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COMMUNICATION

SYNTHESIS, SPECTRAL PROPERTIES AND REACTIONS OF THE NOVEL DINUCLEAR ALKYNE COMPLEXES $[\mathrm{M}(\mu\text{-I})\mathrm{I(CO)(NCMe)}(\eta^2\text{-}\mathrm{PhC_2R})]_2$ (M = Mo OR W, R = Ph OR Me)

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Abstract—$[\mathrm{MI_2(CO)_3(NCMe)_2}]$ (M = Mo or W) and $\mathrm{PhC_2R}$ (R = Ph or Me) react in $\mathrm{CH_2Cl_2}$ to initially afford the "four-electron" alkyne complexes $[\mathrm{MI_2(CO)(NCMe)_2}(\eta^2\text{-}\mathrm{PhC_2R})]$, which subsequently dimerize to the novel iodide-bridged compounds $[\mathrm{M}(\mu\text{-I})\mathrm{I(CO)(NCMe)}(\eta^2\text{-}\mathrm{PhC_2R})]_2$, with loss of acetonitrile. These complexes react *via* symmetrical cleavage of the iodide bridges.

Alkynes are becoming increasingly important as ligands in organometallic chemistry, mainly due to their unique ability to utilize the filled alkyne perpendicular π-bonding orbitals, which permits the possibility of variable electron donor interactions which can formally be two, three or four electrons. This depends on the electronic configuration of the metal and the bonding properties of the other ligands in the coordination sphere.[1] Although a large number of six-coordinate d^4 mononuclear alkyne complexes have been reported for molybdenum(II) and tungsten(II)—$[\mathrm{MX(CO)}(\eta^2\text{-}\mathrm{PhC_2Ph})(\eta^5\text{-}\mathrm{C_5H_5})]$ (M = Mo or W; X = Cl, Br or I);[2] $[\mathrm{Mo(CO)(S_2CNR_2)_2}(\eta^2\text{-}\mathrm{RC_2R})]$ (R = alkyl or aryl);[3] $[\mathrm{M(SR)(CO)}(\eta^2\text{-}\mathrm{R^1C_2R^1})(\eta^5\text{-}\mathrm{C_5H_5})]$ ($\mathrm{R = CF_3}$ or $\mathrm{C_6F_5}$; $\mathrm{R^1 = Me}$, $\mathrm{CF_3}$ or Ph);[4] $[\mathrm{WMe(CO)}(\eta^2\text{-}\mathrm{RC_2R})(\eta^5\text{-}\mathrm{C_5H_5})]$ (R = alkyl or aryl);[5] $[\mathrm{MoLL^1}(\eta^2\text{-}\mathrm{RC_2R^1})(\eta^5\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$ $\{\mathrm{L,L^1 = CO}$ or $\mathrm{PR_3}$; $\mathrm{L = L^1 = P(OMe_3)}$; $\mathrm{R, R^1 = Me}$, Ph etc.$\}$;[6] $[\mathrm{Mo(^tBuS)_2(^tBuNC)_2(RC_2R^1)}]$ ($\mathrm{R,R^1 = H}$ or Ph);[7] $[\mathrm{MoX_2(CO)L_2}(\eta^2\text{-}\mathrm{PhC_2R})]$ (X = Cl or Br, L = phosphine, R = H or Ph);[8] $[\mathrm{Mo(SR)\{P(OMe)_3\}}(\eta^2\text{-}\mathrm{MeC_2Me})(\eta^5\text{-}\mathrm{C_5H_5})]$ (R = Me, p-$\mathrm{NH_2C_6H_4}$, p-$\mathrm{MeOC_6H_4}$, p-$\mathrm{MeC_6H_4}$, $\mathrm{C_6H_5}$ or p-$\mathrm{NO_2C_6H_4}$)[9]—hitherto very few dinuclear compounds of this type have been reported. In this communication we describe the synthesis of the novel iodide-bridged dimers $[\mathrm{M}(\mu\text{-I})\mathrm{I(CO)(NCMe)}(\eta^2\text{-}\mathrm{PhC_2R})]_2$ (M = Mo or W, R = Ph or Me), and preliminary studies of their reactivity.

