^{13}C NMR chemical-shift tensors of interstitial carbides in transition-metal clusters calculated by density-functional theory

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Results of density-functional calculations of ^{13}C chemical-shift tensors for interstitial carbides in transition-metal carbonyl clusters are in excellent agreement with available experimental data and provide valuable additional information on the orientation of the shift tensors and on the relation between shift tensors and electronic structure.

Interstitial main-group atoms enclosed in transition-metal clusters are often identified *via* their NMR signals. The NMR chemical shifts of these interstitials cover a considerable range, indicating a variety of bonding situations. Mason[1,2] recently pointed out a correlation between the shifts and a compression of the interstitial (in carbonyl clusters), *i.e.* the shift appears to increase with a decrease of the effective radius of the cluster cavity. The rationalisation of this observation is still pending. More work is needed to achieve a detailed understanding of bonding in these types of cluster compounds.

Up to now, there has been no quantitative computational evaluation of chemical-shift tensors in transition-metal clusters due to the difficulties of accounting for electron correlation (this is reflected in the statement[3] 'Inevitably, we face with this kind of system the problem that it is presently beyond any quantitative treatment, *e.g.* by *ab initio* MO calculations.'). However, very recently[4,5] we showed that density-functional theory (DFT) allows the accurate calculation of ligand NMR chemical shifts in transition-metal systems, as it implicitly accounts for electron correlation at much lower computational cost than needed for post-Hartree–Fock *ab initio* methods. The results provided here demonstrate that even the ^{13}C chemical-shift tensors of interstitial carbides in transition-metal carbonyl clusters are now accessible to quantitative analysis and prediction. For the first time we can computationally address the orientation of the shift tensors (which is very demanding to obtain experimentally[3]) and attempt to relate the tensors to electronic structure.

Table 1 summarises ^{13}C shift tensors calculated using sum-over-states density-functional perturbation theory (SOS-DFPT),[6]† combined[4] with quasirelativistic effective-core potentials (ECP),[7]‡ for a number of interstitial carbides (the calculations employed experimental structures[8]§). In addition to experimental isotropic shifts,[1,2] we also include two examples {$[Rh_6C(CO)_{13}]^{2-}$ and $[Rh_6C(CO)_{15}]^{2-}$} of the recently obtained[9] first experimental shift tensors for interstitial carbides. The agreement between theory and experiment for the isotropic shifts is equal to or better than 15 ppm, except for $[Rh_6C(CO)_{15}]^{2-}$ which is calculated *ca.* 30 ppm too high, and $[Fe_6C(CO)_{16}]^{2-}$ which is 45 ppm too low. The somewhat larger discrepancy for the latter anion is most probably due to the relatively poor quality of the experimental structure used.[8c] Agreement for the individual tensor elements of the two rhodium clusters is also good (Table 1). Thus, the combined ECP/SOS-DFPT approach gives a reliable quantitative description of shielding tensors even for these very deshielded nuclei and complex molecular systems.

Table 1 Computed (experimental[a]) ^{13}C chemical-shift tensors for interstitial carbides[b]

	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	Metal polyhedron
$[Rh_6C(CO)_{13}]^{2-}$	684 (705)	366 (362)	341 (349)	464 (472)	distorted octahedron
$[Rh_6C(CO)_{15}]^{2-}$	434 (393)	429 (393)	28 (9)	297 (265)	trigonal prism
$[Fe_4C(CO)_{13}]$	703	488	197	463 (478)	butterfly
$[Fe_5C(CO)_{15}]$	748	343	340	477 (486)	square pyramid
$[Os_5C(CO)_{15}]$	518	243	238	333	square pyramid
$[Fe_6C(CO)_{16}]^{2-}$	791	324	210	442 (485)	distorted octahedron

[a] See ref. 9 for the two rhodium clusters, and the bibliography of ref. 2 for the isotropic shifts. [b] In ppm *vs.* $SiMe_4$.

