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An all-electron and effective core potential study of the effects of electron correlation on the Group 7 complexes $[(C_6H_6)X(CO)_3]^+$, with X = Mn, Tc, Re

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Abstract

All-electron ab initio calculations have been performed for the first two members of the series $[(C_6H_6)X(CO)_3]^+$, X = Mn, Tc, Re, and for the whole series using effective core potentials. Hartree–Fock metal-related equilibrium geometries fail to reproduce experimental results. The extent of this discrepancy falls on going down the series. Electron correlation effects on the metal to ring, ring carbon–carbon, metal to carbonyl carbon and carbon–oxygen bond lengths have been examined using second order Møller–Plesset perturbation theory (MP2). These bond lengths are sensitive to MP2 treatment, and the sensitivity decreases in the order Mn > Tc > Re. Correlation enhances the CO σ bonding/π backbonding mechanism.

Key words: Ab initio (calculations); Manganese; Molecular orbital calculations; Rhenium; Technetium; Electron correlation

1. Introduction

The half-sandwich series $[(C_6H_6)X(CO)_3]^+$, X = Mn, Tc, Re, involves metal–carbonyl and metal–ring bonding, both of which have been shown to be difficult to describe via purely SCF means [1–5]. The reproduction of experimental geometries is a particular problem, requiring high quality basis sets and electron correlation to the second order Møller–Plesset (MP2) level or better [6].

We have attempted to solve the problem for the title series by using MP2 theory coupled with moderate sized split valence basis sets. Thus it was possible to perform all-electron calculations on $[(C_6H_6)X(CO)_3]^+$, X = Mn, Tc, as well as effective core potential (ECP) calculations for the whole series, X = Mn, Tc, Re.

2. Calculational details

Ab initio calculations were carried out on the series $[(C_6H_6)X(CO)_3]^+$, using both effective core potentials (X = Mn, Tc, Re) and all-electron basis sets (X = Mn, Tc).

For the ECP calculations the metal core potentials and valence basis sets were those of Hay and Wadt [7], the potentials incorporating mass–velocity and Darwin relativistic effects. The ligand basis sets were the standard 3–21g and 3–21g* sets of Pople and co-workers [8,9]. The final three sets used were ECP, ECP′ and ECP*, the latter two sets involving metal and ligand polarisation functions respectively. Hartree–Fock (HF) optimisations were carried out at all three levels, while MP2 equilibrium geometries were obtained at the ECP′ level.

All-electron calculations were carried out for the systems $[(C_6H_6)X(CO)_3]^+$, X = Mn, Tc, using the metal 3–21g sets of Dobbs and Hehre [10,11]. Ligand atoms were described using the 3–21g and 3–21g* basis sets of Pople and co-workers [8,9]. The final sets were 3–21g, 3–21g′ and 3–21g*, the latter pair involving metal polarisation and ligand polarisation functions respectively.

For all optimisations the ring was kept planar and the C–H bond distances were fixed at 1.07 Å. Geometry optimisations were carried out at both the MP2 and

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TABLE 1. All-electron ground state geometries and energies for the $[(C_6H_6)Mn(CO)_3]^+$ system, bond lengths in ångstroms, angles in degrees, energies in hartrees

Parameter	HF/3-21g	HF/3-21g′	HF/3-21g*	MP2/3-21g′	Experiment
Mn-C(O)	2.024	2.020	2.012	1.716	1.78
Mn-o [a]	1.874	1.845	1.756	1.593	1.68
C-O	1.122	1.123	1.106	1.188	1.15
C-C	1.397	1.397	1.394	1.432	1.39
C(O)Mno	60.0	59.8	58.9	53.7	55.0
Energy	−1709.5682	−1709.5932	−1709.9169	−1711.2132	–

[a] o = ring centroid.

HF levels using the gaussian series of programs of Pople and co-workers [12].

3. Results and discussion

3.1. *All-electron results*

Equilibrium geometries are given in Tables 1 and 2 for the $[(C_6H_6)X(CO)_3]^+$, X = Mn, Tc species respectively, at both the HF and MP2 levels. The Mn-C(O) bond lengths fall slightly upon improvement of the basis set at the HF level, but the distance of 2.012 Å yielded by the 3-21g* set is 0.232 Å too long compared to the X-ray average of 1.78 Å [13]. Similarly the $[(C_6H_6)Mn(CO)_3]^+$ carbonyl C-O distances of 1.122 Å, 1.123 Å and 1.106 Å are too short compared with the X-ray average of 1.15 Å. These results confirm the well-known poor ability of the HF method to describe carbonyl-metal bonding.

Subsequent MP2/3-21g′ optimised results show Mn-C(O) bond shortening by 0.304 Å to 1.716 Å, a difference of 0.064 Å compared with the X-ray average. A simultaneous C-O bond length increase of 0.065 Å to 1.188 Å is also seen to occur, longer than the MP2/3-21g result for free carbonyl of 1.171 Å, implying π backbonding in the complex.