Equimolar quantities of $\mathrm{PhC_2R}$ (R = Ph or Me) and $[\mathrm{MI_2(CO)_3(NCMe)_2}]$[10] react in $\mathrm{CH_2Cl_2}$ to give the crystalline complexes $[\mathrm{M}(\mu\text{-I})\mathrm{I(CO)(NCMe)}(\eta^2\text{-}\mathrm{PhC_2R})]_2$. These complexes are stable in the solid state when stored under argon at 0°C, and have been fully characterized by elemental analysis (C, H and N) and by IR and ^{1}H NMR spectroscopy (Table 1). The complexes are thermally unstable, i.e. similar to the well-known halide-bridged dimers[11] $[\mathrm{M}(\mu\text{-X})\mathrm{X(CO)_4}]_2$ (M = Mo or W; X = Cl, Br and I), and their thermal instability is reflected by their high reactivity. They react via symmetrical cleavage of the iodide bridges (Scheme 1). The ^{13}C NMR spectrum of **4** shows resonances at δ (ppm) = 207.7 and 206.9 (s, CO), 199.7 (s, $\mathrm{Ph\underline{C}{\equiv}}$), 196.9 (s, $\mathrm{Me\underline{C}{\equiv}}$), 136.7 (s, $\mathrm{{\equiv}C{-}\underline{C}}$), 130.6 (s, o-Ph), 129.2 (s, m-Ph), 128.7 (s, p-Ph), 117.48 (s, $\mathrm{N{\equiv}\underline{C}Me}$), 23.52 (s, $\mathrm{{\equiv}C\underline{Me}}$) and 4.55 (s, $\mathrm{NC\underline{Me}}$). The low-field resonances due to the "acetylenic" carbon atoms are typical of terminally bonded "four-electron" alkynes coordinated to molybdenum(II) or tungsten(II).[6–9]

It is proposed that these reactions proceed via the mononuclear intermediates $[\mathrm{MI_2(CO)(NCMe)_2}(\eta^2\text{-}\mathrm{PhC_2R})]$. For example, reaction of $[\mathrm{MoI_2(CO)_3}$

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Table 1. IR and ^{1}H NMR data for $[M(\mu\text{-}I)I(CO)(NCMe)(\eta^2\text{-}PhC_2R)]_2$

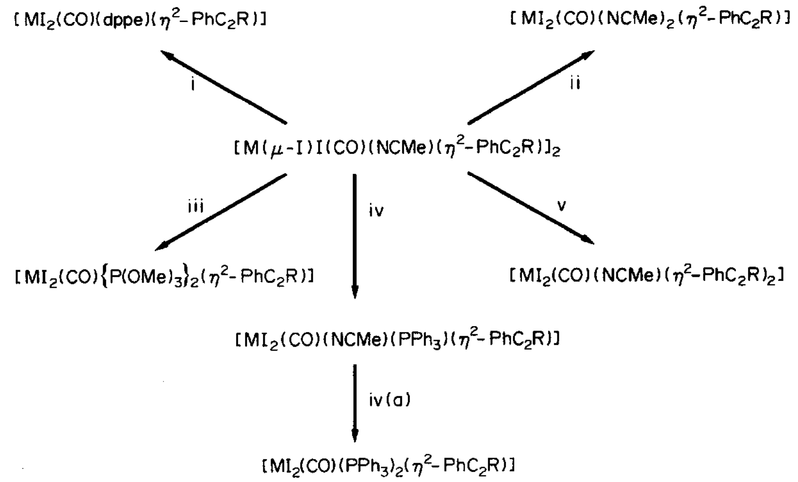
	M	R	$\nu(CO)^a$ (cm^{-1})	$\nu(CN)^a$ (cm^{-1})	$\nu(C{\equiv}C)^a$ (cm^{-1})	^{1}H NMR^b data (δ)
1	Mo	Ph	2050(s), 2005(s)	2315(w), 2290(w)	1690(w)	2.40 (s, 6H, NCMe) 7.49 (m, 20H, Ph)
2	Mo	Me	2045(s), 1990(s)	2315(w), 2240(w)	1620(w)	2.48 (s, 6H, NCMe) 3.54 (s, 6H, $\equiv$CMe) 7.59 (m, 10H, $\equiv$CPh)
3	W	Ph	2065(s), 2000(s)	2310(w), 2290 (w)	1675(w)	2.65 (s, 6H, NCMe) 7.61 (s, 20H, $\equiv$CPh)
4	W	Me	2050(s), 1990(s)	2315(w), 2285(w)	1610(w)	2.72 (s, 6H, NCMe) 3.21 (s, 6H, $\equiv$CMe) 7.62 (m, 10H, $\equiv$CPh)

