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Darmstadtium carbonyl and carbide resemble platinum carbonyl and carbide

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DsC and DsCO are calculated to be very similar to PtC and PtCO, suggesting that even the latest 6d elements resemble the corresponding 5d elements chemically.

The transactinides E104–E108 (Rf–Hs) have been shown experimentally to resemble chemically their lighter homologues Hf–Os[1–3] and thus are chemically assigned to the Groups 4–8, respectively. After a grey zone from E109 to E111 at least one break in the chemical properties may occur: The absorption properties of atomic E112 on gold or ice surfaces have been shown to be more Rn-like than Hg-like.[4] For elements in the zone E109-111 some theoretical data also exist. The halides of eka-gold, E111, have been shown to favour higher oxidation states than the halides of gold.[5] The cation (E112)H$^+$ is calculated to have almost as short a bond length as ZnH$^+$.[6] The question is, whether a sudden *transactinide break* would take place in the chemical properties of the late 6d elements Mt and Ds (E109 and E110) or not. It could be induced by the closely similar 6d and 7s orbital energies. One difference between Pt and Ds is the predicted ground state electron configuration. While for Pt a d^9s^1 configuration is observed, a number of theoretical investigations predict Ds to have a d^8s^2 (or more precisely $d^4_{3/2}d^4_{5/2}s^2$) ground state configuration (see *e.g.* 7). The energy differences between the different states are, however, quite small. A further aspect is that certain neutron-rich isotopes of Ds are calculated to have long lifetimes, of up to 50 years for $^{292}_{110}$Ds.[8]

The Dirac–Coulomb DFT calculations[9] were performed using a development version[10] of DIRAC.[11] The B3-LYP functional was employed. The basis sets of Faegri[12] were used for Pt and Ds. These were uncontracted and augmented with diffuse functions and a set of g-type polarization functions. For C and O cc-pVTZ basis sets were used. The local minimum was obtained by calculating single points on the potential hypersurface and by fitting these points to a Morse potential around the minimum.

The zero order regular approximation (ZORA)[13] calculations were done using the ADF[14,15] code. Calculations were done with the inclusion of scalar relativistic effects and including spin–orbit (SO) coupling. The PBE functional was employed. All electron QZ4P basis sets were used on all atoms. Geometry optimizations were performed without SO. Points on the potential hypersurface were calculated including SO, and using Morse potential fits. The energy decomposition scheme included in ADF[16] was used to study the character of the bonds.

As simple chemical examples, we calculated the properties of diatomic MC and triatomic MCO, M = Pt,Ds. The latter systems could be potentially synthesized by feeding the created metal atoms to CO target gas. Both four-component DFT calculations, ZORA and ZORA-spin–orbit DFT calculations were performed. The results are shown in Table 1. As examples for compounds of the metals in higher oxidation states, MF$_4$ and MF$_6$ were also calculated, the results are included in Table 1. As seen, the bond lengths for Pt and Ds are rather similar. So are in fact the M–L stretching frequencies; note that the metal atoms are heavy. The four-component DFT and the ZORA approximation give closely similar results. Spin–orbit coupling does not change the geometry much. The similarity of Pt and Ds does not mean that relativistic effects are unimportant for Ds. A nonrelativistic Lévy–Leblond DFT calculation gave a Ds–C bond distance of 204.4 pm for DsC. The relativistic contraction of the bond-length is 32.3 pm or 15.8%.

An energy decomposition of the Pt–C, Ds–C, Pt–CO and Ds–CO bonds confirms the similarity of the M–C bonds, see Table 2 for the results. This decomposition shows qualitatively similar σ and π orbital interactions for both metals. Those of Ds are about 1 eV larger than those of Pt. The larger, repulsive, steric interaction of Ds give it, however, a weaker total bond. The Δ part of the orbital interactions in Table 2 can be seen as a static correlation effect between the metal dδ orbitals and the ligand.

Seth *et al.* found that the reaction $MF^{-}_6 \rightarrow MF^{-}_4 + F_2$ is more endothermic by 0.89 eV (B3-LYP) for E111 compared to Au.[5] They also found, that the DFT values are in good agreement with CCSD(T) results. We did similar DFT calculations for the reaction $MF_6 \rightarrow MF_4 + F_2$ (M = Pt,Ds) and found the same trend. The decomposition is more endothermic by 0.2 eV for Ds compared to Pt (PBE ZORA). This shows that already in Group 10 a higher stability of higher oxidation states can be observed. The stability of the higher oxidation state, compared to the lower, increases when going to Group 11.

For the fluorides, Ds is about 5–6 pm larger than Pt. This trend was already seen in Group 4 MH$_4$ and Group 6 MH$_6$[17] where the 6th-row-to-7th-row difference was 3 and 6 pm respectively.

We recently observed a chemical analogy between platinum and oxygen (*e.g.* in species CPt and CPt$_2$, compared with CO and CO$_2$).

