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Preliminary communication

ELECTRONIC STRUCTURES AND REACTIVITIES OF THE ISOELECTRONIC SERIES π-AM(CO)$_3$: AM = C_6H_6Cr, C_5H_5Mn, C_4H_4Fe, C_3H_5Co, C_2H_4Ni.

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Summary

SCCC-MO results have been correlated with relative reactivities for a range of metal tricarbonyls.

Most metal carbonyl complexes undergo carbonyl substitution by an S_N1 dissociative process with a minority reacting by the S_N2 associative process [1,2]. Although correlations between reactivity and metal—ligand bond strength exist in a number of cases for the dissociative mechanism [1,2], the variation of S_N1/S_N2 character through a series of closely related metal carbonyl complexes has not previously been discussed. To correlate both reactivity and S_N1/S_N2 character with theoretical parameters SCCC-MO* calculations [3] have been performed on the isoelectronic series π-AM(CO)$_3$ (AM = C_6H_6Cr, C_5H_5Mn, C_4H_4Fe, C_3H_5Co, C_2H_4Ni) (Table 1). Geometries based on experimental structures [4] were used except for the hypothetical nickel complex where the geometric data were assumed. The coulomb integrals for the $p\pi$ orbitals of the A moiety were altered to give the best fit with experimental photoelectron levels, and with the ionization potential for allyl.

The 4σ and π carbonyl populations are constant across the series. The variations in the antibonding 5σ and π^* orbital populations imply a slightly weaker σ and stronger π C—O bond across the series. This trend is reflected experimentally by an increase in the frequency of both the A_1 and E ν(CO) modes.

The decrease in M—C(O) overlap population and π^* population in the series $C_6H_6Cr(CO)_3 > C_5H_5Mn(CO)_3 > C_4H_4Fe(CO)_3 > C_3H_5Co(CO)_3$ predicts an increase in S_N1 character across this series since both parameters indicate a weakening of the metal—carbonyl bond. According to our previous

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*SCCC-MO calculations = self-consistent charge and configuration molecular orbital calculations.

TABLE 1

SCCC-MO CALCULATIONS FOR π-AM(CO)$_3$ COMPOUNDS

Complex	$C_6H_6Cr(CO)_3$	$C_5H_5Mn(CO)_3$	$C_4H_4Fe(CO)_3$	$C_3H_5Co(CO)_3$	$C_2H_4Ni(CO)_3$
CO populations					
π^*	0.356	0.326	0.208	0.199	0.136
5σ	1.923	1.930	1.930	1.952	1.938
4σ	1.981	1.932	1.983	1.986	1.984
π	3.992	3.992	3.992	3.992	3.990
Charges					
q(A)	0.572	0.566	0.193	0.301	0.032
q(M)	0.182	0.123	0.143	0.085	0.113
q(CO)	−0.251	0.231	−0.113	−0.129	−0.049
q(C) [a]	−0.265	−0.242	−0.130	−0.141	−0.068
Metal configuration					
d	5.360	6.391	7.390	8.509	9.399
s	0.306	0.330	0.331	0.322	0.395
p	0.152	0.151	0.135	0.085	0.094
Overlap populations					
M—C(O) [b]	0.392	0.360	0.287	0.219	0.213
M—C(A) [b]	0.136	0.164	0.193	0.147	0.169
Reactivity	Thermally unreactive	Thermally unreactive	No kinetic data	S_N1	—
ν(CO) A_1 cm^{-1}	1982	2035	2055	2068	—
ν(CO) E cm^{-1}	1915	1949	1985	2000	—

[a] Using q(C) in free CO as reference. [b] This is the overlap population per carbon.

arguments [5*], increasing π^* populations and metal charge (q(M)) suggest a greater tendency for S_N2 behaviour via attack at the metal atom in the cases of $C_6H_6Cr(CO)_3$ and $C_5H_5Mn(CO)_3$ although this process must be inhibited both by the requirement of a seven coordinate transition state for first-row transition elements and by the increase in M—C(O) overlap population; indeed the considerably lower values of the M—C(A) overlap populations suggest that ligand substitution may occur by cleavage of the metal—ring bond as observed, for example in the ligand exchange reactions of labelled benzene and benzenetricarbonylchromium [6].

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* Different allyl functions were used in this reference.