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Reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) with NCPh to Give the Acetonitrile Substituted Products $[WI_2(CO)(NCPh)(\eta^2\text{-}RC_2R)_2]$

ELAINE M. ARMSTRONG and PAUL K. BAKER*

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

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During the past ten years or so there has been a large increase in the number of molybdenum(II) and tungsten(II) alkyne complexes known. Some examples include: $[MX(CO)(\eta^2\text{-}PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W; X = Cl, Br or I) [1]; $[M(SR)(CO)(\eta^2\text{-}R'C_2R')(\eta^5\text{-}C_5H_5)]$ (R = CF_3 or Ph; R' = Me, CF_3 or Ph) [2]; $[W(CO)(\eta^2\text{-}RC_2R)(S_2CNR_2)_2]$ (R = alkyl or aryl) [3]; $[Mo(CO)L(\eta^2\text{-}RC_2R')(\eta^5\text{-}C_5H_5)][BF_4]$ (L = CO, $P(OPh)_3$, PEt_3 or PPh_3; R = R' = H, Me or Ph; R = H, R' = Ph) [4]; $[MoLL'(\eta^2\text{-}RC_2R')(\eta^5\text{-}C_5H_5)][BF_4]$ (L,L' = CO and PR_3; L = L' = $P(OMe)_3$; R,R' = Me, Ph etc.) [5]; $[WI_2(CO)_2L(\eta^2\text{-}PhC_2H)]$ (L = PMe_3, $AsMe_3$ or $CNBu^t$) [6], $[W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R')_2]_2$ (R = R' = Me, Et or Ph; R = Me, R' = Ph) [7]; $[MX_2(CO)L_2(\eta^2\text{-}RC_2R')]$ (M = Mo or W; X = Cl or Br; L = PPh_3, PEt_3 or py; L_2 = $Ph_2P(CH_2)_2PPh_2$) [8].

In recent years 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) [9]. In this communication we wish to describe the reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with NCPh to give the acetonitrile substituted products $[WI_2(CO)(NCPh)(\eta^2\text{-}RC_2R)_2]$.

Experimental

The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) were prepared according to the literature method [9]. All chemicals were purchased from commercial sources. Dichloromethane was distilled before use. ^1H and ^{13}C NMR spectra were recorded on a Jeol FX60 NMR spectrometer (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).

$[WI_2(CO)(NCPh)(\eta^2\text{-}MeC_2Me)_2]$ (1)

To $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (0.500 g, 0.813 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring under a stream of dry nitrogen was added NCPh (0.168 g, 1.629 mmol). After stirring the solution for 17 h, filtration, removal of solvent *in vacuo* and washing with 30 cm^3 of diethylether gave yellow crystals of $[WI_2(CO)(NCPh)(\eta^2\text{-}MeC_2Me)_2]$, which were recrystallized from CH_2Cl_2. Yield = 0.22 g, 40%. *Anal.* Calc. for $C_{16}H_{17}NO_2I_2W$: C, 28.4; H, 2.5; N, 2.1. Found: C, 28.4; H, 2.6; N, 2.4%. IR: $\nu(N\equiv C)$, 2290(w), 2200(w) cm^{-1}; $\nu(C\equiv O)$, 2075(s) cm^{-1}; $\nu(C\equiv C)$, 1652(w) cm^{-1}. NMR: ^1H ($CDCl_3$, +25 °C): δ (ppm) = 8.03 (brm, 2H, *o-Ph*); 7.79 (brm, 2H, *m-Ph*); 7.58 (brs, 1H, *p-Ph*); 2.89 (s, 12H, *Me*C_2). ^{13}C ($CDCl_3$, +25 °C): δ(ppm) = 205.58 (s, *C*O); 166.85, 156.07 (s, *C*≡*C*); 135.28 (s, *i-Ph*); 132.94 (s, *o-Ph*); 129.69 (s, *m-Ph*); 129.04 (s, *p-Ph*); 109.55 (s, *C*N); 19.88 (s, *Me*C_2); 16.11 (s, C_2*Me*).

$[WI_2(CO)(NCPh)(\eta^2\text{-}PhC_2Ph)_2]\cdot O(CH_2CH_3)_2$ (2)

To $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ (0.500 g, 0.579 mmol) dissolved in CH_2Cl_2 (15 cm^3) was added NCPh (0.120 g, 1.164 mmol). After stirring the solution for 17 h, filtration, removal of the solvent *in vacuo* and washing with 60 cm^3 of $O(CH_2CH_3)_2$ gave dark yellow crystals of $[WI_2(CO)(NCPh)(\eta^2\text{-}PhC_2Ph)_2]\cdot O(CH_2CH_3)_2$ which were recrystallized from CH_2Cl_2. Yield = 0.46 g, 86%. *Anal*: Calc. for $C_{40}H_{35}NO_2I_2W$: C, 48.1; H, 3.5; N, 1.4. Found: C, 48.0; H, 2.9; N, 1.4%. IR: $\nu(N\equiv C)$, 2345(w), 2290(w) cm^{-1}; $\nu(C\equiv O)$, 2100(s) cm^{-1}; $\nu(C\equiv C)$, 1650(w) cm^{-1}. ^1H ($CDCl_3$, +25 °C) NMR δ (ppm) = 7.42 (brm, 25H, *Ph*C_2 and NC*Ph*); 4.3 (q, *J* = 10.2 Hz, 4H, O*CH*$_2$); 1.25 (t, *J* = 7.6 Hz, 6H, O CH_2*CH*$_3$).

