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COMMUNICATION

A d^0 TO d^2 TRANSFORMATION OF TUNGSTEN, PROMOTED BY FORMATION OF AN ORGANOIMIDO LIGAND AND INVOLVING DISRUPTION OF THE π-PERPENDICULAR BONDING COMPONENT OF CO-ORDINATED DIPHENYLACETYLENE

ALASTAIR J. NIELSON,* PETER D. W. BOYD, GEORGE R. CLARK, PATRICIA A. HUNT, JAMES B. METSON, CLIFTON E. F. RICKARD and PETER SCHWERDTFEGER

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand

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Abstract—Synthetic, spectroscopic and structural investigations as well as theoretical calculations show that reaction of the d^0, four-electron donor alkyne complex [{$WCl_4(PhC_2Ph)$}$_2$] with the silylamines Me_3SiNHR (R = CMe_3, $CHMe_2$, CH_2Me, 2,6-$CHMe_2Ph$) leads to d^2, two-electron donor alkyne complexes containing an organoimido ligand.

We have recently reported confirmatory evidence for the stabilisation of high oxidation states of tungsten by alkynes, in a manner comparable with an oxo or organoimido ligand.[1] For example the alkyne complex [{$WCl_4(PhC_2Ph)$}$_2$] shows similar chemistry and properties to [{$WCl_4(NPh)$}$_2$][2] and may thus be regarded as a d^0 complex. The alkyne–tungsten bonding in [{$WCl_4(PhC_2Ph)$}$_2$] incorporates the alkyne $\pi_\perp$-bonding components so that the diphenylacetylene ligand acts as a four-electron donor.[3] We report here the disruption of this alkyne–tungsten $\pi_\perp$-donor interaction, by an organoimido ligand which results in a d^0 to d^2 transformation of tungsten.

Reaction of [{$WCl_4(PhC_2Ph)$}$_2$] with *N*-trimethylsilyl-t-butylamine in benzene proceeds according to reaction (1)

$$[\{WCl_4(PhC_2Ph)\}_2] + 4Me_3SiNHCMe_3 \rightarrow 2[WCl_2(NCMe_3)(PhC_2Ph)(NH_2CMe_3)]_x \; (\mathbf{1}) + 4Me_3SiCl \quad (1)$$

The IR spectrum of complex **1** contains a single W—Cl stretch characteristic of *trans*-chloro ligands while the t-butylimido and t-butylamine ligands are confirmed by specific quaternary carbon resonances in the ^{13}C-{^1H} NMR spectrum.[4] The acetylenic carbons appear at δ 156 which is at a similar position to that found for the d^2, two-electron donor alkyne complex [$WCl_2(NPh)(PhC_2Ph)(PMe_3)_2$] (δ 156).[5] In the four-electron donor alkyne complex [$WCl_5(PhC_2Ph)$]NEt_4, a soluble derivative of [{$WCl_4(PhC_2Ph)$}$_2$], the acetylenic carbon resonance occurs at δ 270. The ^{13}C-{^1H} NMR spectra thus indicate the alkyne changes from a four-electron donor to a two-electron donor in reaction (1). Analogues of complex **1** with acetylenic carbon resonances in the vicinity of δ 156 can also be prepared from [{$WCl_4(PhC_2Ph)$}$_2$] and the silylamines Me_3SiNHR (R = $CHMe_2$ and Et). Me_3SiNH-2,6-$CHMe_2Ph$ reacts similarly but requires heating to proceed.

Derivatives of these complexes can be prepared by replacement of the amine ligand with other σ-donor ligands [reactions (2) and (3)].

$$[WCl_2(NR)(PhC_2Ph)(NH_2R)] + 2PMe_3 \rightarrow [WCl_2(NR)(PhC_2Ph)(PMe_3)_2] \quad (2)$$

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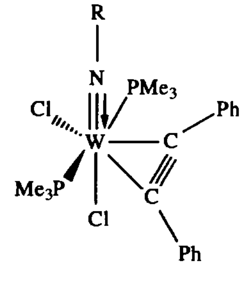
*Author to whom correspondence should be addressed.

$$[WCl_2(NR)(PhC_2Ph)(NH_2R)] + bipy \rightarrow [WCl_2(NR)(PhC_2Ph)(bipy)] \quad (3)$$

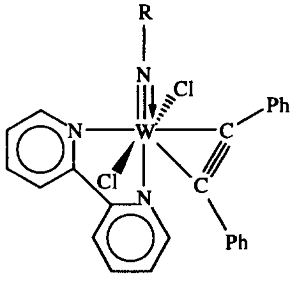
IR spectra of the phosphine adducts show two W—Cl stretches indicating *cis*-chloro ligands and the NMR spectra show *trans*-phosphines (structure I). Conversely, the bipy derivatives show only one W—Cl stretch consistent with *trans*-chloro ligands (structure II). These structures have been confirmed by X-ray crystallography and will be reported elsewhere.



