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The Reactions of $[\mathrm{WI_2(CO)(NCMe)}(\eta^2\text{-}\mathrm{RC_2R})_2]$ (R = Me and Ph).

Part 1. The synthesis and spectral properties of the new bisphosphite complexes $[\mathrm{WI_2(CO)\{P(OR')_3\}_2}(\eta^2\text{-}\mathrm{RC_2R})]$ (R′ = Me, Et, ^{i}Pr and ^{n}Bu)

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There is currently considerable interest in alkyne complexes of molybdenum and tungsten. Although a variety of bisphosphine alkyne complexes of the type $[\mathrm{MoX_2(CO)L_2}(\eta^2\text{-}\mathrm{PhC_2R})]$ (X = Cl and Br; L = phosphines; R = H or Ph) [1] have been made by reaction of the alkyne with $[\mathrm{MoX_2(CO)_3L_2}]$, hitherto only the dibromobistrimethylphosphite analogues $[\mathrm{WBr_2(CO)\{P(OMe)_3\}_2}(\eta^2\text{-}\mathrm{RC_2R'})]$ (R, R′ = Me$_2$, Et$_2$, Ph$_2$ and Me, Ph) have been very recently reported [2], and are prepared by reaction of $[\mathrm{W}(\mu\text{-}\mathrm{Br})\mathrm{Br(CO)}(\eta^2\text{-}\mathrm{RC_2R'})_2]_2$ and $\mathrm{P(OMe)_3}$. Until now no diiodo complexes of this type have been published which is almost certainly due to the difficulty of synthesising the iodide bridged dimers $[\mathrm{M}(\mu\text{-}\mathrm{I})\mathrm{I(CO)_4}]_2$ (M = Mo and W) [3, 4]. The only other bisphosphite alkyne complexes of molybdenum(II) or tungsten(II) to be reported [5, 6] are the cationic molybdenum complexes $[\mathrm{Mo\{P(OMe)_3\}_2}(\eta^2\text{-}\mathrm{RC_2R'})(\eta^5\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$ (R = R′ = Me or Ph; R = ^{t}Bu, R′ = H). In this communication we wish to report the synthesis of the new diiodo complexes $[\mathrm{WI_2(CO)\{P(OR')_3\}_2}(\eta^2\text{-}\mathrm{RC_2R})]$ (R = Me and Ph; R′ = Me, Et, ^{i}Pr and ^{n}Bu).

Results and Discussion

Two molar equivalents of $\mathrm{P(OR')_3}$ (R′ = Me, Et, ^{i}Pr and ^{n}Bu) react with $[\mathrm{WI_2(CO)(NCMe)}(\eta^2\text{-}\mathrm{RC_2R})_2]$ (R = Me and Ph) [7] in $\mathrm{CH_2Cl_2}$ to give the complexes $[\mathrm{WI_2(CO)\{P(OR')_3\}_2}(\eta^2\text{-}\mathrm{RC_2R})]$ in high yield via displacement of an acetonitrile and an alkyne ligand respectively. The complexes are stable

TABLE II. ^{1}H NMR Data for the Complexes $[\mathrm{WI_2(CO)\{P(OR')_3\}_2}(\eta^2\text{-}\mathrm{RC_2R})]$

R	R′	^{1}H NMR[a] (δ)
Me	Me	2.93 (6H, s, MeC≡) 3.49 (9H, d, J_{PH} = 10.8 Hz, OMe) 4.00 (9H, d, J_{PH} = 10.2 Hz, OMe)
Ph	Me	3.49 (9H, d, J_{PH} = 3 Hz, OMe) 3.74 (9H, d, J_{PH} = 5.4 Hz, OMe) 7.40 (10H, m, Ph)
Me	Et	1.21 (9H, t, J = 6.6 Hz, $\mathrm{CH_2\underline{CH}_3}$) 1.41 (9H, t, J = 6.6 Hz, $\mathrm{CH_2\underline{CH}_3}$) 2.93 (3H, t, J_{PH} = 1.8 Hz, MeC≡) 3.10 (3H, t, J_{PH} = 1.8 Hz, MeC≡) 3.42 (12H, m, $\mathrm{\underline{CH}_2CH_3}$)
Ph	Et	1.15 (18H, m, $\mathrm{CH_2\underline{CH}_3}$) 4.00 (12H, m, $\mathrm{\underline{CH}_2CH_3}$) 7.39 (10H, m, Ph)
Me	^{i}Pr	1.20 (36H, d, J_{PH} = 6.35 Hz, Me) 3.09 (6H, s, MeC≡) 4.73 (6H, m, C–H)
Ph	^{i}Pr	1.17 (18H, d, J_{PH} = 6.6 Hz, Me) 1.39 (18H, d, J_{PH} = 6.6 Hz, Me) 4.78 (6H, m, C–H) 7.48 (10H, m, Ph)
Me	^{n}Bu	0.90 (18H, m, Me) 1.47 (24H, m, $\mathrm{\underline{CH}_2\underline{CH}_2CH_3}$) 2.92 (3H, t, J_{PH} = 0.5 Hz, MeC≡) 3.09 (3H, t, J_{PH} = 0.6 Hz, MeC≡) 3.90 (6H, m, $\mathrm{OCH_2}$) 4.24 (6H, m, $\mathrm{OCH_2}$)
Ph	^{n}Bu	0.87 (18H, m, Me) 1.38 (24H, m, $\mathrm{\underline{CH}_2\underline{CH}_2CH_3}$) 3.90 (12H, m, $\mathrm{OCH_2}$) 7.48 (10H, m, Ph)

