Journal of Organometallic Chemistry, 259 (1983) 305–311
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

TRANSITION METAL DERIVATIVES OF ARENEDIAZONIUM IONS

XI. REACTIONS OF SOME MOLYBDENUM(0) ARENEDIAZO COMPLEXES WITH HALOGENS, TIN(IV) HALIDES, MERCURY(II) HALIDES AND RELATED REAGENTS

FERGUS J. LALOR*, MICHAEL E. DEANE and DAVID M. CONDON
Department of Chemistry, University College, Cork (Ireland)

(Received August 1st, 1983)

Summary

The new Mo^{II} arenediazo complexes $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)I_2$, $[(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)I_2]_2$ and $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)(SnI_3)I$ have been isolated from the reaction of the Mo^0 complex $(\eta\text{-}C_5H_5)Mo(CO)_2N_2C_6H_4CH_3\text{-}p$ with I_2 and SnI_4 respectively. The W^{II} complex $(\eta\text{-}C_5H_5)W(CO)(N_2C_6H_4CH_3\text{-}p)I_2$ has also been prepared. In the reactions with chlorine and bromine analogous complexes could be detected in solution but were too labile to be isolated. No reaction occurs with C_3F_7I, $(CH_3)_3SnCl$, $(C_6H_5)_3SnCl$ or mercuric halides but $(\eta\text{-}C_5H_5)Mo(CO)(PPh_3)N_2C_6H_4CH_3\text{-}p$ yields a 1 : 2 adduct $(\eta\text{-}C_5H_5)Mo(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)(HgBr_2)_2$. The structures of the products are discussed.

Introduction

In 1967 King reported that the Mo^0 nitrosyl complex $(\eta\text{-}C_5H_5)Mo(CO)_2NO$ (I) underwent oxidative displacement of CO when treated with iodine to yield the dimeric Mo^{II} nitrosyl $[(\eta\text{-}C_5H_5)Mo(NO)I_2]_2$ (II) [1]. Subsequent work, much of it due to McCleverty and his co-workers, has shown that complex II (as well as its chloro and bromo analogues) has an extremely rich derivative chemistry leading to many molybdenum complexes of unusual structure [2]. Complexes analogous to II but containing the closely-related arenediazo ligand instead of nitrosyl would therefore be potentially useful starting materials for the synthesis of structurally novel arenediazo complexes. In a 1966 paper [3] King and Bisnette referred briefly to the fact that the Mo^0 arenediazo complex $(\eta\text{-}C_5H_5)Mo(CO)_2N_2C_6H_4CH_3\text{-}p$ (III) (which is structurally and electronically related to I) reacted with iodine to yield a material of approximate composition $[(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)I_2]_n$ which could not be fully characterised. A subsequent brief investigation of the same reaction in