(I)

The ^{13}C-$\{^1H\}$ NMR spectra of these derivatives again show acetylenic carbon resonances in the vicinity of δ 156. X-ray photoelectron spectroscopy (XPS) shows the complexes have $W(4f_{7/2})$ binding energies in the range considered to be tungsten(IV). For example the $W(4f_{7/2})$ binding energy found for $[WCl_2(NCMe_3)(PhC_2Ph)(bipy)]$ is 33.8 eV which is below that observed for $[\{WCl_4(PhC_2Ph)\}_2]$ where the $W(4f_{7/2})$ binding energy (35.1 eV)[1] falls in the range considered to be tungsten(VI).[6]

Hartree Fock (HF)[7] as well as scattered wave Xα calculations (MSXα),[8] suggest that the model complex $[WCl_2(NCH_3)(HC_2H)(PH_3)_2]$ (**3**) is best described as a d^2 tungsten system. The 5*d* populations, n_{5d}, are presented in Fig. 1 along with data obtained from SWXα calculations made on WCl_6 and the d^0, d^1 and d^2, four-electron donor alkyne model systems $[WCl_5(HC_2H)]^-$, $[WCl_3(HC_2H)(PH_3)_2]$ and $[WCl_2(HC_2H)(PH_3)_3]$.[1] The n_{5d} value for the imido complex is clearly greater than that obtained for $[WCl_5(HC_2H)]^-$. The calculated charge for the imido complex (SWXα calculation) is significantly smaller than that found for $[WCl_5(HC_2H)]^-$ and this difference correlates well with the lower $W(4f_{7/2})$ binding energy found for the analogous complex $[WCl_2(NCMe_3)(PhC_2Ph)(bipy))]$.



(II)

The presence of the imido ligand, another π-donor, significantly affects the characteristics of the acetylene ligand bond. The imido ligand Frontier Molecular Orbitals (FMOs) are able to interact extensively with the same *d* Atomic Orbitals (dAOs) as the acetylene ligand. Population analysis shows a distinct difference in the ligand donor properties in $[WCl_5(HC_2H)]^-$ and $[WCl_2(NMe)(HC_2H)(PH_3)_2]$. In both complexes $W(5d_\pi)$ to $C_2H_2(\pi^*)$ back donation (b_2 interaction in the local C_{2v} point group) and $C_2H_2(\pi_\parallel)$ to $W(5d_\pi)$ donation (a_1 interaction) operate, but in the imido complex $C_2H_2(\pi_\perp)$ to $W(5d_\pi)$ donation (b_1 interaction) is minimised as the nitrogen p_z (N_{p_z}) orbital overlap with the d_{yz} AO dominates (Fig. 2). $W(5d_\pi)$ to $C_2H_2(\pi^*)$ back-bonding is activated by overlap of the N_{p_x} donor

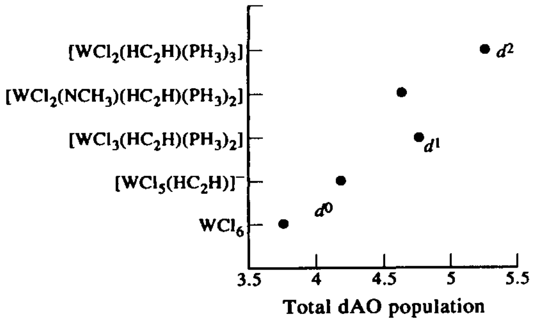


Fig. 1.

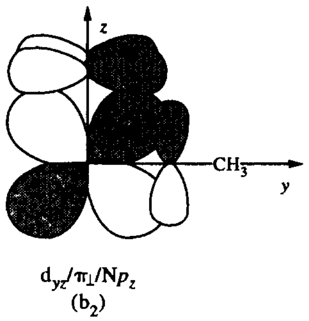


Fig. 2.

orbital with the d_{xy} AO which also overlaps with the $\pi_\perp{}^*$ FMO of acetylene.

The combined results of these studies show that the four-electron donor alkyne ligand in $[\{WCl_4(PhC_2Ph)\}_2]$ may be formally considered a net two-electron donor alkyne after an organoimido ligand is added to the complex. The properties associated with $[\{WCl_4(PhC_2Ph)\}_2]$ all point to a d^0 system, formally tungsten(VI).[1] Addition of the organoimido ligand disrupts the alkyne–metal $\pi_\perp$ bonding component leading to a d^2 complex formally considered as tungsten(IV). Alternatively, the alkyne ligand in $[\{WCl_4(PhC_2Ph)\}_2]$ may be regarded as being in a reduced state compared with the alkyne ligand in the organoimido complexes. Overall, reaction (1) represents a change at the metal centre, effectively of two electrons, and thus the alkyne ligand in $[\{WCl_4(PhC_2Ph)\}_2]$ may be regarded as an internal redox ligand.

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