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Preliminary communication

Transition metal derivatives of aryl diazonium ions: arylazo molybdenum clusters

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Although the reactions of aryl diazonium ions with transition metal halides have extensive synthetic applications[1] few arylazo derivatives of the transition metals have been reported. Complexes containing arylazo ligands as well as cyclopentadienyl[2] or pyrazolylborate[3] and carbonyl groups are known for molybdenum and tungsten. Attempts to prepare analogous complexes of chromium and iron have not been successful[2,4]. We now describe a new series of arylazo-molybdenum complexes containing carbonyl as the only other π-acidic ligand.

$$ArN_2^+ + [Mo_4(CO)_{12}(OH)_4]^{4-} \rightarrow \underset{\text{(I–VI)}}{[ArN_2Mo(CO)_2OH]_4} + 4CO$$

Aryl diazonium tetrafluoroborates[5] react smoothly with the caesium salt of the hydroxo carbonylmetallate anion[6,7] **, $[Mo_4(CO)_{12}(OH)_4]^{4-}$ in a nitrogen-saturated water–ether two-phase system. Four moles of carbon monoxide are evolved per mole of carbonylmetallate salt and the intensely red neutral coupling products (I–VI) (see Table 1) could be isolated in ca. 70% yield from the organic phase. The coupling products retain solvent very strongly and microanalytical data were generally slightly high in carbon and hydrogen and correspondingly low in the other elements. Nonetheless two complexes were obtained in analytical purity, compounds (I) and (VI). (Representative analysis: Found: C, 34.91; H, 2.44; Mo, 34.83; N, 10.04. Calcd. for (I) C, 35.07; H, 2.21; Mo, 35.01; N, 10.22%). The remaining compounds in Table 1 were characterised spectroscopically or by derivative formation. Molecular-weight determinations confirm that the Mo_4 unit of the parent carbonylmetallate[7] is not cleaved during the coupling reaction.

The arylazo ligand is isoelectronic with nitric oxide and our complexes are thus

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**Prepared by the action of boiling ethanolic KOH on $Mo(CO)_6$ [6], followed by metathesis of the potassium salt with CsBr. The caesium salt (ν(CO), 1864, 1685 cm^{-1}) was chosen since it could be handled briefly in the air without decomposition.

TABLE 1

SPECTROSCOPIC DATA FOR THE ARYLAZO-MOLYBDENUM COMPLEXES: $[ArN_2Mo(CO)_2OH]_4$ AND DERIVATIVES

No.	R in Ar	Addend	ν(CO)(cm^{-1}) [a]	ν(N=N)(cm^{-1}) [a]	Ultraviolet visible (mμ) [b]
(I)	H	–	1992 s, 1921 s(sh), 1893 s	1550 s	419(2.96)272(10.35)216(6.85)
(II)	*o*-Cl	–	2000 s, 1910 s	1550 s	422(3.05)274(9.06)215(6.79)
	o-Cl	4(TPPO)	1996 s, 1908 s(sh), 1896 s	1540 s	
	o-Cl	4(TPAO)	1994 s, 1900 s(sh), 1890 s	1535 s	
(III)	*p*-Cl	–	1995 s, 1904 s	1550 s	423(3.36)280(10.00)218(7.29)
(IV)	*o*-Br	–	2000 s, 1907 s	1552 s	423(2.86)277(8.90)216(6.62)
	o-Br	4(TPPO)	1995 s, 1904 s, 1894 s(sh)	1538 s	
	o-Br	4(TPAO)	1987 s, 1893 s(sh), 1884 s	1533 s	
	o-Br	4(PyO)	1990 s, 1895 s	1539 s	
	o-Br	4(*o*-Phen)	1999 s, 1905 s	1522 s	
(V)	*p*-Br	–	1997 s, 1902 s	1540 s	422(3.47)282(10.3)218(7.35)
	p-Br	4(TPPO)	1993 s, 1898 s(sh), 1889 s	1534 s	
(VI)	*o*-CH_3	–	1991 s, 1892 s	1560 s	424(2.67)272(8.95)217(5.80)
	o-CH_3	4(TPAO)	1993 s, 1882 s(sh), 1867 s	1535 s	

[a] In KBr disc. s, strong; s(sh), strong shoulder. [b] In methanol. Figures in parentheses are extinction coefficients $\times 10^{-4}$.