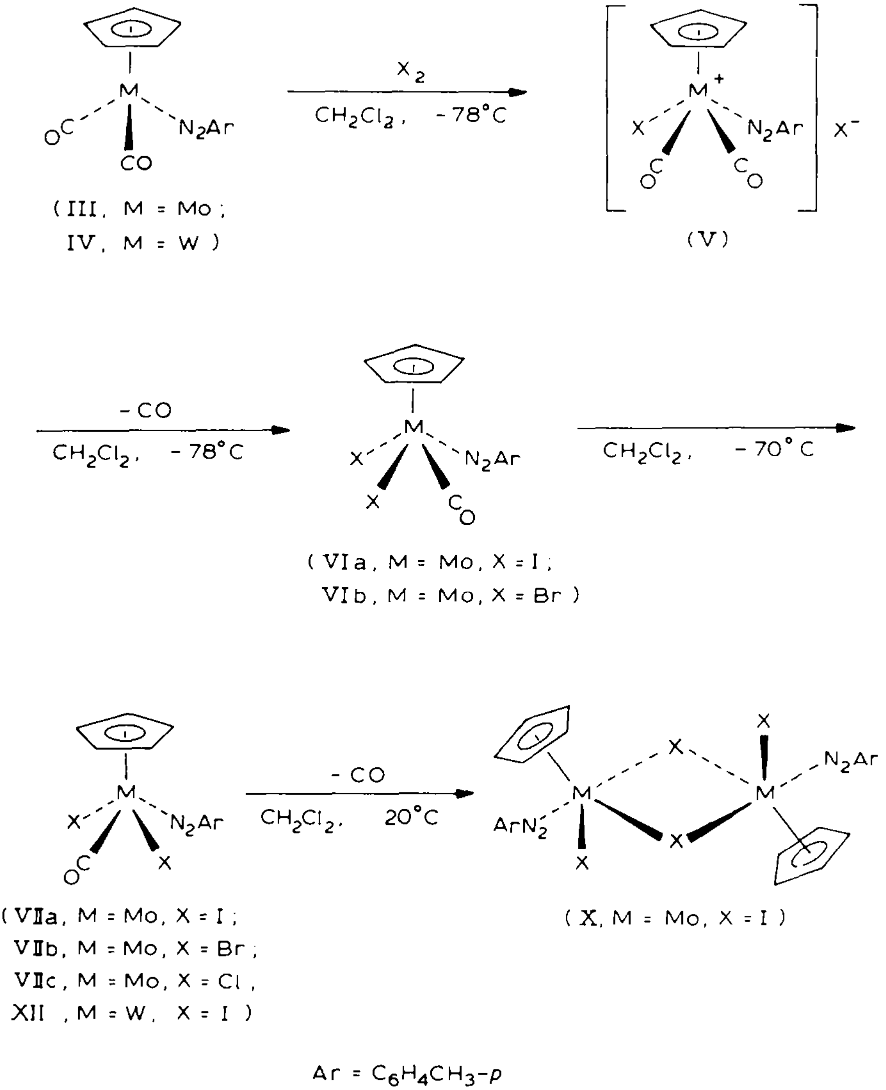
0022-328X/83/$03.00

these laboratories was equally unproductive [4]. We now wish to report the successful reinvestigation and extension of this chemistry.

Results and discussion

We have studied the reactions of III with Cl_2, Br_2 and I_2 at low temperature (−78°C) in CH_2Cl_2 and also the reaction of the analogous tungsten complex $(\eta\text{-}C_5H_5)W(CO)_2N_2C_6H_4CH_3\text{-}p$ (IV) with I_2 under similar conditions.

The only reactions which yielded pure isolable solid products were those employing iodine as the oxidant. However IR monitoring of the Cl_2 and Br_2 reactions and



SCHEME 1

comparison of the data with the results of similar monitoring of the I_2 oxidation (Table 1) allows us to infer the course of the former reactions with reasonable confidence. The probable sequence of events is summarised in Scheme 1. By analogy with the behaviour of related complexes [5] the first step is likely to be electrophilic attack of halogen at the Mo atom to produce a cationic dicarbonyl complex (V, only one of two possible isomers illustrated). If V is indeed formed it is extremely labile even at −78°C. Upon addition of I_2 in CH_2Cl_2 to a stirred solution of III in the same solvent gas evolution is immediate and the originally red solution becomes deep green. The presence of V could not be detected spectroscopically. Within ca. 5 min at −78°C the IR bands at 1997 and 1925 cm^{-1} due to III have disappeared and are replaced by a single strong band at 1968 cm^{-1}. With continued stirring at −78°C this IR band slowly decreases in intensity and is replaced by another strong band at 2040 cm^{-1}. If the solution is then warmed to room temperature and rapidly worked up a green solid is isolated which shows $\nu(CO)$ at 2040 cm^{-1} (CH_2Cl_2 solution) and gives correct microanalytical data (Table 1) for the Mo^{II} monocarbonyl formulation $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)I_2$. We interpret these results as indicating that attack of iodide anion on the transient cation V and displacement of CO leads first to a neutral monocarbonyl complex VIa which is the product of kinetic control and that VIa then isomerises to a thermodynamically favoured monocarbonyl VIIa which is the species which can be isolated in the solid state. Assuming that the complex formulated as $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)I_2$ has the common "four-legged piano-stool" structure it may exist in two geometrically isomeric forms, with either *cis* or *trans* arrangements of CO and arenediazo ligands. We have no conclusive evidence which would allow us to assign *cis* or *trans* geometries to VIa and VIIa. However it will be noted from the IR data that the extent of back-bonding to the single CO ligand is clearly reduced in the thermodynamically favoured isomer VIIa as compared to the kinetically favoured isomer VIa. We suggest that the π-acceptor ability of a *trans* arenediazo ligand * is likely to reduce back-bonding to CO more effectively than the inductive effect of a *trans* iodine ligand. On these grounds we tentatively assign the structures illustrated in Scheme 1, *cis* to VIa and *trans* to VIIa. That the thermodynamically most stable monocarbonyl should be that in which the CO ligand receives least π-bonding from the metal is unexpected but the IR data necessitates this conclusion, irrespective of the details of the structural model used to interpret it. It may be noted that monocarbonyl intermediates analogous to VIa and VIIa have not been detected in the reaction of the nitrosyl I with Cl_2, Br_2 [6] or I_2 [1]. A related tungsten complex formulated as $(\eta\text{-}C_5H_5)W(CO)(NO)I_2$ (VIII) ($\nu(CO)$ 2040 cm^{-1}) of unknown isomeric structure has been detected spectroscopically in the reaction of $(\eta\text{-}C_5H_5)W(CO)_2NO$ (IX) with I_2 but was too labile towards further loss of CO to permit of isolation in the solid state [7]. The greater stability of the arenediazo analogue VIIa is not unexpected given the reduced π-acceptor capacity of ArN_2^+ compared with NO^+ but the fact that the two complexes exhibit identical $\nu(CO)$ values is surprising.

