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Preliminary communication

BIS-ARYLDIAZO COMPLEXES OF MANGANESE

BARRY L. HAYMORE
Department of Chemistry, Indiana University, Bloomington, Indiana 47401 (U.S.A.)
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Summary

The first bis-aryldiazo complexes containing manganese of the type MnX-$(N_2Ph)_2(PPh_3)_2$ and $Mn(CO)(N_2Ph)_2(PPh_3)_2{}^+PF_6{}^-$ have been prepared from $Mn(CO)_2(N_2Ph)(PPh_3)_2$ (X = Cl, Br, NCO). In addition, the mixed aryldiazo—nitrosyl analogues and the dinitrosyl analogues have been prepared in order to compare their spectroscopic properties with the bis-aryldiazo complexes. The preparation of the rhenium complex $Re(CO)_2(N_2Ph)(PPh_3)_2$ is also reported.

In order to study the chemistry of the aryldiazo ligand bound to transition metals, we have prepared several stable bis-aryldiazo complexes of manganese in high yield according to the outlined reaction scheme (see Fig. 1). To date, only two bis-aryldiazo complexes have been mentioned in the literature [1], RuCl-$(N_2Ar)_2(PPh_3)_2{}^+PF_6{}^-$ and $(C_5H_5)Mo(N_2Ph)_2(PPh_3)^+BF_4{}^-$.

The starting material [2] $MnH(CO)_3(PPh_3)_2$, which was prepared by a new, convenient high-yield method, reacts with benzenediazonium salts to form stable *cis*-phenyldiazene complexes which in turn undergo deprotonation and decarbonylation in the presence of base to form orange crystals of $Mn(CO)_2(N_2Ph)$-$(PPh_3)_2$ (II) in good yield. This complex can be prepared less conveniently from $Mn_2(CO)_8(N_2Ph_2)_2$ which in turn is prepared from the reaction of $MnBr(CO)_5$ with $PhN{=}NSiMe_3$ over a period of six days [3]. The analogous nitrosyl starting material, $Mn(CO)_2(NO)(PPh_3)_2$ (I), was prepared by a modification of the literature method [4]. Both I and II undergo successive carbonyl displacement reactions in the presence of arenediazonium, nitrosonium and halide ions to yield a series of dinitrosyl, aryldiazonitrosyl and bis-aryldiazo complexes (see Table I). Brown colored compounds of the type $MnX(NO)_2(PPh_3)_2$ have been prepared previously by the action of NO on $MnX(CO)_3(PPh_3)_2$ [4]. Chromatographic purification of the bromide prepared by this method yields an orange product identical to ours and also a dark brown impurity. Spectroscopic data for the five-coordinate nitrosyl and aryldiazo complexes are all consistent with trigonal bipyramidal geometries about the metal, axial phosphine ligands and singly bent

TABLE 1

INFRARED SPECTRAL DATA FOR MANGANESE COMPLEXES (cm^{-1})

	Compound[a]	ν(CO)	ν(NO)	ν(NN)[b]
	$MnBr(CO)_3(PPh_3)_2$	1919, 1951, 2040		
	$MnH(CO)_3(PPh_3)_2$[c]	1894, 1908		
XV	$Mn(CO)_3(HN_2Ph)(PPh_3)_2^+PF_6^-$*[e]	1945, 1980, 2060		
	$Mn_2(CO)_8(PPh_3)_2$	1900, 1914, 1936 1954, 1978, 1986, 2060		
	$Mn_2(CO)_8(PPh_3)_2$*	1956, 1982		
	$Mn(CO)_3(NO)(PPh_3)$	1916, 1966, 2035	1703	
I	$Mn(CO)_2(NO)(PPh_3)_2$	1857, 1943	1655	
II	$Mn(CO)_2(N_2Ph)(PPh_3)_2$	1849, 1925		1476, 1543, 1612
III	$Mn(CO)(NO)_2(PPh_3)_2^+PF_6^-$*	2065	1738, 1778	
IV	$Mn(CO)(NO)(N_2Ph)(PPh_3)_2^+PF_6^-$*	2035	1753	1577, 1691
V	$Mn(CO)(N_2Ph)_2(PPh_3)_2^+PF_6^-$*	2015		1574, 1668, 1709
VI	$MnCl(NO)_2(PPh_3)_2$		1659, 1703	
VII	$MnBr(NO)_2(PPh_3)_2$		1658, 1702	
VIII	$Mn(NCO)(NO)_2(PPh_3)_2$	2195, 1334[d]	1656, 1698	
IX	$MnCl(NO)(N_2Ph)(PPh_3)_2$		1676	1476, 1564, 1630
X	$MnBr(NO)(N_2Ph)(PPh_3)_2$		1677	1476, 1565, 1631
XI	$Mn(NCO)(NO)(N_2Ph)(PPh_3)_2$	2225, 1432[d]	1680	1476, 1560, 1627
XII	$MnCl(N_2Ph)_2(PPh_3)_2$			1471, 1542, 1569, 1611, 1630
XIII	$MnBr(N_2Ph)_2(PPh_3)_2$			1471, 1543, 1570, 1607, 1632
XIV	$Mn(NCO)(N_2Ph)_2(PPh_3)_2$	2225, 1438[d]		1471, 1540, 1570, 1612, 1629