$[(C_6H_6)Tc(CO)_3]^+$ geometries at both the HF and MP2 levels are given in Table 2. The HF treatment again overestimates metal to C(O) bond lengths by an average of 0.188 Å, less than the 0.238 Å value for the X = Mn case. The C-O bond distances are found to vary between 1.108 Å and 1.127 Å. MP2 equilibrium geometries show a decrease in the Tc-CO bond length by 0.112 Å to 1.949 Å, overestimating X-ray averages by 0.069 Å. The MP2 CO bond length is 1.179 Å compared with the value for the Mn complex of 1.188 Å, showing that there is a decrease in metal to carbonyl backbonding upon moving down the group.

C-C bond length in the benzene ligand increases between the HF and MP2 optimised geometries by 0.035 Å and 0.033 Å for the Mn and Tc cases respectively, while the free benzene change is 0.022 Å, indicating that some backbonding to benzene takes place. Geometry optimisations on $[Mn(CO)_6]^+$ at the MP2/3-21g′ level give a CO bond length of 1.178 Å, a decrease of 0.01 Å from the $[(C_6H_6)Mn(CO)_3]^+$ value, indicating that electron density preferentially backbonds to the CO π^* orbitals rather than to the benzene δ orbitals. The MP2/3-21g′ $[Tc(CO)_6]^+$ value for $r(CO)$ is 1.172 Å, 0.007 Å less than the $[(C_6H_6)Tc(CO)_3]^+$ value of 1.179 Å, showing that the effect weakens slightly on going down the group.

Mulliken carbon and oxygen population analyses are given in Table 3 for the all-electron calculations. This method of population calculation is known to be unreliable if metal s and p populations are negative [14], and only trends, rather than absolute values, should be considered. With this in mind, in Table 3 we show the populations for both free and complexed CO. The C(O) p population shows an increase of 0.2303e upon complexation at the HF/3-21g′ level due to backbond-

TABLE 2. All-electron ground state geometries for the $[(C_6H_6)Tc(CO)_3]^+$ system, bond lengths in ångstroms, angles in degrees, energies in hartrees

Parameter	HF/3-21g	HF/3-21g′	HF/3-21g*	MP2/3-21g′	Experiment
Tc-C(O)	2.055	2.061	2.089	1.949	1.88
Tc-o [a]	2.104	2.081	2.026	1.860	–
C-O	1.126	1.127	1.108	1.179	1.15
C-C	1.401	1.401	1.400	1.434	–
C(O)Tco	54.6	54.8	54.3	53.1	–
Energy	−4750.4586	−4750.492	−4750.7908	−4752.844	–

[a] o = ring centroid.

TABLE 3. All-electron Mulliken populations for the $[(C_6H_6)X(CO)_3]^+$ systems, X = Mn, Tc

Calculation	p C(O)	s C(O)	p O	s O
$[(C_6H_6)Mn(CO)_3]^+$				
HF/3-21g	2.1328	3.5338	4.4110	4.0017
HF/3-21g′	2.0926	3.5474	4.4175	4.0162
HF/3-21g*	2.1344	3.4979	4.3735	3.9144
MP2/3-21g′	2.4875	3.3909	4.2748	4.0131
$[(C_6H_6)Tc(CO)_3]^+$				
HF/3-21g	2.1480	3.4779	4.4287	3.9892
HF/3-21g′	2.0672	3.4349	4.4349	4.0162
HF/3-21g*	2.1229	3.4587	4.3889	3.9047
MP2/3-21g′	2.2985	3.4162	4.2746	4.0050
Free CO				
HF/3-21g	1.8623	3.7003	4.4983	3.9391
MP2/3-21g	1.9827	3.7538	4.3242	3.9393

ing, yet the increase at the MP2 level is 0.5048*e*. Similarly, C(O) s populations decrease by 0.1529*e* and 0.3629*e* at the HF/3-21g′ and MP2/3-21g′ levels, respectively. Surprisingly these differences at the HF level yield little variation in CO bond lengths upon complexation, while an increase of similar order at the MP2 level over the HF level yields large CO bond length changes.

In the $[(C_6H_6)Tc(CO)_3]^+$ case the populations show a similar increase in C(O) p values upon complexation at the HF level of 0.2049*e* yet yield an increase of only 0.3158*e* at the MP2 levels, while the respective s populations decline by 0.2654*e* and 0.3376*e*, indicating a weakening of the importance of CO σ/π bonding with the application of correlation upon progression down the series.