The absolute orientation of the shift tensors is indicated in Fig. 1. While we cannot support the hybridisation arguments of Heaton *et al.*[9] (the hybridisation concept is not applicable in a straightforward way to strongly delocalised systems[10]), our calculations confirm their suggestion that the shielding anisotropy is closely related to the detailed structure of the cluster cavity (which in turn is connected to the distribution of the peripheral carbonyl ligands). Thus, the very large δ_{11} principal component of the shift tensor in $[Rh_6C(CO)_{13}]^{2-}$ points towards the axial sites [Rh(2), Rh(4)] in this somewhat elongated[8a] Rh_6 octahedron [Fig. 1(*a*)]. The large shifts are due to deshielding contributions involving the C–M bonding orbitals within the cluster (this holds for all of the systems studied). A calculation with a hypothetical structure featuring a regular Rh_6 octahedron (a C–Rh distance of 1.963 Å was assumed), one threefold bridging, and twelve terminal carbonyl ligands (this would also give the correct electron count for a *closo* cluster) gives a much smaller and almost completely isotropic shift (δ_{iso} 336). The relatively poor C–Rh_{axial} overlap in the 'real' structure[8a] gives rise to a low-lying π^*-type orbital, which apparently accounts for the extremely large δ_{11} and subsequently for the overall dramatic deshielding. In the case of trigonal-prismatic $[Rh_6C(CO)_{15}]^{2-}$ [Fig. 1(*b*)], the smallest tensor component (δ_{33}) is oriented parallel to the 'threefold axis' of the Rh_6 trigonal prism (δ_{11} and δ_{22} are oriented equatorially).

The very large δ_{11} in $[Fe_6C(CO)_{16}]^{2-}$ also appears to be directed between two iron atoms with somewhat elongated C–M distances [Fig. 1(*c*)].[8c] The deviations from axial symmetry in the computed shift tensor might be artifacts due to the poor input structure (*cf.* above). Therefore, the tensor orientation for this cluster is probably the least reliable of the six systems studied. In $[Fe_5C(CO)_{15}]$, the largest principal component (δ_{11}) is directed along the C–Fe_{apical} axis [Fig. 1(*d*)], as one might expect. In $[Fe_4C(CO)_{13}]$, the largest component (δ_{11}) also points to an open face of the cluster, parallel to the backbone [Fe(1), Fe(2)] of the Fe_4 butterfly, whereas δ_{22} is directed away from the midpoint of the two backbone atoms [Fig. 1(*e*)]. The smallest component (δ_{33}) points approximately along a line connecting the wingtips [Fe(3), Fe(4)]. This agrees with previous suggestions that the bonds from the interstitial to the wingtips are the strongest[11] [which is also supported by the bond distances,[8e] *cf.* Fig. 1(*e*)]. Even though the individual tensor elements for $[\mathrm{Fe_5C(CO)_{15}}]$ and $[\mathrm{Fe_4C(CO)_{13}}]$ are very different, the isotropic shifts (δ_{iso}) are similar, due to compensation between the δ_{11} and δ_{22} contributions. $[\mathrm{Os_5C(CO)_{15}}]$ exhibits the same orientation of the shift tensor as its lighter iron homologue. However, all three principal components are considerably reduced. As the carbide atom in $[\mathrm{Ru_6C(CO)_{16}}]^{2-}$ is only 36 ppm more shielded than that in $[\mathrm{Fe_6C(CO)_{16}}]^{2-}$,[1,2] we suspect that our calculated value for the osmium complex is considerably too low, possibly due to the neglect of spin–orbit coupling in our calculations.[4]

To investigate the proposed correlation between the shifts and the cavity size,[1,2] we have also carried out two calculations on $[\mathrm{Fe_5C(CO)_{15}}]$ where all C–Fe bonds have been stretched (by 0.1 and 0.2 Å, respectively). This leads to δ_{iso} 527, 586, respectively. Thus, the expansion of the cavity for this given cluster increases the shifts considerably, and almost linearly. This contradicts the notion[1,2] that a 'compression' of the cavity increases the shift of the interstitial. Obviously, the expansion of the C–Fe bonds lowers the band gap (the calculated Kohn–Sham orbital band gap decreases from *ca.* 1.46 to *ca.* 1.28 to *ca.* 1.10 eV) and thus increases the paramagnetic contributions to the shift tensor (as frequently observed[12]). Therefore, the relation between cavity size and shift must be more indirect. In particular, the larger shift of the octahedral compared to the trigonal-prismatic cluster is probably connected to the different electron count (and to the deformation of the octahedron, *cf.* above). It is notable that, *e.g.* the colour of compounds with the octahedral $[\mathrm{Rh_6C(CO)_{13}}]^{2-}$ anion (with a formal cluster electron count of 86) is red–brown[8a] whereas that of the trigonal-prismatic $[\mathrm{Rh_6C(CO)_{15}}]^{2-}$ cluster (90 cluster electrons) is yellow.[8b] The computed Kohn–Sham orbital energies confirm a *ca.* 0.3 eV larger band gap for the trigonal-prismatic compared to the octahedral cluster. This may account for the reduced paramagnetic contributions to the carbide chemical shift. More detailed analyses of these questions, on a larger number of interstitial main group atoms in transition-metal clusters, are in progress. Preliminary results support the notion that the largest shift tensor components are connected to the presence of low-lying π^*-type orbitals.

