18-Electron $\mathrm{Os(X)(CHR)(Cl)(CO)L_2}$ (X = H, Cl): not octahedral and metastable?

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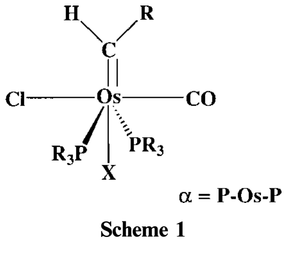
The differences in the geometries of $\mathrm{Os(X)(CHR)(Cl)(CO)L_2}$ (X = H, Cl; L = $\mathrm{PPr^i_3}$; R = $\mathrm{SiMe_3}$, Ph), where X and CHR are mutually *trans*, have been studied through *ab initio* MP2 calculations (L = $\mathrm{PH_3}$, R = H). The optimized structures are in good agreement with the experimental data (P—Os—P = 141.4° for X = H; 167.5° for X = Cl) and show the electronic origin of the distortion. A molecular orbital analysis explains why the P—Os—P angle is small for X = H and larger, but not 180°, for X = Cl. For X = H, the isomer in which H and $\mathrm{CH_2}$ are mutually *cis* is shown to be more stable than the corresponding experimental isomer in which they are mutually *trans*. However, the 16-electron product resulting from insertion of the carbene into the Os—H bond is shown to be considerably more stable than the 18-electron hydrido-carbene parent compound. Thus, the isolated metastable isomer is kinetically protected by a high barrier for site exchange in $\mathrm{d^6}$ hexacoordinated complexes. Recent experimental observations by Caulton *et al.* have shown that $\mathrm{Os(H)(CH_2)(Cl)(CO)L_2}$ transforms into $\mathrm{Os(CH_3)(Cl)(CO)L_2}$ when the kinetic barrier is removed by loss of phosphine.

It is commonly believed that 18-electron hexa-coordinated complexes have a "regular" octahedral geometry with ligand–metal–ligand angles that deviate only slightly from 90°. While the electronic origin of small distortions has been discussed,[1] any large geometrical distortion is surprising and the differences between the structures of the recently reported complexes $\mathrm{Os(X)(CHR)(Cl)(CO)L_2}$ (X = H and R = $\mathrm{SiMe_3}$ **1H**; X = Cl and R = Ph **1Cl**; L = $\mathrm{PPr^i_3}$), by Werner *et al.*, in which X and CHR are mutually *trans*, are therefore remarkable.[2] The X-ray structures of these complexes show that the two phosphine ligands are bent toward X (P—Os—P = 167.5° for X = Cl and 141.4° for X = H, Scheme 1). While the distortion is slight in the case of Cl, this is not the case for X = H. Steric effects cannot explain this distortion since the plane of the carbene is perpendicular to the P—Os—P plane and therefore an electronic origin seems possible.

The formation of the carbene complex for X = H is also surprising since the reaction of diazomethane with the 16-electron unsaturated $\mathrm{OsH(Cl)(CO)(PPr^i_3)_2}$ complex was expected to give $\mathrm{Os(CH_3)(Cl)(CO)(PPr^i_3)_2}$, **2**, and not $\mathrm{OsH(Cl)(CH_2)(CO)(PPr^i_3)}$.[2]

In this work we have used *ab initio* MP2 calculations to analyse the origin of the geometrical distortion. We also discuss the relative stabilities of saturated **1H** and unsaturated **2**. We thus obtain insights concerning some limitations of the commonly accepted ideas that hexa-coordinated 18-electron species are octahedral and more stable than the corresponding 16-electron isomers.



Scheme 1

Computational details

All the calculations were performed with the Gaussian 94 set of programs.[3] Osmium was represented with the Hay–Wadt relativistic core potential (ECP) for the 60 innermost electrons and its associated double-ζ basis set.[4] Cl, P and Si were also described with Los Alamos ECPs and their associated double-ζ basis set augmented by a d polarization function.[5,6] A 6-31G(d,p) basis set[7] was used for all other atoms except the hydrogen atoms of the phosphine ligands ($\mathrm{PH_3}$ and $\mathrm{PMe_3}$) and the carbon atoms of the phosphine ligands ($\mathrm{PMe_3}$) for which a minimal STO-3G basis set was used.[8] Full geometry optimizations without any symmetry constraints have been carried out at the MP2 level.