[a] Spectra recorded in $\mathrm{CDCl_3}$ (25 °C) and referenced to $\mathrm{SiMe_4}$.

TABLE I. Analytical (C, H and N) Data and IR Data for $[\mathrm{WI_2(CO)\{P(OR')_3\}_2}(\eta^2\text{-}\mathrm{RC_2R})]$

R	R′	Analysis (%)[a]	ν(CO)[b] (cm^{-1})	ν(C≡C)[b] (cm^{-1})
Me	Me	C, 17.50(17.21); H, 3.25(3.15)	1980(s)	1715(w)
Ph	Me	C, 28.56(28.27); H, 2.84(3.16)	1970(s)	1700(w)
Me	Et	C, 24.16(23.96); H, 4.31(4.26)	1978(s)	1658(w)
Ph	Et	C, 33.84(33.22); H, 4.12(4.13)	1965(s)	1655(w)
Me	^{i}Pr	C, 29.21(29.51); H, 5.12(5.17)	1958(s)	1718(w)
Ph	^{i}Pr	C, 37.79(37.38); H, 4.93(4.94)	1963(s)	1692(w)
Me	^{n}Bu	C, 34.75(34.14); H, 6.22(5.93)	1978(s)	1658(w)
Ph	^{n}Bu	C, 41.18(40.93); H, 6.00(5.64)	1963(s)	1720(w)

[a] Calculated values in parenthesis. [b] Spectra recorded in $\mathrm{CHCl_3}$. s, strong; w, weak.

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when stored under argon, and have been fully characterised by elemental analysis (C, H and N), IR spectroscopy (Table I) and ^{1}H NMR spectroscopy (Table II). The ^{13}C NMR spectrum ($CDCl_3$) of $[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}PhC_2Ph)]$ shows resonances at δ(ppm) = 220.51 (t, J_{PC} = 7.8 Hz, $Ph\underline{C}\equiv$), 218.17 (t, J_{PC} = 14 Hz, $Ph\underline{C}\equiv$), 203.56 (s, $\underline{C}O$), 139.55 (s, $\equiv C-\underline{C}$), 129.80 (s, *o*-Ph), 129.15 (s, *m*-Ph), 127.15 (s, *p*-Ph), 71.34 (s, $O-\underline{C}$), 44.69 (s, Me). The very low field acetylenic shifts at 220.51 and 218.17 ppm are indicative that the alkyne ligand is bonded as a '4-electron' donor to the tungsten in view of Templeton and Ward's [8] correlation relating the number of electrons donated by the alkyne to a transition-metal and the ^{13}C chemical shifts of the 'acetylenic' carbon atoms. Details of the fluxional behaviour of the but-2-yne complexes $[WI_2(CO)\{P(OR')_3\}_2(\eta^2\text{-}MeC_2Me)]$ will be presented at a later date.

It is interesting to note that the reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with an equimolar quantity of $P(OPh)_3$ gives the monotriphenylphosphite product $[WI_2(CO)\{P(OPh)_3\}(\eta^2\text{-}MeC_2Me)_2]$, whereas reaction of equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ and $P(OMe)_3$ gives 50% $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ and 50% $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$. This is likely to be due to the larger 'cone angle' [9] of $P(OPh)_3$.

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