Journal of Organometallic Chemistry, 301 (1986) C31—C34
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE ELECTRONIC STRUCTURES OF $[(C_5H_4XC_6H_5)Cr(CO)_3]^-$ AND $(C_6H_5XC_5H_4)Mn(CO)_3$, (X = —, CO, CH_2, C_2H_2)

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(Received October 25th, 1985)

Summary

SCCC calculations are reported for $[(C_5H_4XC_6H_5)Cr(CO)_3]^-$ and $(C_6H_5XC_5H_4)Mn(CO)_3$, with X = —, CO, CH_2 and C_2H_2. The calculated charges and Mulliken populations correlate in general with the frequencies. The results are interpreted consistently in terms of two extreme structures $(ABX)^-$=M—C≡O and (ABX)—M=C=O^-. The importance of delocalisation is noted.

The electronic structures of neutral $AM(CO)_3$ complexes, such as $(C_6H_6)Cr(CO)_3$, $(C_5H_5)Mn(CO)_3$ and related complexes and of charged species such as $[(B)Fe(CO)_3]^+$, B = C_5H_5, C_6H_7, C_7H_9, have been studied theoretically for a number of years, using approximate molecular orbital methods [1—7]. Substituted complexes, $(C_6H_5XC_5H_4)Mn(CO)_3$ and $(CO)_3Mn(C_5H_4XC_6H_5)Cr(CO)_3$, X = —, CO, CH_2, C_2H_2, have been prepared and studied using various spectroscopic techniques [8,9]. In the present study the IR frequencies are compared with the results obtained from Self-Consistent Charge and Configuration calculations on $[(C_5H_4XC_6H_5)Cr(CO)_3]^-$ and $(C_6H_5XC_5H_4)Mn(CO)_3$ (a and b), using the QCPE 256 program [10]. The atomic orbitals were those of Richardson and coworkers and of Clementi and Raimondi [11—13].

For the complexes with X = — and CO the ligands were planar and for those with X = CH_2 and C_2H_2 the C_5H_4 ring was tilted to decrease non-bonding interactions. Separate calculations, with the same geometries, were also considered for the free ligands. Standard geometries were used in the calculations.

Results and discussion

(a) [$C_5H_4XC_6H_5Cr(CO)_3$]$^-$. Table 1 gives the calculated charges on the various moieties for the [$(C_5H_4XC_6H_5)Cr(CO)_3$]$^-$ series. The trends in q_{Cr}, $q_{(CO)_3}$ and $q_{Cr(CO)_3}$ are CO > C_2H_2 > CH_2 > —, while the q_{AXB} trend is the reverse. Thus the electronegative oxygen in $C_5H_4COC_6H_5$ minimises the electron donation to the $Cr(CO)_3$. Also in $C_5H_4C_6H_5$, as maximum delocalisation occurs, the donation to $Cr(CO)_3$ is greatest while in the two cases where the rings are non-planar the donation is intermediate. It is of interest to note that the trends in q_{Cr} and $q_{(CO)_3}$ are identical and opposite to that of q_{AXB}. In all cases the $Cr(CO)_3$ behaves as an electron acceptor from the AXB^- group. The variation in metal charge is small, while that of the $(CO)_3$ groups is larger, the ranges being 0.012 for the former and 0.047 for the latter. However the range in q_{AXB} is greater still being 0.059. These results show that, to a certain extent, the metal behaves as a conduit, transferring charge to the carbonyls. Formally two extremes represented by $(AXB)^-$ = M—C≡O (X = CO) and (AXB)—M=C=O$^-$ (X = —) occur. It is of interest to see whether this formalism is supported by other calculated values and the experimental IR. The trend in the average Mulliken populations of a CO group in each complex is CO > C_2H_2 = CH_2 > —. This agrees with the trend in the charges and in the model proposed. The trend in carbonyl frequencies for $(CO)_3Mn(C_5H_4XC_6H_5)Cr(CO)_3$ are CO > — > CH_2 > C_2H_2 for the A_1 case and CO > — > C_2H_2 > CH_2 for the E case.

TABLE 1

SCCC RESULTS AND IR DATA FOR [$(AXB)Cr(CO)_3$]$^-$, A = C_5H_4, B = C_6H_5

X [a]	—	CO	CH_2	C_2H_2
q_{Cr}	0.341	0.353	0.346	0.348
$q_{(CO)_3}$	—0.454	—0.407	—0.436	—0.428
q_{AXB}	—0.887	—0.946	—0.910	—0.920
Sum of electron populations on carbons of C_6H_5 ring, Δ in parentheses				
σ	18.530(0.62)	18.576(0.49)	18.611(0.50)	18.507(0.50)
π	5.556(—0.62)	5.449(—0.56)	5.451(—0.60)	5.534(—0.59)
Total	24.088(—0.02)	24.025(—0.07)	24.062(—0.10)	24.041(—0.09)
MP(C—O)	1.436	1.440	1.438	1.438
$\nu(CO)(A_1)$	1979	1989	1977	1975
$\nu(CO)(E)$	1913	1925	1908	1910

[a] q_A = charge on A; Δ = complex-ligand populations; MP = Mulliken population; The frequencies refer to $(CO)_3Mn(C_5H_4XC_6H_5)Cr(CO)_3$.

Thus in both cases X = CO has the greatest frequency as predicted but the trends for the other complexes differ. However, in these three complexes, it may be noted that the range in frequencies is 5 cm^{-1} or less.