Results

Non-octahedral geometry

Before moving on to the quantitative calculations, we first show how a simple molecular orbital analysis can predict the orientation of the carbene ligand as well as the possibility for distortion to occur. An interaction diagram between $\mathrm{CH_2}$ and the $\mathrm{Os(X)(Cl)(CO)(PH_3)_2}$ fragment (**3X**) for an ideal octahedral geometry shows a preference for the plane of the carbene to be perpendicular to the P—Os—P direction. The three occupied non-bonding d orbitals of **3H**, calculated at the EHT level, are shown in Fig. 1. The highest occupied orbital, d_{xz}, has the proper symmetry to interact with the empty p orbital of the carbene when the carbene ligand is coplanar with Os—Cl and Os—CO. Rotating the carbene by 90° makes the empty carbene p orbital interact with d_{yz}, which is stabilized by a push–pull effect[9] and is thus a less efficient electron donor. The d_{xy} orbital does not have the proper symmetry to interact with the carbene p orbital for any orientation of the carbene ligand.

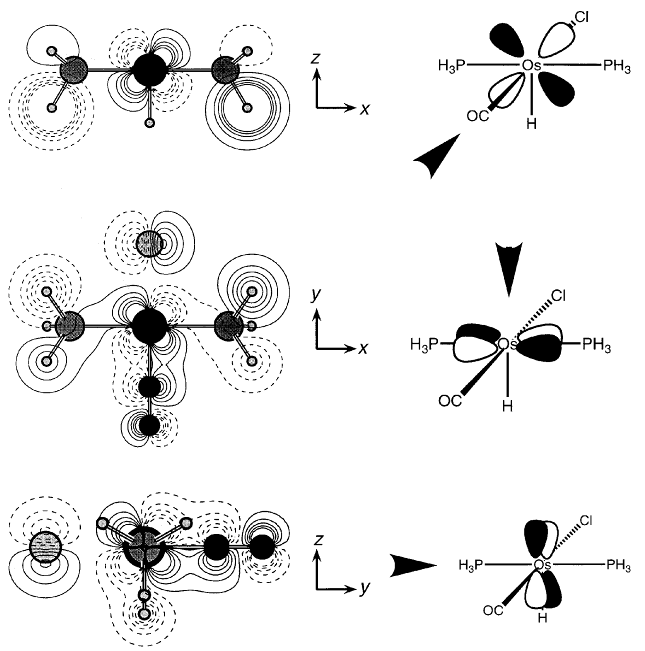
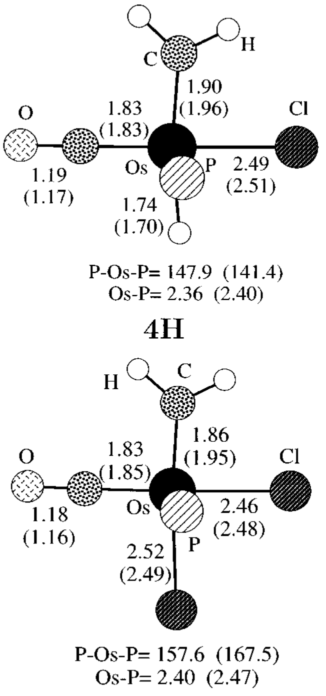


Fig. 1 Occupied non-bonding d orbitals of **3H** calculated at the EHT level. (The EHT program was downloaded from the web site http://overlap.chem.cornell.edu:8080/yaehmop.html)

The interaction between the occupied σ orbital of the carbene and the LUMO of **3H**, which is responsible for the Os—C σ bond, is independent of the orientation of the carbene plane. A similar analysis was carried out for the orientation of H_2 in $OsH(Cl)(CO)(PH_3)_2(H_2)$.[10]

This back-donation from d_{xz} to the carbene creates a partial double bond between the metal and the carbon.[11] Decreasing the P—Os—P angle α causes the phosphine ligands to bend away from the carbene. This leads to a larger mixing between d_{xz} and p_x on Os and thus to an increase in its ability to back-donate into the carbene p orbital.[12] Thus, this improved back-donation is in competition with the increase in energy of fragment **3X** (through destabilization of d_{xz}) as α decreases. Quantitative calculations are thus necessary to determine the final result, which is a compromise between these two effects.