Table 1 Bond lengths (in pm) and selected vibrational frequencies (in cm^{-1}) for the investigated species

		Pt		Ds		
Molecule	Property	Exp	ZORA	ZORA	ZORA + SO[a]	4comp-DFT[a]
MC	$R_{M–C}$	167.67[b]	167.8	171.8	172.7	172.1
	$\nu_{M–C}$	1051.13[b]	1096	1148	1147	1134
MCO	$R_{M–C}$	176.046[c]	175.6	176.1	177.8	178.9
	$R_{C–O}$	114.354[c]	116.0	116.7	116.5	115.7
	$\nu_{M–C}$		606	705	646	636
	$\nu_{C–O}$	2065.5[d]	2037	2054	2043	2045
MF$_4$	$R_{M–F}$		187.3	192.7	—	—
MF$_6$	$R_{M–F}$		188.7	194.9	—	—

[a] From Morse-potential fits. [b] Ref. 19 [c] Ref. 20 [d] Ref. 21

Table 2 Energy decomposition of the M–C bonds in PtC, DsC, PtCO and DsCO, all energies in eV

	Pt–C	Ds–C	Pt–CO	Ds–CO
Steric interaction				
Pauli repulsion	33.45	39.56	24.00	30.71
Electrostatic interaction	−13.01	−15.21	−13.29	−16.73
Total steric interaction	20.43	24.35	10.71	13.98
Orbital interactions				
Σ	−17.10	−19.43	−1.03	−2.17
Π	−7.38	−9.62	−9.52	−10.62
Δ	−6.07	−5.01	−5.54	−4.81
Total orbital interactions	−30.54	−34.05	−16.09	−17.60
Total bonding energy	−10.11	−9.71	−5.38	−3.62

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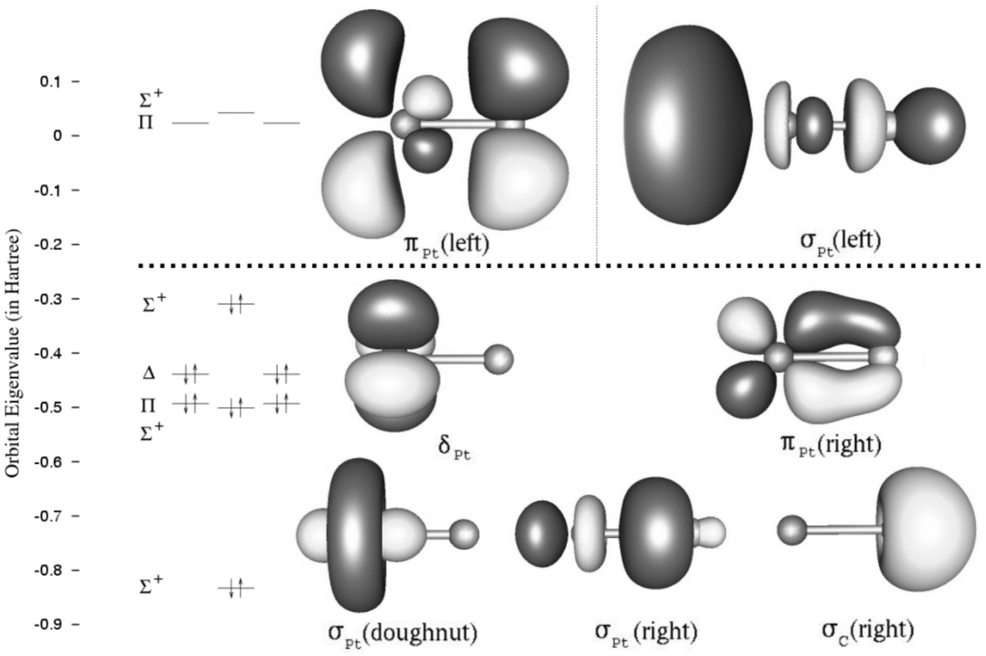

Fig. 1 Calculated molecular orbitals for PtC (platinum left, carbon right). The occupied orbitals have been localized with the Boys scheme. The energy spectrum is given for the unlocalized orbitals. The calculated orbitals support the schematic picture in Fig. 2. See also there for an explanation of the shape of the orbitals.

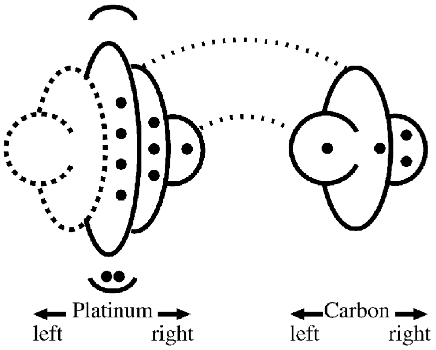

Fig. 2 Schematic picture of orbital interactions in PtC. For platinum the "doughnut σ" and "δ lone pair" orbitals are fully occupied and the "left π" and "left σ" are empty. The bonds towards right are accomplished using the "right π" and "right σ" orbitals, which together introduce four electrons. For carbon the "right σ" is a lone pair, while the "left σ" and "π" participate in bonding. The six bonding electrons form a $\sigma^2\pi^4$ MO system.

We also noted that the mixed species PtCO has analogous bonding orbitals as OCO.[18] The calculated molecular orbitals of PtC are shown in Fig. 1 and support the qualitative interpretation in the cartoon of Fig. 2. Very similar bonding occurs for DsCO.

In conclusion, the systems studied here reveal no striking chemical differences between platinum and darmstadtium. Darmstadtium may therefore be a normal member of Group 10.

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