

Preliminary communication

A CONVENIENT SYNTHETIC ROUTE TO NEW BIS(ARENEDIAZO) COMPLEXES OF MOLYBDENUM AND TUNGSTEN

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Summary

Complexes of the type $[(C_5H_5)Mo(N_2Ar)(N_2Ar')(PPh_3)] [PF_6]$ have been prepared and shown to be useful starting materials for the synthesis of a variety of neutral, cationic or anionic compounds containing $[cis-Mo(N_2Ar)(N_2Ar')]^{2+}$ units.

Complexes containing two arenediazo ligands terminally bonded to the same metal atom are quite rare. Chatt and co-workers [1] have recently described complexes of the type $[(R_2NCS_2)_2Mo(N_2R')_2]$ ($R, R' = \text{aryl or alkyl}$) and their report prompts us to communicate the details of a versatile synthesis of bis(arenediazo) complexes which has been developed in these laboratories***.

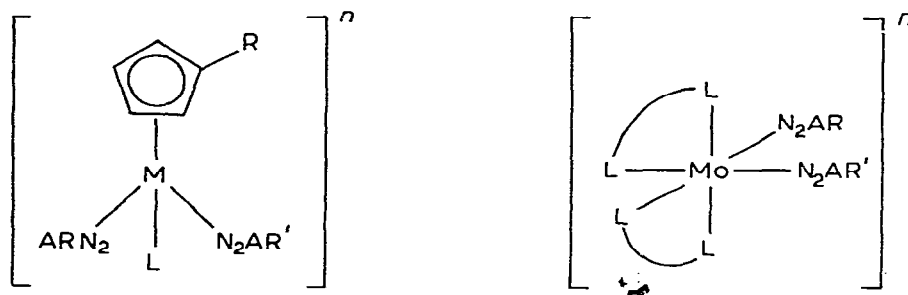
Reaction of $(\eta-C_5H_4R)M(N_2C_6H_4CH_3-p)(CO)_2$ (I, $R = H$) [2] with $[ArN_2]^+$ in acetone at $-78^\circ C$ produces purple reactive solutions which, by analogy with Stewart's synthesis of $[(\eta-C_5H_5)M(NO)_2(CO)]^+$ [3], are presumed to contain the bis(arenediazo) monocarbonyl cations $[(\eta-C_5H_4R)M(N_2Ar)(N_2Ar')(CO)]^+$ (II, $R = H, M = Mo, Ar = C_6H_4CH_3-p, Ar' = C_6H_4CH_3-p$ or $C_6H_4F-p; M = W, Ar = Ar' = C_6H_4CH_3-p$). Although Stewart's results [3] and the relative π -acceptor capacities $[NO]^+$ and $[ArN_2]^+$ [4] would suggest that cations of type II should be stable enough to isolate, we were not successful in this. However, addition of Ph_3P or halide anion to the reaction mixture at low temperatures yielded stable purple cationic complexes $[(\eta-C_5H_4R)Mo(N_2Ar)(N_2Ar')(PPh_3)]^+$ (III, $R = H, Ar = C_6H_4CH_3-p, Ar' = C_6H_4CH_3-p$ or C_6H_4F-p) which were isolated as $[BF_4]^-$ or $[PF_6]^-$ salts, or stable red neutral compounds $(\eta-C_5H_4R)MoX(N_2Ar)(N_2Ar')$ (IV, $R = H, M = Mo, Ar = Ar' = C_6H_4CH_3-p, X = Cl, I; M = W, Ar = Ar' = C_6H_4CH_3-p, X = I$) in excellent yield. Alternatively, the cationic complexes of type III ($R = H, Ar = Ar' = C_6H_5, Ar = Ar' = C_6H_4CH_3-p; Ar = C_6H_5, Ar' = C_6H_4CH_3-p; Ar = C_6H_4CH_3-p,$

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***All new compounds have given satisfactory microanalytical data.