4H

4Cl

Fig. 2 Optimized structure for **4H** and **4Cl** (distances in Å, angles in degrees). Experimental values for **1H** and **1Cl** are reported in parenthesis for comparison.

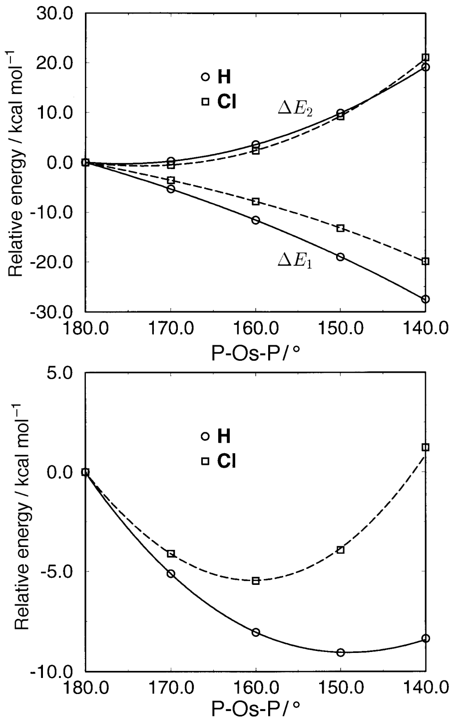


Fig. 3 Top: Variation of ΔE_1 and ΔE_2 (in kcal mol^{-1}, see text for definition) as a function of the P—Os—P angle. Solid lines: X = H; dashed lines: X = Cl. Bottom: Variation of $\Delta E_t(\alpha) = \Delta E_1 + \Delta E_2$ (in kcal mol^{-1}, see text for definition) as a function of the P—Os—P angle. Solid lines: X = H; dashed lines: X = Cl.

The MP2-optimized geometries of the model systems $Os(X)(CH_2)(Cl)(CO)(PH_3)_2$, **4X**, for X = H and Cl are shown in Fig. 2. Experimental values for **1H** and **1Cl** are reported in parenthesis for comparison. The metal–ligand bond lengths are in good agreement with the experimental values. The Os—C bond length for the carbene is significantly longer for X = H (1.90 Å) than for X = Cl (1.86 Å), as expected from the stronger *trans* influence of H. Direct comparison with the experimental values is made difficult by the presence of substituents on the carbene that influence the Os—C bond length.[13] The Os—H distance, not accurately determined in the X-ray structure, is close to that calculated in other Os^{II} complexes.[14] The carbene is coplanar with the Os—Cl and Os—CO bonds in **4H** and **4Cl**, as observed in experimental structures of **1H** and **1Cl**. The trend in the P—Os—P angle is properly reproduced: α = 147.9° in **4H** (141.4° in **1H**) and 157.6° in **4Cl** (167.5° in **1Cl**).

The key actors in these complexes are the phosphine and carbene ligands, but in both cases we have used a simplified model for the experimental ligands. It is thus necessary to determine the dependence of the optimized geometry on the nature of both the phosphine and carbene substituents. Replacing PH_3 by PMe_3 (**4X′**) and keeping CH_2 as the model carbene leads, suprisingly, to a marginal increase (<3°) of the P—Os—P angle for both X = H and Cl. Increasing the bulk of the phosphine maintains the distortion, which shows that the electronic effects are not overwhelmed by steric repulsions between Cl and phosphine ligands. Replacing CH_2 by $CH(SiH_3)$ and keeping PH_3 as the phosphine, to give **4H″**, does not lead to any significant change in the value of α

Table 1 NPA population of the p_x orbital (see Fig. 1) for the carbene carbon atom as a function of the P—Os—P angle