[a] Spectra measured in Fluorolube mulls (no designation) or in CH_2Cl_2 solution (*). [b] Verified by ^{15}N isotopic substitution. Resonance interaction of ν(NN) with phenyl vibrational modes is usually observed. [c] The third C—O stretching vibration is not observed; ν(MnH) 1827 cm^{-1}. [d] These are values for ν_s(NCO) and ν_{as}(NCO). [e] The N—N mode is not visible in the infrared spectrum.

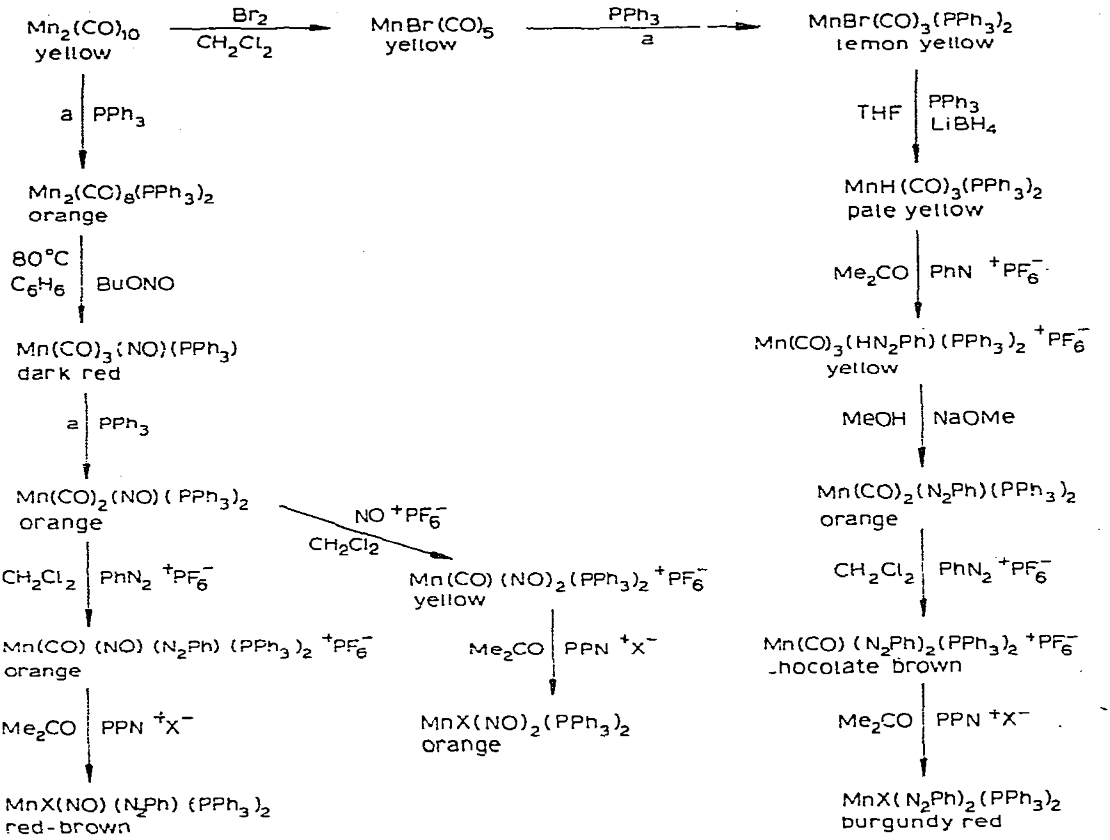
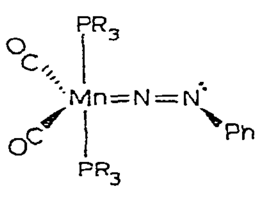
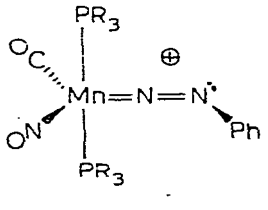