3.2. ECP results

Tables 4–6 give the ECP optimised geometries and energies for the three systems $[(C_6H_6)X(CO)_3]^+$, X = Mn, Tc, Re. The $[(C_6H_6)Mn(CO)_3]^+$ results at the HF level are unrepresentative, giving long metal related bond lengths. As with the all-electron results the CO lengths are too short, attaining values of 1.120–1.121 Å. MP2 results are in good accord with experiment, the Mn–C(O) and Mn–o distances of 1.773 Å and 1.716 Å being within 0.007 Å and 0.036 Å respectively of the X-ray averages.

TABLE 4. ECP ground state geometries and energies for the $[(C_6H_6)Mn(CO)_3]^+$ system, bond lengths in ångstroms, angles in degrees, energies in hartrees

Parameter	HF/ECP	HF/ECP′	HF/ECP*	MP2/ECP′	Experiment
Mn–C(O)	2.342	2.309	2.337	1.773	1.78
Mn–o	2.381	2.335	2.383	1.716	1.68
C–O	1.121	1.120	1.120	1.182	1.15
C–C	1.393	1.394	1.393	1.432	1.39
C(O)Mno	56.7	56.7	56.6	54.3	55.0
Energy	−580.4943	−580.5084	−580.5087	−581.7965	–

TABLE 5. ECP ground state geometries and energies for the $[(C_6H_6)Tc(CO)_3]^+$ system, bond lengths in ångstroms, angles in degrees, energies in hartrees

Parameters	HF/ECP	HF/ECP′	HF/ECP*	MP2/ECP′	Experiment
Tc–C(O)	2.021	2.007	2.030	1.892	1.88
Tc–o [a]	2.137	2.108	2.000	1.951	–
C–O	1.127	1.127	1.109	1.181	1.15
C–C	1.401	1.402	1.401	1.433	–
C(O)Tco	53.7	53.5	53.4	52.2	–
Energy	−577.1265	−577.1429	−577.4812	−578.5042	–

[a] o = ring centroid.

The results for the Tc and Re species are given in Tables 5 and 6. The ECP HF geometries still fail to include correct descriptions of the ring metal and carbonyl to metal bonding but are in closer agreement with the all-electron results. Subsequent MP2 optimisations show a Tc–C(O) decrease of 0.115 Å to 1.892 Å and a Re–C(O) decrease of 0.09 Å to 2.047 Å. The MP2 C–O bond length values decrease upon moving down the series with values 1.182 Å, 1.181 Å and 1.177 Å for the Mn, Tc, and Re cases, revealing the decreasing importance of correlation to the σ/π CO bonding mechanism.

Mulliken population analyses, as with the all-electron case, are in general agreement with this trend (Table 7). The HF free to complexed carbonyl carbon s population for $[(C_6H_6)Mn(CO)_3]^+$ decreases by 0.1438*e*, while the MP2 decrease is 0.5017*e*. The corresponding p values increase to 0.1143*e* and 0.2960*e*. The low value for the s population change and the p population gain at the HF level compared to the all-electron

TABLE 6. ECP ground state geometries and energies for the $[(C_6H_6)Re(CO)_3]^+$ system, bond lengths in ångstroms, angles in degrees, energies in hartrees

Parameter	HF/ECP	HF/ECP′	HF/ECP*	MP2/ECP′	Experiment
Re–C(O)	2.213	2.137	2.203	2.047	1.936
Re–o	2.232	2.189	2.150	2.060	–
C–O	1.118	1.127	1.107	1.177	1.145
C–C	1.406	1.406	1.405	1.406	–
C(O)Reo	54.2	54.3	53.9	53.4	–
Energy	−576.3963	−576.4259	−576.7365	−577.7248	

[a] o = ring centroid.

TABLE 7. ECP Mulliken populations for the $[(C_6H_6)X(CO)_3]^+$ systems, X = Mn, Tc, Re

Calculation	p C(O)	s C(O)	p O	s O
$[(C_6H_6)Mn(CO)_3]^+$				
HF/3-21g	2.0189	3.5620	4.4005	3.9525
HF/3-21g′	1.9766	3.5565	4.4058	3.9782
HF/3-21g*	2.0401	3.5765	4.3725	3.9461
MP2/3-21g′	2.2787	3.2511	4.2477	3.9897
$[(C_6H_6)Tc(CO)_3]^+$				
HF/DH/3-21g	2.0909	3.3873	4.4265	3.9652
HF/3-21g′	2.0705	3.3926	4.4291	3.9743
HF/3-21g*	2.0529	3.3901	4.3922	3.8889
MP2/3-21g′	2.2826	3.2222	4.2582	3.9785
$[(C_6H_6)Re(CO)_3]^+$				
HF/3-21g	2.0507	3.4349	4.41548	3.9531
HF/3-21g′	2.0107	3.4219	4.4202	3.9709
HF/3-21g*	2.0527	3.4009	4.3792	3.8673
MP2/3-21g′	2.2156	3.2447	4.2573	3.9715
Free CO				
HF/3-21g	1.8623	3.7003	4.4983	3.9391

calculations, in conjunction with long equilibrium bond lengths, implies a poor molecular description at the ECP/HF level, while both the MP2 bond lengths and population changes imply an improved description.