Table 1 also reports electron populations. The trend in total electron populations of the carbons in the complexed ring is the same as q_{AXB} (— > CH_2 > C_2H_2 > CO). This is approximately the trend in π populations. However the σ population trend is different: CH_2 > CO > — > C_2H_2. Thus it is not adequate to rationalise the results in terms of the populations in the C_6H_5 ring in isolation, since these suggest that X = — and CH_2 should have the most negative and X = C_2H_2 and CO the least negative AXB groups, where the reverse is the case. Thus the importance of delocalisation is noted.

A comparison of the complex and ligand carbon populations in the C_6H_5 ring shows larger ligand populations in all cases. Thus the ligand C_6H_5 ring donates 0.6 π electrons approximately in every case and accepts slightly less into the σ orbitals of the carbons resulting in a net donation of 0.10 electrons or less. Again the importance of the second ring and the role of both σ and π electrons are inferred.

The results show that when X = CO the total electron population in the carbons of the C_6H_5 ring are least yet the relative charges on the AXB moiety is greatest, while with X = — the corresponding electron populations are the largest while the AXB negative charge is the least. This clearly shows the importance of delocalisation in the ligand. With X = CO conjugation does not occur and the C_6H_5 ring is isolated from the rest of the ligand; thus in this case charge donation occurs from the C_6H_5 ring, hence the smallest carbon C_6H_5 ring populations and the most negative ring, while when maximum conjugation is possible in X = — the reverse occurs.

TABLE 2

SCCC RESULTS AND IR DATA FOR $(BXA)Mn(CO)_3$, B = C_6H_5, A = C_5H_4

X	—	CO	CH_2	C_2H_2
q_{Mn}	0.329	0.338	0.323	0.329
$q_{(CO)_3}$	−0.287	−0.253	−0.314	−0.290
q_{BXA}	−0.042	−0.085	−0.009	−0.039
Sum of electron populations on carbons of C_5H_4 ring.				
σ	15.401	15.386	15.340	15.402
π	4.605	4.586	4.672	4.605
Total	20.006	19.972	20.012	20.007
MP(C—O)	1.471	1.475	1.470	1.471
$\nu(CO)(A_1)$	2025	2034	2024	2022
$\nu(CO)(E)$	1941	1958	1938	1942

(b) $(C_6H_5XC_5H_4)Mn(CO)_3$, $C_6H_5XC_5H_4Mn(CO)_3$. The results for $(BXA)Mn(CO)_3$ are given in Table 2. The trends for q_{Mn} and $q_{(CO)_3}$ are CO > — ≈ C_2H_2 > CH_2 and for q_{BXA} $CH_2 > C_2H_2 \gtrsim - > CO$. Thus the q_{BXA} trend is the reverse of the q_{Mn} and $q_{(CO)_3}$ trends. This charge trend differs from the chromium series (a), except that for X = CO the largest metal and $(CO)_3$ charges and the most negative organic ligand occur. The variation in metal charge is small the range being 0.015, the ranges in $q_{(CO)_3}$ and q_{AXB} charges are 0.061 and 0.076. These ranges show the role of metal as a conduit for charge to the carbonyls. The trend in MP is the same as that for the charges supporting the model presented for (a) where negative carbonyls and low MPs are correlated.

The trend in IR frequencies is

$$CO \gg - \gtrsim CH_2 > C_2H_2 \; (A_1) \text{ and } CO \gg C_2H_2 \gtrsim - > CH_2 \; (E)$$

Thus in both the A_1 and E cases the complex with X = CO has the largest frequency. The range in frequencies of the other three complexes is 4 cm^{-1} or less. The trend in E vibrations is closer to the trend in MPs. Thus in this case, the frequencies, Mulliken populations and charges correlate.

References

1 D.A. Brown, N.J. Fitzpatrick and N.J. Mathews, J. Organomet. Chem., 88 (1975) C27.
2 R. Hoffmann and P. Hofmann, J. Am. Chem. Soc., 98 (1976) 598.
3 N.J. Fitzpatrick, J.-M. Savariault and J.-F.R. Labarre, J. Organomet. Chem., 127, (1977) 325.
4 T.H. Whitesides, D.L. Lichtenberger and R.A. Budnik, Inorg. Chem., 14 (1975) 68.
5 D.L. Lichtenberger and R.F. Fenske, J. Am. Chem. Soc., 98 (1976) 50.
6 D.A. Brown, J.P. Chester and N.J. Fitzpatrick, J. Organomet. Chem., 155 (1978) C21.
7 N.J. Fitzpatrick, N.J. Gogan and I.J. King, J. Organomet. Chem., 166 (1979) 45.
8 N.J. Gogan and C.-K. Chu, J. Organomet. Chem., 132 (1977) 103.
9 N.J. Gogan, C.-K. Chu and P.A. Narayana, J. Organomet. Chem., 92 (1975) 207.
10 P. Dibout, QCPE Program 256.
11 J.W. Richardson, W.C. Nieuwpoort, R.R. Powell and W.F. Edgell, J. Chem. Phys., 36 (1962) 1057.
12 J.W. Richardson, R.R. Powell and W.C. Nieuwpoort, J. Chem. Phys., 36 (1963) 796.
13 E. Clementi and D.L. Raimondi, J. Chem. Phys., 38 (1963) 2686.