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* We assume that in this and the other complexes discussed in this communication the arenediazo ligands are in the "singly bent" (formal ArN_2^+) coordination mode as is required to maintain the favoured 18-electron configuration at the metal atom.

Although complex VIIa is sufficiently stable to be isolated in the solid it contains a carbonyl ligand bonded to Mo^{II} and moreover *trans* to a strongly π-accepting arenediazo ligand. Accordingly it is readily decarbonylated in CH_2Cl_2 at room temperature (reaction completed in ca. 20 min) or by maintaining a water-aspirator vacuum over the solid complex for ca. 8 h. The product is a black crystalline solid X which gave correct microanalytical data for the formulation $[(\eta\text{-}C_5H_5)\text{-}Mo(N_2C_6H_4CH_3\text{-}p)I_2]_n$ where *n* is probably 2, i.e. X is the arenediazo analogue of the nitrosyl II. We suggest that X has a structure similar to that proposed for II [1] and for its tungsten analogue $[(\eta\text{-}C_5H_5)W(NO)I_2]_2$ (XI) [7] with a planar $[Mo(\mu\text{-}I)_2Mo]$ core and each molybdenum atom being further coordinated by η-C_5H_5, terminal iodine and terminal singly-bent arenediazo ligands. The structure illustrated in Scheme 1 is only one of several isomers differing in the relative disposition of the latter ligands with respect to the core. Direct information on the structure (or structures) actually present is not available since we were unable to obtain crystals of X which were suitable for an X-ray crystallographic study.

IR monitoring of the reactions of III with Cl_2 and Br_2 indicates that they follow the sequence outlined above for I_2. With Br_2 both the kinetically favoured monocarbonyl VIb and its thermodynamically stable isomer VIIb can be observed in solution (Table 1) but attempts to isolate VIIb always yielded CO-free material. In the reaction of III with Cl_2 the first observable product is the thermodynamically favoured monocarbonyl isomer VIIc. In the related groups of monocarbonyl isomers VIa, VIb and VIIa, VIIb, VIIc the CO stretching frequencies increase with increasing electronegativity of the halogen ligands which progressively reduces the availability of metal *d*-electron density for back-bonding to the CO ligand. The general decrease in stability of the complexes in the same sequence is therefore to be expected. Both VIIa and VIIb are readily decarbonylated in solution at room temperature but the

TABLE 1

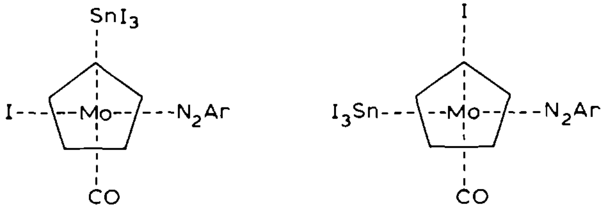
INFRARED AND MICROANALYTICAL DATA

Complex	$\nu(CO)$ [a] (cm^{-1})	Analysis (Found (calcd.) (%))		
		C	H	N
VIa	1968			
VIIa	2040	28.01 (27.78)	2.16 (2.15)	5.05 (4.98)
VIb	1985			
VIIb	2061			
VIIc	2071			
X		26.85 (26.99)	2.20 (2.26)	5.17 (5.25)
XII	2040	24.12 (24.02)	1.85 (1.86)	4.39 (4.31)
XIII	1965			
XIV	2040	16.90 (16.71)	1.74 (1.29)	2.50 (3.00)
XVII	1970	29.30 (28.83)	2.31 (2.11)	1.85 (2.17)