[a] Spectra recorded in $CHCl_3$: s, strong; w, weak.

[b] Spectra recorded in $CDCl_3$ (+25°C) and referenced to $SiMe_4$.

$(NCMe)_2]$ with PhC_2Ph in CH_2Cl_2 at room temperature proceeds rapidly with effervescence of CO which ceases after 15 min. An IR spectrum of this solution shows not only carbonyl bands due to the dimer at $\nu = 2050$ and $2005\ cm^{-1}$, but also a very intense carbonyl band at $1978\ cm^{-1}$. This band is due to $[MoI_2(CO)(NCMe)_2(\eta^2\text{-}PhC_2Ph)]$ (**5**) and decreases with time until after 12 h only the bands due to the dimer **1** are observed. **5** can be prepared by reacting $[MoI_2(CO)_3(NCMe)_2]$ with PhC_2Ph in acetonitrile at 40°C for 2 h, when removal of solvent affords very air-sensitive red crystals of **5** which has been fully characterized by elemental analysis (C, H and N), and IR and ^{1}H NMR spectroscopy. The room-temperature ^{1}H NMR spectrum of **5** in $CDCl_3$ showed a methyl resonance at $\delta = 2.45$ ppm which after 12 h shows two MeCN resonances at $\delta = 2.40$ (dimer **1**) and 2.12 ppm (uncoordinated MeCN). Hence the proposed mechanism for the formation of the dimer is given in Scheme 2.

The preparation of a wide variety of these dinuclear complexes of molybdenum(II) and tungsten(II) with different alkynes, RC_2R^1 (R, R^1 = Me and Me, CH_2Cl and CH_2Cl, Me and SPh, Me and *p*-tolS etc.) has been carried out and a wide range of different rates of dimerization has been observed. It appears that the larger and more electron-deficient alkynes dimerize more slowly (probably due to there being less electron density on the metal,



Scheme 1. M = Mo or W; R = Me and Ph. Reagents: (1) dppe in CH_2Cl_2; (ii) NCMe, warm to 40°C; (iii) $P(OMe)_3$ in CH_2Cl_2; [iv and iv(a)] PPh_3 in CH_2Cl_2; and (v) PhC_2R in CH_2Cl_2.

(a) $[\mathrm{MoI_2(CO)_3(NCMe)_2}] \longrightarrow [\mathrm{MoI_2(CO)_2(NCMe)_2}] + \mathrm{CO}$

(b) $[\mathrm{MoI_2(CO)_2(NCMe)_2}] \xrightarrow{\mathrm{PhC_2Ph}} [\mathrm{MoI_2(CO)_2(NCMe)_2(\eta^2\text{-}PhC_2Ph)}]$

(c) $[\mathrm{MoI_2(CO)_2(NCMe)_2(\eta^2\text{-}PhC_2Ph)}] \longrightarrow [\mathrm{MoI_2(CO)(NCMe)_2(\eta^2\text{-}PhC_2Ph)}] + \mathrm{CO}$

(d) $2[\mathrm{MoI_2(CO)(NCMe)_2(\eta^2\text{-}PhC_2Ph)}] \longrightarrow [\mathrm{Mo(\mu\text{-}I)I(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)}]_2 + 2\mathrm{NCMe}$

Scheme 2.

and hence a stronger M—N bond). The chemistry of these complexes is currently being investigated in this laboratory and is extremely diverse (Scheme 1).

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