Journal of Organometallic Chemistry, 67 (1974) C19—C22

Preliminary communication

TRANSITION METAL DERIVATIVES OF ARYL DIAZONIUM IONS

V. OXIDATIVE ADDITION OF HALOGENS TO ARYLAZO AND NITROSYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN

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(Received December 10th, 1973)

Summary

The oxidative addition of halogens to various arylazo derivatives of Mo and W has been studied. Several different types of product are formed depending on the nature of the metal atom and the co-ligand; among these are probable first examples of a bridging ArN_2 ligand and of an ArN_2^- derivative of a Group VI metal.

Oxidative addition reactions [1] and the chemistry of arylazo complexes [2] have separately aroused much recent interest. We have now extended our earlier observations in both these fields [3] to the oxidative addition reactions of several Group VI arylazo and nitrosyl complexes with halogens. Compounds of novel structure result including probable first examples of a bridging ArN_2 ligand and of a tungsten complex of ArN_2^-.

McCleverty [4] has shown that oxidative additions of halogens to $(\pi\text{-}C_5H_5)Mo(CO)_2NO$ yields $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ with terminal NO ligands (formal NO^+) and both bridging and terminal X groups. The present work confirms a brief report by King [5] that addition of iodine to $(\pi\text{-}C_5H_5)Mo(CO)_2\text{-}N_2Ph$ yields the analogous $[(\pi\text{-}C_5H_5)Mo(N_2Ph)I_2]_2$ but like him, we found this material difficult to purify. The IR spectrum (CH_2Cl_2) shows a strong band at 1630 cm^{-1} consistent with a terminal PhN_2^+ ligand. A structure analogous to that of the nitrosyl seems likely. $(HBPz_3)M(CO)_2NO$ (Pz = 1-Pyrazolyl, M = Mo or W) reacts cleanly with halogens in CH_2Cl_2 at −70° to yield $[(HBPz_3)Mo(NO)X_2]_2$ (Ia, X = Cl, Ib, X = Br*; Ic, X = I) or $[(HBPz_3)W(NO)X_2]_2$ (IIa, X = Cl; IIb, X = Br; IIc, X = I). All these compounds show a strong ν(NO) absorption at ca. 1718 cm^{-1} (M = Mo) and 1645 and (M = W), (CH_2Cl_2), consistent with

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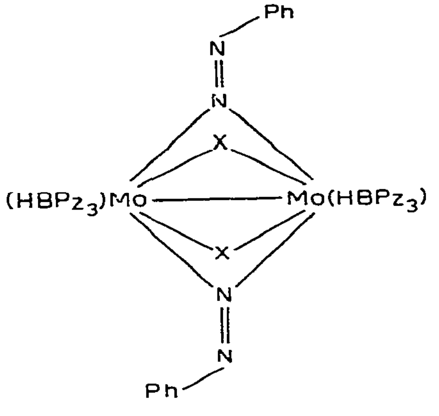
*This compound has evidently been synthesised by McCleverty, private communication to S. Trofimenko [6], but no details have appeared.

terminal NO^+ ligands and again supporting a structure analogous to $[(\pi\text{-}C_5H_5)Mo(NO)I_2]_2$. The halogen bridges in complex (IIc) are cleaved by PPh_3 in refluxing acetone to give the monomeric $(HBPz_3)W(NO)(PPh_3)I_2$, $\nu(NO)$ at 1610 cm^{-1} (KBr).

Treatment of $(HBPz_3)Mo(CO)_2N_2Ph$ with equimolar quantities of halogens under conditions similar to those described above for the nitrosyls does not lead to analogous products. Instead very stable intensely blue crystalline solids result for which the analytical data (all elements except B) are in agreement with the formula $[(HBPz_3)Mo(N_2Ph)X]_n$ (IIIa, X = Cl; IIIb, X = Br; IIIc, X = I). Molecular weight determinations on all three compounds indicate $n = 2$ and the highly resolved NMR spectra suggest diamagnetism and hence a Mo—Mo bond. A probable cyclopentadienyl analogue of (IIIc), $[(\pi\text{-}C_5H_5)Mo(NO)I]_2$ has been synthesised by the reaction of C_3F_7I with $(\pi\text{-}C_5H_5)Mo(CO)_2NO$ [4]. The structure suggested for the mono-iodo compound involved an Mo—Mo bond bridged by two μ_2-NO groups and two μ_2-I ligands. Evidence from a variety of sources suggests a similar structure for complexes (IIIa - IIIc) which may thus be the first examples of complexes containing bridging arylazo groups:



(III)

(i) The very intense blue colour of complexes (IIIa - IIIc) (λ_{max} = 630 nm, $E_{max} \sim 1.9 \times 10^4$ in methanol, acetone or ether) is unique among molybdenum arylazo complexes. All previous examples contain formal PhN_2^+ terminally coordinated to Mo and are either orange or red. This suggests the presence of different chromophores in the two types of complex.