[a] Dichloromethane solution, all absorptions are strong. All the complexes showed a number of bands in the 1570–1650 cm^{-1} region, some of which may be due to $\nu(NN)$ of the arenediazo ligand. Definite assignment is not possible without ^{15}N labelling.

products, which we presume to be the chloro and bromo analogues of X, were unstable and could not be obtained analytically pure. We did not attempt to observe the kinetically controlled monocarbonyl isomer in the reaction of the tungsten complex IV with iodine but the thermodynamically stable isomer XII was isolated and characterised (Table 1). Complex XII could be decarbonylated in a manner similar to its molybdenum congener VIIa but the product, although similar in its general properties to X, proved to be intractable. King has also reported that III reacts with n-C_3F_7I under unspecified conditions to yield an uncharacterised red CO-free solid [3]. We were unable to detect any reaction between III and this reagent in CH_2Cl_2 at room temperature.

Complex III fails to react with either $(CH_3)_3SnCl$ or $(C_6H_5)_3SnCl$ but reacts rapidly with SnX_4 (X = Cl, Br, I) in CH_2Cl_2 at −78°C. The reactions may be presumed to parallel those with halogens with initial oxidative displacement of CO by $X-SnX_3$ (rather than X–X) followed by decarbonylation. As in the halogen reactions, stable isolable products were found only with the least electronegative reagent, i.e. SnI_4. In this reaction also, a kinetically favoured monocarbonyl complex formulated as $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)(SnI_3)I$ (XIII) is the first spectroscopically detectable product (Table 1). This is then converted into a thermodynamically stable isomer XIV which could be isolated and characterised by microanalysis. By analogy with the iodine reaction we suggest that XIV has a *trans* arrangement of CO and arenediazo ligands. The structural possibilities for XIII are more complex since there are now two isomers in which the CO and arenediazo ligands are mutually *cis*:



(XII)

Beyond the fact that the single CO stretching frequency obtained for XIII indicates that only one of these isomers is present we have no information that would allow a distinction to be made between them. Complex XIV was further decarbonylated in CH_2Cl_2 solution at room temperature. The black CO-free product is presumed to have a structure similar to that of X in which SnI_3 groups replace the terminal iodine ligands but satisfactory microanalytical data could not be obtained. Treatment of III with either $SnCl_4$ or $SnBr_4$ in CH_2Cl_2 at −78°C results in vigorous evolution of CO and formation of black solutions. IR monitoring revealed that even at this low temperature the presumed monocarbonyl intermediates had undergone complete decarbonylation. Attempted work-up of the reactions yielded only intractable black solids. It should be noted that the rapid reaction of III with SnX_4 at −78°C contrasts sharply with the failure of the related nitrosyl I to react with $SnCl_4$ even at 20°C [5] although reaction does take place with the phosphine-substituted nitrosyl $(\eta\text{-}C_5H_5)Mo(CO)(PPh_3)(NO)$ (XV) [5,8]. We believe that this is a further demonstration [5] that interaction of the relatively weakly electrophilic (vis-a-vis halogen) SnX_4 with the metal atom of transition metal carbonyl complexes is critically dependent on the relative electron releasing or withdrawing capacity of the other ligands present. The strongly π-accepting character of the nitrosyl ligand in I renders the metal centre too electron-poor to react with SnX_4. An increase in available electron density, either via replacement of CO by the donor ligand PPh_3 or by replacement of the nitrosyl ligand with the less powerfully electron withdrawing arenediazo ligand allows reaction to take place.