Fig. 1. Synthetic scheme for aryldiazo complexes of manganese. All reactions were carried out at 25°C under a nitrogen atmosphere except as noted. Acceptable C, H and N elemental analyses have been obtained for all complexes. PPN = Ph_3PNPPh_3; X = Cl, Br, NCO; THF = tetrahydrofuran; Ar = aryl. Reactions a performed in a PPh_3 melt (no solvent) at 150°C.

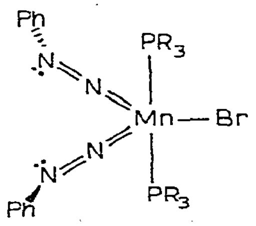
aryldiazo ligands [5]. The isoelectronic compounds $Fe(CO)_2(N_2Ph)(PPh_3)_2{}^+$ and $OsH(CO)(N_2Ph)(PPh_3)_2$ have similar structures [6].



(II)



(IV)



(XIII)

The comparison of C—O stretching frequencies in I and II and also in III, IV and V reaffirm the previously observed trends that the N_2Ph ligand is a very good π-acceptor ligand, but not quite as good as NO. Although the C—O stretching frequencies are much more sensitive to the substitution of N_2Ph for NO, the N—O stretching frequencies also show small but consistent decreases when NO is replaced by N_2Ph. Thus ν(NO) for III (1758 cm^{-1}, average) is higher than that for IV (1753 cm^{-1}), and ν(NO) for VII (1680 cm^{-1}) is higher than that for X (1677 cm^{-1}). In the mixed nitrosyl-aryldiazo complexes (IV, IX, X, XI), the N—O and N—N stretching vibrations seem to be weakly coupled, thus increasing the observed ν(NO) and decreasing the observed ν(NN) by 2—5 cm^{-1}.

The N—N stretching frequencies of the aryldiazo complexes are more difficult to obtain from the infrared spectra owing to the vibrational resonance interactions with one or two weak phenyl vibrational modes located near 1600 and 1475 cm^{-1}. Thus, XIII appears to have six interacting vibrational modes, and five bands are seen to shift upon ^{15}N substitution. Solution spectra are essentially the same as mull spectra indicating the absence of solid state splitting. With judicious choice of multiple isotopic labels (^{15}N and ^{2}H), however, the decoupled values of ν(NN) have been determined, and they follow the same trends as do the nitrosyl stretching frequencies noted above. The N—N stretching frequency for IV (1689 cm^{-1}) is higher than that for V (1686 cm^{-1}, average of 1666 and 1706), and ν(NN) for X (1598 cm^{-1}) is higher than that for XII (1578 cm^{-1}, average of 1555 and 1601). It is noteworthy that ν(NN) is consistently lower than ν(NO) by 60—80 cm^{-1} in analogous aryldiazo and nitrosyl complexes and also in mixed aryldiazo-nitrosyl complexes.

The orange-brown Re analogue of II, $Re(CO)_2(N_2Ph)(PPh_3)_2$, has also been prepared in a manner similar to that for the Mn complex; $ReH(CO)_2(PPh_3)_3$ was used as the starting material instead of the bis-phosphine tricarbonyl complex owing to the greater reluctance of the Re complexes to loose CO. The infrared spectrum of the Re aryldiazo complex shows C—O stretching frequencies (1848, 1920 cm^{-1}) and N—N stretching frequencies (1471, 1538, 1604 cm^{-1}) near those belonging to the Mn analogue but shifted by about 5 cm^{-1} to lower energy. The decoupled value of the ν(NN) is 1536 cm^{-1} and is the lowest yet recorded for a singly bent aryldiazo ligand (probable ligand geometry assumed).

Earlier two groups of workers using $Mn(CO)_5^-$ and benzenediazonium salts failed to generate the expected aryldiazo complexes, even at low temperature and in the presence of phosphine ligands [7]. It appears, however, that once the diazo group is attached to the metal, the resulting mono- and bis-aryldiazo complexes of manganese are more stable than had been expected. The aryldiazo complexes of manganese and rhenium are useful synthetic intermediates and readily undergo a number of reactions similar to aryldiazo complexes of Ru and Os [8].

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