2$Me)][BF$_4$] (2)

To [WI(CO)(NCMe)(dppm)(η^2-MeC$_2$Me)] [BF$_4$] (0.5 g, 0.552 mmol) dissolved in CH_2Cl_2 (20 cm^3) with continuous stirring under a stream of dry nitrogen was added CN^{t}Bu (0.0459 g, 0.552 mmol). After the solution had been stirring for 3 h it was filtered and the solvent volume reduced to 2 cm^3 *in vacuo*. Dropwise addition of Et_2O precipitated the cationic red–brown complex [WI(CO)(CN^{t}Bu)(dppm)(η^2-MeC$_2$Me)] [BF$_4$] (**2**), which was recrystallised from CH_2Cl_2/Et_2O, yield 0.32 g, 62%. *Anal.* Calc. for $C_{35}H_{37}N_1O_1P_2I_1W_1B_1F_4$: C, 44.4; H, 3.9; N, 1.5. Found: C, 44.6; H, 3.9; N, 1.5%. ^{1}H NMR (+25 ℃. $CDCl_3$) 7.35 (bm, 20H, *Ph*); 4.52 (bm, 2H, CH_2); 3.30 (s, 6H, ≡C*Me*); 2.2 (s, 9H, CH_3). ^{13}C NMR (+25 ℃, $CDCl_3$) 221.99 (s, *C*≡C), 205.27 (s, *C*≡O); 180.4 (s, *C*≡N); 133.59–129.75 (m, *Ph*); 59.8 (s, C≡N*C*); 32.15 (t, *C*H$_2$, J_{pc} = 21.9 Hz); 30.12 (s, C*Me*$_3$); 20.58 (s, ≡C*Me*). IR ($CHCl_3$ film) ν(C≡N), 2200(m) and 2150(w) cm^{-1}, ν(C≡O) 1995(s) cm^{-1} and ν(C≡C), 1645(vw) cm^{-1}

Results and Discussion

Carbon monoxide when bubbled through a CH_2Cl_2 solution of [WI(CO)(NCMe)(dppm)(η^2-MeC$_2$Me)] [BF$_4$] afforded the new acetonitrile displaced product [WI(CO)$_2$(dppm)(η^2-MeC$_2$Me)] [BF$_4$] (**1**) in good yield. The dicarbonyl complex **1** was fully characterised by elemental analysis (C, H and N), infrared, ^{1}H and ^{13}C NMR spectroscopy (see 'Experimental'). The complex is stable in the solid state when stored under nitrogen, however it decomposes in air, particularly in solution, and is soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$, but as expected since it is a salt it is insoluble in diethylether and hydrocarbon solvents.

The infrared spectrum shows two carbonyl bands at 1985 and 1975 cm^{-1}, which suggests a *cis*-dicarbonyl structure. The structure of **1** is likely to have the iodide ligand *trans* to the but-2-yne ligand since the X-ray crystal structure of the closely related triisopropylphosphite [18] and thiourea [19] containing cationic complexes [WI(CO)L(dppm)(η^2-MeC$_2$Me)]$^+$ {L = P(O^{i}Pr)$_3$ [18] and SC(NH$_2$)$_2$ [19]} have been determined and have this arrangement of ligands. Hence, the structure of **1** will have the two *cis*-carbonyls and bis(diphenylphosphino)methane ligand in the equatorial plane as shown in Fig. 1.

The room temperature ^{1}H NMR spectrum of **1** shows only a single resonance for the but-2-yne methyl groups which may be due to rapid rotation of the but-2-yne ligand at room temperature (faster than the NMR time scale). This fluxional behaviour of a coordinated but-2-yne ligand has been previously observed by other workers [8, 11, 13, 14 and 17–19] for monobut-2-yne complexes of molybdenum(II) or tungsten(II). However, the equivalence of the but-2-yne methyl groups in **1** could result from a static structure if the but-2-yne plane is oriented with the bisdiphenylphosphinomethane ligand on one side and the two carbon monoxide ligands on the other, i.e. perpendicular to the structure shown in Fig. 1. The ^{13}C NMR spectrum for **1** shows a single resonance at δ = 222.92 ppm which suggests [20] the but-2-yne is utilizing both of its filled pπ-orbitals and is donating four electrons to the metal.

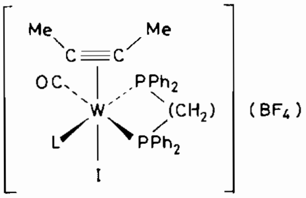

Fig. 1. Proposed structure of the complexes [WI(CO)L(dppm)(η^2-MeC$_2$Me)] [BF$_4$] (L = CO or CN^{t}Bu).