A further example of the effect described above is provided by the behaviour of the arenediazo complex III towards mercuric halides. Complex III does not react with HgX_2 ($X = Cl, Br, I$) in CH_2Cl_2/CH_3OH either at −78°C or at room temperature. However the triphenylphosphine derivative of III, $(\eta\text{-}C_5H_5)Mo(CO)(PPh_3)N_2C_6H_4CH_3\text{-}p$ (XVI) gives moderate yield of a yellow crystalline product XVII when treated with excess $HgBr_2$ in CH_2Cl_2/CH_3OH at room temperature. Microanalytical data for XVII (Table 1) indicated that it is formally a 1 : 2 adduct of XVI and $HgBr_2$. Initially we were inclined to formulate the complex as an ionic species $[(\eta\text{-}C_5H_5)Mo(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)(HgBr)][HgBr_3]$ analogous to the known $[(\eta\text{-}C_5H_5)Mo(CO)(PPh_3)(NO)(SnCl_3)][SnCl_5(H_2O)]$ (XVIII) [8]. However the conductivity of solutions of XVII in nitromethane is not compatible with an ionic formulation and since the IR spectrum in CH_2Cl_2 (ν(CO) at 1970 cm^{-1} compared with 1860 cm^{-1} for XVI) shows that the adduct does not revert to its components in solution the two $HgBr_2$ moieties must be strongly covalently bound to XVI. We propose that one $HgBr_2$ unit in XVII is directly bound to molybdenum via a Lewis acid-base interaction as has been suggested for the 1 : 1 adduct $(\eta\text{-}C_5H_5)Mo(CO)(PPh_3)(NO)(HgCl_2)$ (XIX) [8]. The location of the second $HgBr_2$ unit is less certain. It may be attached to the Mo-bound $HgBr_2$ via halogen bridging as has been found in the dimeric 1 : 2 adduct $[\{\eta\text{-}1,3,5\text{-}(CH_3)_3C_6H_3\}Mo(CO)_3(HgCl_2)_2]_2$ (XX) in which a further network of halogen bridges then unites two monomers [9]. However, unlike the nitrosyl XV, the arenediazo complex XVI has two Lewis base sites, the metal atom and the arenediazo nitrogen atom β to the metal which carries a potentially available lone pair of electrons and which is known to be capable of donating these to a metal centre [10]. Crystals of XVII suitable for X-ray studies have not so far been obtainable although our efforts in this direction are continuing. In the absence of such data it is difficult to speculate further on the structure of this complex. We are also investigating the derivative chemistry of the complexes described here and these studies will be the subject of a subsequent communication.

Experimental

The complexes III, IV and XVI were prepared by the published procedures [3]. Other reagents and solvents were commercial samples and were used as received. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer calibrated with respect to standard polystyrene film. Microanalyses were carried out by the staff of the Microanalytical Laboratory of University College, Cork. IR and microanalytical data are summarised in Table 1.

Reaction of arenediazo complexes III and IV with halogens and tin(IV) halides

The reaction of III with I_2 is representative of the procedures used. A solution of I_2 (0.38 g, 1.5 mmol) in 10 ml CH_2Cl_2 was added dropwise to a stirred, nitrogensaturated solution of III (0.50 g, 1.5 mmol) in 60 ml CH_2Cl_2 at −78°C. Gas was evolved and the red solution became deep green in colour. After ca. 1 h at −78°C the reaction mixture was allowed to warm to room temperature and the solvent was rapidly removed in vacuo at that temperature. The residue was washed several times with cold hexane and the dark green monocarbonyl complex VIa (0.73 g, 90%) was collected by filtration and dried in vacuo.

A CH_2Cl_2 solution of VIa, prepared as described above, was allowed to stir at room temperature for 2 h during which time the colour changed from deep green to a very dark red. The solvent was removed in vacuo at room temperature and the residue was washed with cold hexane to yield 0.78 g (94%) of black crystalline X.

Reaction of (η-C_5H_5)Mo(CO)(PPh_3)$N_2C_6H_4CH_3$-p (XVI) with $HgBr_2$

A solution of $HgBr_2$ (1.80 g, 5 mmol) in methanol was added to a stirred solution of XVI (1.14 g, 2 mmol) in 50 ml CH_2Cl_2. After 30 min at room temperature 100 ml of diethyl ether was added to precipitate the yellow adduct XVII (0.97 g, 37.6%).

Acknowledgement

We are grateful to the Department of Education of the Irish Republic for Post-graduate Maintenance Awards to M.D. and D.C.

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