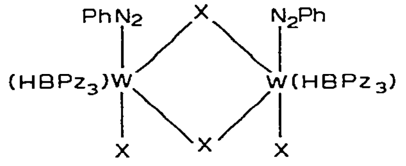
(ii) Preparation of (IIIc) from $(HBPz_3)Mo(CO)_2N_2Ph$ involves an increase in the Mo oxidation state but the frequency position of $\nu(NN)$ verified by ($^{14}N^{15}N$) labelling, decreases from 1556 to 1530 cm^{-1} (CH_2Cl_2). This trend is opposite to that expected for a terminal PhN_2^+ ligand but a shift to lower wavenumber would be expected to result from the formation of a μ_2-PhN_2 structure.

(iii) The Mo—Mo bond in (IIIc) is extremely unreactive and is not affected by excess iodine in boiling benzene. Such behaviour would be expected if, as suggested, the metal—metal bond is buried inside a cylindrical array of four bridging ligands.

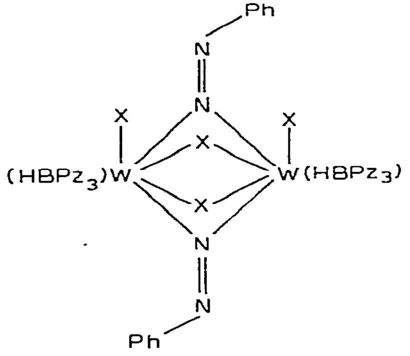
(iv) Finally, we might point out that the proposed structure for (IIIa - IIIc) is consistent with other observations on polypyrazolyl borate complexes which contain a metal—metal bond. Thus, while $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$ is known [7] to have two terminal and one μ_2-CO group the IR spectrum of the analogous complexes $(HBPz_3)Rh_2(CO)_3$ and $(BPz_4)Rh_2(CO)_3$ indicates that all three CO groups are doubly bridging [8]. The evident preference of polypyrazolylborate complexes for highly bridged structures is a natural consequence of the considerable steric bulk of the ligand.

The tungsten complex $(HBPz_3)W(CO)_2N_2Ph$ also reacts readily with Cl_2 and Br_2 in CH_2Cl_2 at low temperature but the products are the dihalide dimers $[(HBPz_3)W(N_2Ph)X_2]_2$, (IVa, X = Cl; IVb, X = Br)*. In the reaction with Br_2 the reaction mixture before work-up shows a single strong ν(CO) at 1977 cm^{-1} consistent with initial formation of $(HBPz_3)W(CO)(N_2Ph)Br_2$ (Va) but this complex does not survive work-up. In contrast the analogous reaction with I_2 yields the stable $(HBPz_3)W(CO)(N_2Ph)I_2$ (Vb) ν(CO) 1983 cm^{-1}, ν(NN) (confirmed by ($^{14}N^{15}N$) labelling) at 1634 cm^{-1} (CH_2Cl_2), as the only product. Complex (Vb) is quantitatively decarbonylated to $[(HBPz_3)W(N_2Ph)I_2]_2$, (IVc) in refluxing benzene. Three possible structures, (IV) (singly-bent terminal ArN_2^+), (IV′), and (IV″) (doubly-bent terminal ArN_2^-) must be considered for these complexes.

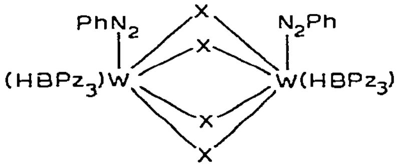
All three complexes show only weak IR peaks in the 1700 - 1500 cm^{-1} region and a medium-intensity peak at ca. 1435 cm^{-1} (thin film) was confirmed by ($^{14}N^{15}N$) labelling in (IVc) to be ν(NN). The exceptionally low value of



(IV)



(IV′)



(IV″)

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*Dimeric structure confirmed by molecular weight determination on (IVa).

ν(NN) for these complexes* rules out structure (IV) since the analogous nitrosyls of both the cyclopentadienyl and pyrazolylborate series have high ν(NO) values fully in keeping with the proposed structures. Structure (IV′), with a μ_2-PhN_2 group, seems also to be somewhat unlikely by analogy with μ_2-CO and μ_2-NO groups which are rarely found in the absence of a metal—metal bond. We are forced to the conclusion that structure (IV″) in which the arylazo ligand behaves as formal PhN_2^- is the most likely of all three structures.

Further investigations are continuing on these interesting new complexes. All compounds analysed correctly unless the contrary is stated.

One of us (M.E.D.) is grateful for a Department of Education Maintenance Grant.

References

1 L. Vaska, Accounts Chem. Res., 1 (1968) 335.
2 B.L. Haymore and J.A. Ibers, J. Amer. Chem. Soc., 95 (1973) 3052.
3 M.E. Deane and F.J. Lalor, J. Organometal. Chem., 57 (1973) C61.
4 T.A. James and J.A. McCleverty, J. Chem. Soc. (A), (1971) 1068.
5 R.B. King and M.B. Bisnette, Inorg. Chem., 5 (1966) 300.
6 S. Trofimenko, Chem. Ber., 72 (1972) 497.
7 O.S. Mills and J.P. Nice, J. Organometal. Chem., 10 (1967) 337.
8 D.J. O'Sullivan and F.J. Lalor, J. Organometal. Chem., 65 (1974) C47.

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*Compare the data for complex (Vb) in which the metal atom has the same formal oxidation state.