$\text{Ar}' = \text{C}_6\text{H}_4\text{F}-p$; $\text{R} = \text{CH}_3$, $\text{Ar} = \text{Ar}' = \text{C}_6\text{H}_4\text{CH}_3-p$) could be prepared by the reaction of $[\text{Ar}'\text{N}_2]^+$ with $(\eta\text{-C}_5\text{H}_4\text{R})\text{Mo}(\text{N}_2\text{Ar})(\text{PPh}_3)(\text{CO})$ [2] in acetone at -78°C . The IR spectrum [4] of the cation III ($\text{Ar} = \text{Ar}' = \text{C}_6\text{H}_5$) both singly- and doubly-labelled with ^{15}N at the metal-bonded nitrogen atom identified bands at ca. 1650, 1620 and 1550 cm^{-1} as associated with $\bar{\nu}(\text{NN})$ and indicated the presence of coupling with arenediazo phenyl vibrational modes [4–6]. If (as seems likely) the metal atom attains the favoured 18-electron configuration, we must assume that both arenediazo ligands in III and IV are in the singly-bent $[\text{ArN}_2]^+$ coordination mode. It is probable that the complexes adopt “piano-stool” structures such as those illustrated in Fig. 1.



(III) $\text{L} = \text{PPh}_3$; $n = 1$

(V) $\text{LL} = 2,2'$ -bipy, o -phen; $n = 2 +$

(IV) $\text{L} = \text{halide anion}, \text{CN}^-$; $n = 0$

$\text{LL} = \text{dtc}^-, \text{acac}^-$, $n = 0$

$\text{LL} = \text{dtdt}^{2-}$; $n = 2 -$

Fig. 1.

Although stable to storage in the solid state, the cationic complexes III have an extensive chemistry and act as a starting-point for the synthesis of a wide range of compounds containing $[\text{cis-Mo}(\text{N}_2\text{Ar})(\text{N}_2\text{Ar}')]^{2+}$ structural units. Nucleophilic anions readily displaced Ph_3P to yield the neutral species IV ($\text{R} = \text{H}$, $\text{Ar} = \text{C}_6\text{H}_5$, $\text{Ar}' = \text{C}_6\text{H}_4\text{CH}_3-p$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$ or CN). Cleavage of both phosphine and cyclopentadienyl groups from III was induced by bidentate chelating ligands such as 2,2'-bipyridyl or o -phenanthroline (2,2'-bipy, o -phen) ($\text{R} = \text{CH}_3$, $\text{Ar} = \text{C}_6\text{H}_4\text{CH}_3-p$, $\text{Ar}' = \text{C}_6\text{H}_4\text{F}-p$), diethyldithiocarbamate or acetylacetonate anions (dtc^- , acac^-) ($\text{R} = \text{H}$, $\text{Ar} = \text{C}_6\text{H}_5\text{CH}_3-p$, $\text{Ar}' = \text{C}_6\text{H}_4\text{F}-p$; $\text{R} = \text{CH}_3$, $\text{Ar} = \text{Ar}' = \text{C}_6\text{H}_4\text{CH}_3-p$) or 1,1-dicyanoethylene-2,2-dithiolate dianion (dcdt^{2-}) ($\text{R} = \text{H}$, $\text{Ar} = \text{Ar}' = \text{C}_6\text{H}_4\text{CH}_3-p$). The products were new octahedral bis(arenediazo) complexes of the type $[(\text{LL})_2\text{Mo}(\text{N}_2\text{Ar})(\text{N}_2\text{Ar}')]^n$ (V) where $n = 2+$ ($\text{LL} = 2,2'$ -bipy, o -phen); $[\text{PF}_6]^-$ salts), $n = 0$ ($\text{LL} = \text{dtc}^-$, acac^-) or $n = 2-$ ($\text{LL} = \text{dcdt}^{2-}$; $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt), respectively (Fig. 1). The dtc complex appears to be similar to the complexes reported by Chatt et al. [1] but our route is more versatile than theirs in that the two arenediazo ligands need not be identical. The other species are representatives of previously unknown classes of bis(arenediazo) complexes. The dcdt complex is moreover the first reported example of an anionic arenediazo complex of any type. The ^1H NMR spectrum of the dtc complex confirms the cis -geometry and fluxional character reported by Chatt for his compounds [1] while that of the acac species indicates a rigid cis -geometry. The dicationic and dianionic complexes are also likely to have mutually cis -arenediazo ligands. The IR spectra

show a number of intense peaks in the $1500\text{--}1650\text{ cm}^{-1}$ area but firm assignment of $\bar{\nu}(\text{NN})$ must await the results of labelling experiments. Current research indicates that other complexes of unusual structure may be obtained from III and work in this area is continuing.

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