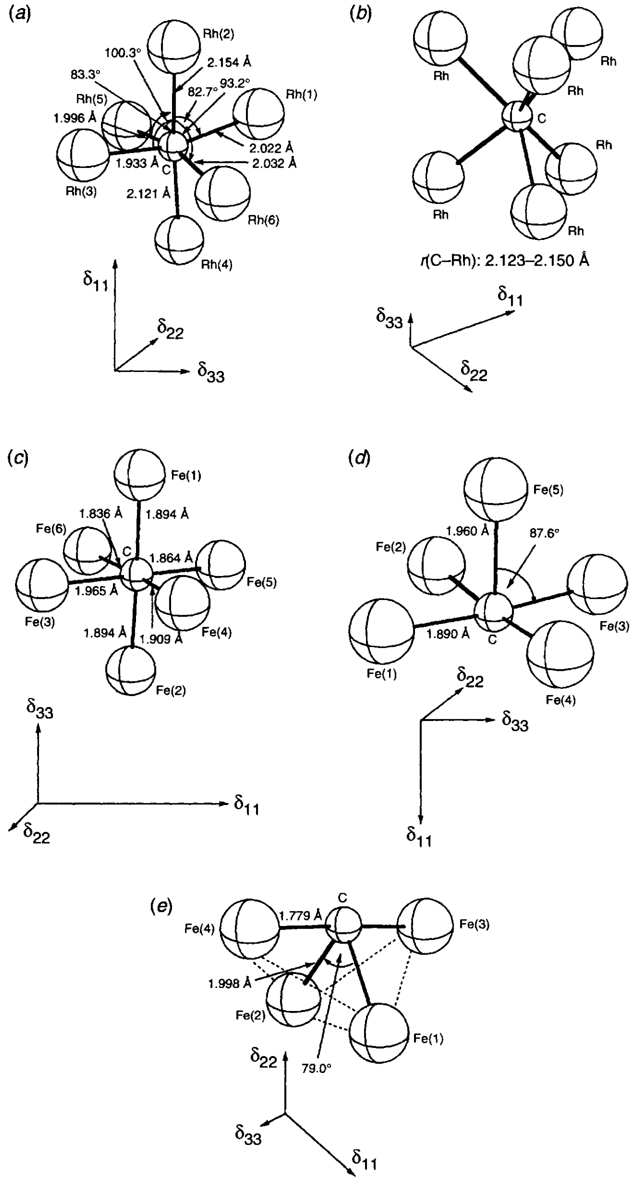

Fig. 1 Cluster backbone structures (the carbonyl ligands have been omitted) with the orientation of the principal axes of the shift tensors: (*a*) $[\mathrm{Rh_6C(CO)_{13}}]^{2-}$, (*b*) $[\mathrm{Rh_6C(CO)_{15}}]^{2-}$, (*c*) $[\mathrm{Fe_6C(CO)_{16}}]^{2-}$, (*d*) $[\mathrm{Fe_5C(CO)_{15}}]$, (*e*) $[\mathrm{Fe_4C(CO)_{13}}]$

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Footnotes

† More details of the SOS/DFPT computations are described in ref. 4 and 5.

‡ Quasirelativistic ECPs and valence basis sets[7a,b] were used for Rh and Fe, IGLO-II all-electron basis sets[7c] for the carbide carbon, and for one carbonyl group out of each unique set. DZ all-electron bases[7d] were used for the remaining carbonyl ligands.

§ The structures have been slightly idealised in some cases, in particular some unreasonable C–O distances[8c] in $[\mathrm{Fe_6C(CO)_{16}}]^{2-}$ have been modified.

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