Results and Discussion

The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) and an excess of NCPh react in CH_2Cl_2 at room temperature to give the new complexes $[WI_2(CO)(NCPh)(\eta^2\text{-}RC_2R)_2]$ by substitution of the acetonitrile ligand. Both complexes have been fully characterized by elemental analysis (C, H and N), IR and ^1H NMR spectroscopy (see 'Experimental'). The bisdiphenylacetylene complex $[WI_2(CO)(NCPh)(\eta^2\text{-}PhC_2Ph)_2]\cdot O(CH_2CH_3)_2$ was confirmed as a diethylether solvate from repeated elemental analyses and ^1H NMR spectroscopy. The complexes are stable in the solid state when stored under nitrogen at 0 °C, and only slowly decompose in solution when exposed to air. They are soluble in $CHCl_3$ and CH_2Cl_2 and only slightly soluble in diethylether.

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*Author to whom correspondence should be addressed.

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The reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with NCPh are likely to proceed via an associative mechanism whereby the NCPh becomes coordinated to give the seven-coordinate intermediate $[WI_2(CO)(NCMe)(NCPh)(\eta^2\text{-}RC_2R)_2]$. The alkyne ligands can rearrange their mode of bonding from supplying a total of six electrons as in $[WI_2(CO)(NCPh)(\eta^2\text{-}RC_2R)_2]$ (see later in the paper) to both alkynes being two electron donors. The acetonitrile ligand can then be lost to give the observed products. Evidence to support this associative mechanism comes from the fact that the complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ do not lose acetonitrile to give the iodide-bridged dimers $[W(\mu\text{-}I)I(CO)(\eta^2\text{-}RC_2R)_2]_2$ even after refluxing in $CHCl_3$ for 24 h [9].

Since the spectral properties of the complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ and $[WI_2(CO)(NCPh)(\eta^2\text{-}RC_2R)_2]$ are very similar the structures of the benzonitrile complexes are likely to be comparable to the acetonitrile complexes which have been determined by X-ray crystallography [9]. Hence the proposed structure of **1** and **2** is given in Fig. 1.

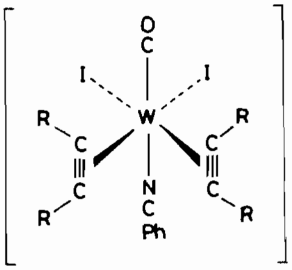

Fig. 1. Proposed structure for $[WI_2(CO)(NCPh)(\eta^2\text{-}RC_2R)_2]$.

Complexes **1** and **2** both have single carbonyl bands in their IR spectra of slightly higher wavenumber than their acetonitrile counterparts. This was expected since NCPh is a slightly poorer σ-donor and better π-acceptor ligand than NCMe. The alkyne (C≡C) stretching bands at 1652 and 1650 cm^{-1} for **1** and **2** respectively are considerably lower than for the 'free' alkyne ligands. Hence there is considerable back donation of electron density from filled metal d-orbitals to empty π*-orbitals upon coordination of these alkyne ligands.

The ^1H NMR spectra of **1** and **2** showed the expected features for the structures shown in Fig. 1. The ^{13}C NMR spectrum of **1** showed alkyne carbon (C≡C) resonances at $\delta = 166.85$ and 156.07 ppm. These values suggest that the two alkyne ligands in **1** donate a total of six electrons to the metal, since Templeton and Ward [10] have correlated the values of ^{13}C alkyne contact carbon chemical shifts with the average number of electrons donated to the metal, *i.e.* in **1** and **2** it is three electrons from each alkyne ligand. However, it is very likely that one alkyne ligand is donating four electrons and the other two electrons with rapid exchange between these resonance hybrids (faster than the NMR time scale) hence it appears that each alkyne is donating the same number of electrons, *i.e.* three, to the tungsten centre.

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References

1 J. L. Davidson and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.*, 2531 (1975).
2 J. A. K. Howard and R. F. D. Stansfield, *J. Chem. Soc., Dalton Trans.*, 246 (1976).
3 L. Ricard, R. Weiss, W. E. Newton, G.J.-J. Chen and J. W. McDonald, *J. Am. Chem. Soc., 100,* 1318 (1978).
5 K. Sünkel, U. Nagel and W. Beck, *J. Organomet. Chem., 222,* 251 (1981).
5 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.*, 873 (1981).
6 P. Umland and H. Vahrenkamp, *Chem. Ber., 115,* 3580 (1982).
7 J. L. Davidson and G. Vasapollo, *J. Chem. Soc., Dalton Trans.*, 2239 (1985).
8 P. B. Winston, S. J. N. Burgmayer, T. L. Tonker and J. L. Templeton, *Organometallics, 5,* 1707 (1986).
9 E. M. Armstrong, P. K. Baker and M. G. B. Drew, *Organometallics,* (1988), in press.
10 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc., 102,* 3288 (1980).