Journal of Organometallic Chemistry, 61 (1973) C45–C47

Preliminary communication

Theoretical studies of nitrogen bonded organometallic carbonyls

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(Received September 17th, 1973)

SUMMARY

Molecular orbital calculations on $AM(CO)_{3-n}(N_2)_n$ ($AM = \pi\text{-}C_6H_6Cr$; $n = 0, 1$ and $AM = \pi\text{-}C_5H_5Mn$; $n = 0, 1$) have shown that N_2 is a weaker π-acceptor than the CO ligands in the tricarbonyls and the dinitrogen complexes, and a stronger ($\sigma + \pi$) electron donor than a CO ligand in the corresponding tricarbonyl complexes.

The complexes $\pi\text{-}C_5H_5Mn(CO)_2N_2$ (I)[1] and $\pi\text{-}C_6H_6Cr(CO)_2N_2$ (II)[2] have been prepared by the oxidation of the hydrazines of $\pi\text{-}C_5H_5Mn(CO)_3$ (III) and $\pi\text{-}C_6H_6Cr(CO)_3$ (IV). To study the relative bonding effects of the carbonyl and dinitrogen ligands in these complexes, self-consistent charge and configuration molecular orbital[3] (SCCC-MO) calculations were performed on the four complexes. Experimental geometries[4,5,6], where available, were used and the eigenvalues and eigenvectors for N_2 and CO were those used in an SCCC-MO study of $Cr(CO)_5N_2$ [7]. Table 1 gives the pertinent calculated results and also some experimental carbonyl stretching frequencies.

The π^* populations in all four complexes are much greater for CO than N_2 thus confirming that the carbonyl is the greater π acceptor. The carbonyl π^* populations reflect the trend in experimental carbonyl frequencies and thus, $\nu(CO)$ ($\pi\text{-}C_6H_6Cr(CO)_2N_2$) $<$ $\nu(CO)$ ($\pi\text{-}C_5H_5Mn(CO)_2N_2$) is predicted.

The 4σ orbital populations are constant throughout the series both for dinitrogen and carbonyl (1.982 ± 0.001) while the 5σ orbital populations of N_2 and of CO in the tricarbonyls differ little. Thus N_2 has a similar σ donating ability to a carbonyl in the tricarbonyl complexes. However, including π donation, the total electron donations from the dinitrogens in $\pi\text{-}C_6H_6Cr(CO)_2N_2$ and $\pi\text{-}C_5H_5Mn(CO)_2N_2$ are 0.121 and 0.114 electrons respectively while the corresponding values for each carbonyl in the tricarbonyls are 0.104 and 0.096. Thus the dinitrogens are better ($\sigma + \pi$) electron donors than the carbonyls in the tricarbonyls in agreement with Sellmann[1].

TABLE 1

Orbital populations	Charges	π-$C_5H_5Mn(CO)_2N_2$[a] (I)	π-$C_6H_6Cr(CO)_2N_2$[a] (II)	π-$C_5H_5Mn(CO)_3$ (III)	π-$C_6H_6Cr(CO)_3$ (IV)
π^*		0.412 (0.111)	0.439 (0.117)	0.327	0.356
π		3.992 (3.973)	3.992 (3.971)	3.992	3.992
5σ		1.910 (1.930)	1.901 (1.926)	1.930	1.923
4σ		1.982 (1.983)	1.981 (1.982)	1.982	1.981
Total forward donation/ligand		0.116 (0.114)	0.126 (0.121)	0.096	0.104
	q_A	0.472	0.462	0.558	0.572
	q_M	0.116	0.160	0.132	0.182
	q_{CO}	−0.296	−0.313	−0.231	−0.251
	q_{N_2}	0.003	.004		
	π donation from ring	0.535	0.844	0.610	0.868
	π^* donation to ring	0.063	0.382	0.053	0.296
$\nu(CO)\ A_1\ (cm^{-1})$		1980[1]	–	2035[8]	1982[9]

[a] Dinitrogen values in parentheses.

The large differences between the π^*(CO) populations and the π^* (N_2) populations are major factors in determining the relative charge distribution. Thus the metal in I and II, due to the decrease in back-bonding acquires a lower positive charge than in III and IV. Secondly there is an increase of back donation to the two remaining carbonyls in the dinitrogen complexes with a resultant increase in forward 5σ donation (synergic effect). The net effect is a lowering of carbonyl charge relative to the tricarbonyl complexes and the carbonyl frequencies are decreased relative to the tricarbonyls. Thirdly, larger charge donation from metal to ring in I and II coupled with smaller donation from ring to metal results in lower positive ring charges for the dinitrogen complexes.

It is interesting to note that in II, in which the ring is a good electron acceptor, the decrease in charge on C_6H_6 relative to IV results mainly from an increase in back-donation whereas with C_5H_5, which is a weak acceptor, the reduction in charge from III to I results almost totally from a decrease in forward donation.

The orbital populations and charges for N_2 in both dinitrogen complexes are remarkably similar. However, the π^* population in II is slightly greater than in I while the other populations are slightly less. Thus it is expected that the ν(N≡N) in II will be slightly less than 2169 cm^{-1}, the value in I[1].

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