COMMUNICATION

COORDINATIVELY UNSATURATED ALKYNE COMPLEXES: SYNTHESIS OF MONO AND BIS-ALKYNE COMPLEXES OF TUNGSTEN (II)

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Summary. $[WBr_2(CO)_{l_{j_n}}]_n$ reacts with alkynes to give complexes $[WBr_2CO(RC\equiv CR)_2]_2$ (1) (R = R' = Me, Et, Ph; R = Me, R' = Ph), which react with nucleophiles L{L = CN Bu^t, PPh₃, or P(OMe)₃} to give monoalkyne derivatives $[WBr_2(CO)(RC\equiv CR')L_2](2)$. An intermediate bis-alkyne adduct $[WBr_2CO(MeC\equiv CMe)_2(CNBu^t)]$ (3) was isolated in the reaction of $[WBr_2(CO)(MeC\equiv CMe)_2]_2$ with CNBu^t illustrating that cleavage of the dimer(1) is the first stage in these reactions.

In recent years it has become clear that alkyne ligands can involve both sets of filled π -orbitals in bonding with a transition metal and thus stabilise coordinative unsaturation^{1,2}. This phenomenon is particularly pronounced in divalent molybdenum and tungsten, (d⁴), complexes containing one or two coordinated alkyne ligands. Following recent indications that 4-electron donation may lead to activation of a coordinated alkyne towards nucleophilic rather than electrophilic attack, ^{2a,b,3} we now report the synthesis of new alkyne complexes of W(II) and their reactions with nucleophiles.

Reactions of $[WBr_2(CO)_{4}]_{n}$ with alkynes RCECR' (R = R' = Me, Et, Ph: R = Me, R' = Ph) in hexane at 20°C give good yields of alkyne complexes $[WBr_2CO(RCECR)_2]_{n}$ which according to molecular weight studies in solution are dimeric i.e. n = 2. However the mass spectra in each case only gives identifiable peaks due to mononuclear fragments $[P/2 = CO]_{n}^{+}[P/2 - (CO + RCECR')]_{n}^{+}[P/2 - (CO + Br)]^{+}$ although very weak dinuclear ions were observed in some cases. Spectroscopic data : e.g. $[WBr_2(CO)(MeCECMe)_2]_2$; i.r., (CCl_4) , 2098 cm⁻¹, wm, 2060 cm⁻¹, vs; ¹H nmr., $\delta 2.96(s, 6H) 2.33(s, 6H)$. The two ¹H nmr resonances suggest two sets of inequivalent alkynes or that all four alkynes are equivalent but the two substituents are magnetically non-equivalent and on this basis structures (la) or (lb) are proposed. However, since alkynes are able to function as ⁴-electron donors an alternative structure to (l) without a metal-metal double bond is equally plausible. Interestingly CF_3CECCF_3 and $[WBr_2(CO)_4]_n$ give a mononuclear complex $[WBr_2CO(CF_3CECF_3)_2]$ under similar reaction conditions^{2b} while $[Mo(SBu^{t})_2(CNBu^{t})_4]$ reacts with alkynes to give $[Mo(SBu^{t})_2(CNBu^{t})_2 (RCECR)] (R = H, Ph)^3$.

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Mononuclear complexes $[WBr_2CO(RC \equiv CR)L_2]$, (2) were readily obtained from reactions of (1) with nucleophiles L = PFh₃, P(OMe)₃ or CNBu^t and in one case an intermediate bis alkyne complex $[WBr_2CO(MeC \equiv CMe)_2(CNBu^t)]$ (3), was also isolated. Spectroscopic data: $[WBr_2CO(MeC \equiv CMe)_2(CNBu^t)]$; i.r. $(CHCl_3)$, $vC \equiv N \ 2218 \ cm^{-1}s$. vCO 2092 $cm^{-1}vs$; ¹H nmr $(CDCl_3)$, $\delta 2.93$ (q, J = 0.79 Hz, 6H), 2.89 (q, J = 0.79 Hz, 6H), 1.80 (s 9H); mass spectrum-highest peak $[WBr_2(MeC_2Me)_2]^{+}$. The presence of CH_3-CH_3 coupling in the ¹H nmr spectrum indicates inequivalence of the CH_3 groups at either end of each acetylene rather than inequivalent acetylene ligands and structure (3) is therefore proposed. Structures with *trans* alkynes are also possible but six-coordinate bis alkyne d⁴ metal complexes appear to prefer *cis* alkyne ligands^{2a}.