Table 7 shows how this description improves rapidly upon proceeding down the group, the HF s populations decreasing by 0.3077*e* and 0.2784*e* for Tc and Re respectively while the HF p values increase by 0.2082*e* and 0.1482*e*. The HF all-electron and ECP trends are therefore in general agreement with the experimental trends going down the group. The HF description is more adequate for the Tc complex than for the Mn one, due to the more diffuse nature of the valence d orbitals used for bonding.

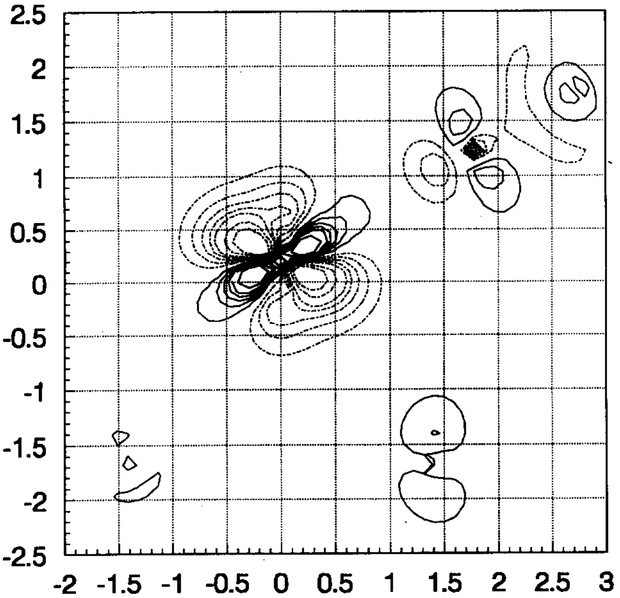

Fig. 1. An (MP2–HF)/3–21g′ density difference contour map through the C_{3v} plane of the $[(C_6H_6)Mn(CO)_3]^+$ system. The contour values used are −0.01, −0.02, −0.03, −0.04, −0.05, −0.075, −0.1, 0.01, 0.02, 0.03, 0.04, 0.05, 0.07.

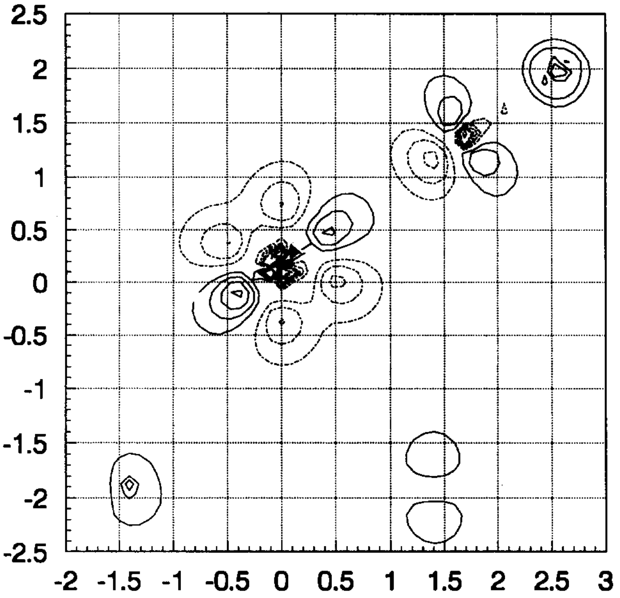

Fig. 2. An (MP2–HF)/3–21g′ density difference contour map through the C_{3v} plane of the $[(C_6H_6)Tc(CO)_3]^+$ system. The contour values used are −0.01, −0.02, −0.03, −0.04, −0.05, −0.075, −0.1, 0.01, 0.02, 0.03, 0.04, 0.05, 0.07.

4. Conclusion

All-electron geometry optimisations on the series $[(C_6H_6)X(CO)_3]^+$, X = Mn, Tc, at the HF level yield unsatisfactory metal related geometries.

Subsequent MP2 equilibrium geometries are in closer accord with X-ray averaged geometries. The correlation treatment is seen to be more important in the description of the Mn than the Tc species, being demonstrated by comparison of the MPA and bond length trends at the HF and MP2 optimised geometries. Density difference plots (Figs. 1, 2) indicate that this is due to the higher degree of contraction of the 3d orbitals on Mn than of the 4d orbitals on Tc.

ECP HF calculations on the species $[(C_6H_6)X(CO)_3]^+$, X = Tc, Re yield bond lengths in acceptable agreement with their all-electron counterparts while for the Mn complex the lengths are too long. MP2 ECP geometries are in close accord with the X-ray averaged geometries for all three species.

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