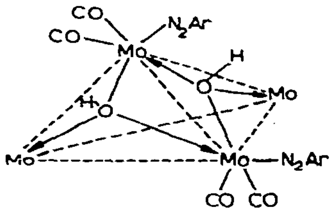
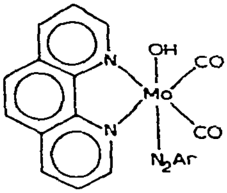


Fig.1. Proposed structure of $[ArN_2Mo(CO)_2OH]_4$. For clarity only two μ_3-OH groups and two sets of terminal ligands are shown. The dotted lines merely define the Mo_4 tetrahedron.

closely related to the complex $[Mo(CO)_2(NO)OH]_4$ first synthesised by Canziani[8] the structure of which has been established by Bellon[7]. It is reasonable to assume that our complexes are isostructural with Canziani's nitrosyl. Essential details of the proposed structure are illustrated in Fig.1. The complexes (I)–(VI) are reddish-purple poorly-crystalline solids, unaffected by exposure to the air for up to six months and stable in organic solvents for at least several hours. The arylazo compounds are soluble in acid and complex (V) was recovered quantitatively from concentrated sulphuric acid after six hours at room temperature. Decomposition was rapid in sulphuric acid at 60° or in 30% aqueous hydrochloric acid at room temperature. The complexes are not affected by reflux with excess triphenylphosphine in benzene.

Since the molecule is otherwise devoid of π-acceptor ligands back-bonding from the molybdenum atoms to the carbonyl and arylazo ligands would be expected to be extensive. The carbonyl absorptions in (I)–(VI) occur at somewhat lower frequencies than in either the related cyclopentadienyl[2] or pyrazolylborate[3] complexes in agreement with this prediction. However, the increased back-bonding is not reflected in the (N=N) stretching frequency which occurs at slightly higher frequency than in the related cyclopentadienyl complex[2,9]. Assuming little mutual conjugation of the arylazo ligands the extinction coefficient of the $n\rightarrow\pi^*$ absorption of the isolated chromophore in compound (I) is 7400. The arylazo absorption is, therefore, somewhat weaker than in the related cyclopentadienyl compound[2] and approximately of equal intensity to that in the analogous pyrazoylborate[3]. This indicates, in contrast to the IR evidence, greater back-bonding[9] to the arylazo group in our compounds than in the π-cyclopentadienyl analogues. Evidently the (N=N) stretching frequency of the arylazo ligand is not a sensitive probe for electron density on the metal.

Canziani's nitrosyl reacts with four moles of triphenylphosphine oxide to form an 1/4 adduct[8] which has been shown[7] to involve strong hydrogen-bonding between the oxide oxygens and the four facial μ_3-OH groups of the nitrosyl. Arylazo compounds (II), (IV) and (VI) form similar stable crystalline adducts with triphenylphosphine-, triphenylarsine- or pyridine-oxides (TPPO, TPAO and PyO respectively). The adducts separate from a methylene-chloride/ether solution of the components in analytical purity but deteriorate on attempted recrystallisation. Molecular weight studies show that these adducts are highly dissociated in solution. (Representative analysis: Found: C, 49.20; H, 3.10; Br, 12.46; Mo, 15.43; N, 4.20; P, 4.88. Compound (IV) + 4TPPO calc.: C, 49.48; H, 3.20; Br, 12.66; Mo, 15.21; N, 4.43; P, 4.92%). Interestingly azo-complexes lacking an *ortho*-substituent on the aromatic ring did not form insoluble adducts. A crystalline adduct of the *para*-substituted



(VII)

complex (V) and TPPO was isolated by slow evaporation of a benzene–petroleum solution of the components but could not be obtained completely pure. The IR OH-stretching absorptions which appears as a very broad medium-intensity band covering the range 3660–2880 cm^{-1} in the parent arylazo compounds (KBr disc) are found as a similarly broad band covering the range 3060–2320 cm^{-1} in the adducts. The site of adduct-formation is, therefore, confirmed to be at the facial-OH groups. Interestingly, adduct formation is in all cases accompanied by a lowering of the (CO) and (N=N) stretching frequencies (See Table 1). Complex (IV) reacts with *o*-phenanthroline (*o*-Phen) to form a complex for which the analytical data indicates the composition [(IV) + 4(*o*-Phen)]. A possible structure for this complex would be the mononuclear (VII).

Unfortunately, the complex was insufficiently soluble for accurate molecular weight determination. However, the IR spectrum of the solid shows a broad medium-intensity band covering the range 3060–2310 cm^{-1} assignable to a strongly hydrogen-bonded OH group. Moreover, the IR spectrum of the complex in the (CO) and (N=N) stretch regions is similar to that of the other hydrogen-bonded adducts of complex (IV). We feel that the four *o*-phenanthroline residues in [(IV) + 4(o-Phen)] are similarly hydrogen-bonded to the μ_3-OH groups. 2,2′-Dipyridyl does not form a similar adduct.

The interaction of diazonium ions with other metal carbonyl species is currently being investigated.

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