(3)

Spectroscopic data: $[WBr_2CO(MeC \equiv CMe)(CNBu^{t})_2]$ i.r. $(CHCl_3)$, $vC \equiv N \ 2194$ s, 2160 cm⁻¹s; $vCO \ 2002 \ cm^{-1}vs$, ¹H nmr δ 3.16 (s, 6H), 1.74 (s, 9H), 1.36 (s, 9H) mass spectrum decomposition observed in the probe. The ¹H nmr spectrum of $[WBr_2CO(MeC \equiv CMe)(CNBu^{t})_2]$ indicates two inequivalent isocyanide ligands and a single acetylenic CH₃ resonance in accord with *cis* CNBu^t groups. ¹H and ³¹P nmr spectra of $[WBr_2CO(RC \equiv CR'){P(OMe)_3}_2]$ similarly suggest *cis* phosphite ligands with R = R' = Me. Spectroscopic data: ¹H nmr: $\delta = 3.9^4$ (d, $J_{P-H} = 9.81$ Hz, 9H) 3.47 (d, $J_{P-H} = 10.46$ Hz, 9H) 3.03 (d, $J_{P-H} = 1.77, 6H$); ${}^{31}P[^{1}H]$ 119.95 (AB quartet), but trans P(OMe)₃ ligands with R = R' = Ph ${}^{1}H$ nmr δ 7.75 (m, 4H), 7.48 (m, 6H), 3.61 (t, $J_{P-H} = 5.42$ Hz, 18H); ${}^{31}P[^{1}H]$, δ 117.96 (s). However monitoring of the spectra of [WBr₂CO(MecECMe){P(OMe)₃}₂ lrevealed that isomerisation of the kinetic *cis* isomer occurs to a more stable trans form: ${}^{1}H$ nmr δ 3.66 (t, $J_{P-H} = 5.38$ Hz, 18H), 3.14 (t, $J_{P-H} = 1.59$ Hz, 6H); ${}^{31}P[^{1}H]$, δ 120.03 (s). Variable temperature ${}^{1}H$ nmr spectra also revealed that the CH₃CECCH₃ doublet δ 3.03 of the *cis* isomer splits into two equal intensity multiplets at low temperatures (T. coalescence = 14°C) whereas no change is observed in the spectrum of the *trans* isomer down to -85° C. This suggests propeller rotation of the alkyne ligand but with significantly higher barriers to rotation in the *cis* isomer. Such a conclusion is based on the proposal that in both isomers the alkyne should be in an asymmetric environment as in the illustrated structures (2a,b,c). This follows from simple bonding arguments^{1,3} which dictate that for the alkyne to function as a four electron donor ligand in (2) the CO and RCECR ligands must be mutually *cis* while the most stable alkyne orientation will be that in which the C=C bond lies parallel to the M-CO bond.



(2a)



These structures are based on the premise that the phosphines are coordinated to the metal a fact confirmed by the presence of ${}^{31}P - {}^{183}W$ coupling in the ${}^{31}P$ nmr spectra of the complexes. In contrast P(OMe)₃ reacts with [WBr₂CO(CF₃C≡CCF₃)₂] to give a vinyl derivative as a result of addition to an acetylenic carbon^{2b}. Thus, although nucleophilic attack at

an acetylenic carbon may be promoted by four-electron donation to a metal 2a,b,3 these results indicate that the presence of electron withdrawing groups (CF₃) also appears to be necessary in some circumstances.

Finally we note the increasing range of stoichiometries exhibited by d^4 Mo(II) and W(II) alkyne complexes.¹⁻⁵ Since coordinative unsaturation in d^4 complexes can also be stabilised by inorganic donor ligands¹⁸ it seems probable that the wide range of stoichiometries available to the alkyne complexes may be a consequence of π -donation by both the alkynes and the inorganic ligands. Thus differences in the π -donor abilities of SBu^t and Br could account for the preference for five coordination in [Mo(SBu^t)₂(CNBu^t)₂(PhC=CPh)]³ relative to six coordination found with [WBr₂CO(CNBu^t)₂(PhC=CPh)].

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