Equimolar quantities of [WI(CO)(NCMe)(dppm)(η^2-MeC$_2$Me)] [BF$_4$] and CN^{t}Bu react in CH_2Cl_2 to afford the mono-^{t}butylisonitrile complex [WI(CO)(CN^{t}Bu)(dppm)(η^2-MeC$_2$Me)] [BF$_4$] (**2**) via displacement of the labile acetonitrile ligand. Complex **2** was characterised by elemental analysis (C, H and N), IR, ^{1}H and ^{13}C NMR spectroscopy (see 'Experimental'). The complex is stable when stored under nitrogen, and is considerably more soluble than the dicarbonyl complex **1**.

The infrared spectrum of **2** as expected shows a single carbonyl band at ν(CO) = 1995 cm^{-1}, nitrile bands ν(C=N) at 2200 and 2150 cm^{-1}. Complex **2** also shows a weak ν(C≡C) band at 1645 cm^{-1} which is at a considerably lower wavenumber compared to free but-2-yne and hence suggests that electron density is being donated from filled metal orbitals to empty π*-orbitals of the but-2-yne. The structure of **2** is likely to be similar to **1** (see Fig. 1).

The room temperature ^{1}H NMR spectrum of **2** shows a single but-2-yne resonance at δ = 3.30 ppm, which suggests rapid but-2-yne rotation at room temperature, since a static structure for **2** does not allow equivalence of the but-2-yne methyl groups. The ^{13}C NMR spectrum of **2** has a low field alkyne contact carbon resonance at δ = 221.99 ppm suggesting [20] the but-2-yne ligand is acting as a four-electron donor.

We are currently studying the reactions of **1** and **2** with nucleophiles since in recent years Green and co-workers [6, 8, 21] have developed a wide range of new organotransition-metal chemistry from reactions of their related cationic alkyne complexes [Mo(CO)(η^2-RC$_2$R')$_2$(η^5-C$_5$H$_5$ or C$_9$H$_7$)] [BF$_4$] and their derivatives with nucleophiles.

Acknowledgement

We wish to thank the S.E.R.C. for support.

References

1 D. P. Tate and J. M. Augl, *J. Am. Chem. Soc., 84* (1963) 2174.
2 R. B. King, *Inorg. Chem., 7* (1968) 1044.
3 R. M. Laine, R. E. Moriarty and R. Bau, *J. Am. Chem. Soc., 94* (1972) 1402.
4 J. L. Davidson and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.*, (1975) 2531.
5 J. A. K. Howard, R. F. D. Stansfield and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1976) 246.
6 M. Bottrill and M. Green, *J. Chem. Soc., Dalton Trans.*, (1977) 2365.
7 L. Ricard, R. Weiss, W. E. Newton, G. J.-J. Chen and J. W. McDonald, *J. Am. Chem. Soc., 100* (1978) 1318.
8 S. R. Allen, P. K. Baker, S. G. Barnes, M. Green, L. Trollope, L. M. Muir and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, (1981) 873.
9 J. W. Faller and H. H. Murray, *J. Organomet. Chem., 172* (1979) 171.
10 P. L. Watson and R. G. Bergman, *J. Am. Chem. Soc., 102* (1980) 2698.
11 H. G. Alt, M. E. Eichner and B. M. Jansen, *Angew. Chem., Int. Ed. Engl., 21* (1982) 861.
12 R. S. Herrick and J. L. Templeton, *Organometallics, 1* (1982) 842.
13 J. L. Davidson and G. Vasapollo, *J. Chem. Soc., Dalton Trans.*, (1985) 2239.
14 P. B. Winston, S. J. N. Burgmayer, T. L. Tonker and J. L. Templeton, *Organometallics, 5* (1986) 1707.
15 A. Mayr, K. S. Lee, M. A. Kjelsberg and D. Van Engen, *J. Am. Chem. Soc., 108* (1986) 6079.
16 E. M. Armstrong, P. K. Baker and M. G. B. Drew, *Organometallics, 7* (1988) 319.
17 E. M. Armstrong, P. K. Baker, M. E. Harman and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1989) 295.
18 P. K. Baker, K. R. Flower, M. G. B. Drew and G. Forsyth, *J. Chem. Soc., Dalton Trans.*, (1989) 1903.
19 P. K. Baker, K. R. Flower, P. A. Bates and M. B. Hursthouse, *J. Organomet. Chem., 372* (1989) 263.
20 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc., 102* (1980) 3288.
21 M. Green, *J. Organomet. Chem., 300* (1986) 93, and refs. therein.