α/°	180	170	160	150	140
X = H	0.670	0.676	0.695	0.724	0.761
X = Cl	0.761	0.754	0.761	0.779	0.809

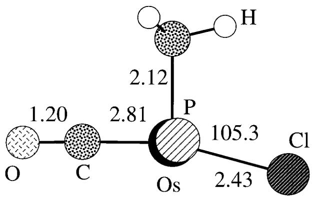
(147.9° for **4H** and 147.4° for **4H″**). The Os—C(carbene) bond is still shorter (1.91 Å) than the experimental value (1.96 Å). Our results show that the significant decrease of the P—Os—P angle and its dependence on the nature of X is well reproduced with the simplest model ($L = PH_3$, and carbene $= CH_2$) and we will use this model for the following quantitative analysis.

Starting from an idealized geometry close to the optimized **4X**,[15] the P—Os—P angle α was varied from 180° to 140° in 10° steps and the total energy $E_t(\alpha)$ was computed at the MP2 level. The complex **4X** was then considered to be formed of two interacting fragments: a carbene ligand CH_2 (constant energy E_c) and a 16-electron fragment $OsX(Cl)(CO)(PH_3)_2$ with variable energy $E_m(\alpha)$. The interaction energy $E_i(\alpha)$ between the two fragments is defined in eqn. (1):

$$E_i(\alpha) = E_t(\alpha) - [E_m(\alpha) + E_c] \quad (1)$$

Using $\alpha = 180°$ as a reference angle, the variation in the interaction energy $\Delta E_1(\alpha) = E_i(\alpha) - E_i(180)$ and the variation in the energy of the 16-electron fragment $\Delta E_2(\alpha) = E_m(\alpha) - E_m(180)$ are plotted as a function of α [Fig. 3(a)] for X = Cl and H. The sum of $\Delta E_1(\alpha)$ and $\Delta E_2(\alpha)$ is the total energy $\Delta E_t(\alpha)$ of the complex relative to its value at 180°, $E_t(180)$ [Fig. 3(b)]. The two functions, $\Delta E_t(\alpha)$ (X = H, Cl) in Fig. 3(b) present a minimum for α_{min}, which is smaller for X = H ($\alpha_{min} = 149°$) than for X = Cl ($\alpha_{min} = 160°$). These numbers compare well with the optimized values for **4X** and validate the choice made to vary only α and freeze all other structural parameters.

The relative destabilization ($\Delta E_2 > 0$) of the metal fragment $Os(X)(Cl)(CO)(PH_3)_2$, **3X**, upon decreasing α is identical for X = H and Cl [Fig. 3(a)], which shows that X plays no role in determining this quantity. In contrast, the absolute value of the relative stabilization energy ($\Delta E_1 < 0$) increases more rapidly for **4H** than for **4Cl** as α diminishes and leads to a larger distortion for H. The Os-to-carbene σ and π bonds both participate in ΔE_1, but only the π bonding varies strongly with α because of the large change in overlap between d_{xz} and the phosphine ligands. A numerical evaluation of the importance of this back-donation has been carried out with the natural population analysis (NPA) method of Weinhold and co-workers.[16] The p orbital is empty in free $^1CH_2$ but partially occupied after coordination to the 16-electron metal fragment. The population in the p_x orbital on the carbene carbon atom is thus a measure of the back-donation from the metal and is given as a function of the P—Os—P angle (Table 1). In agreement with the earlier MO analysis, it increases with decreasing α. It is also more important for **4Cl** than for **4H** at any value of α angle since the Cl p_x lone pair raises the energy of the d_{xz} orbital responsible for back-donation (Fig. 1).[17] However, the back-donation increases by 13.6% in the case of X = H while it increases only by 6.3% for X = Cl when α goes from 180° to 140° (Table 1). For X = Cl, additional diminuation of α is thus not necessary to achieve efficient back-donation.

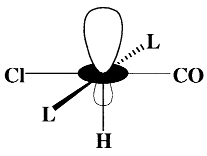


P-Os-P= 174.1
Os-P= 2.35

Fig. 4 Optimized structure for **5H** (distances in Å, angles in degrees).

Isomeric structures

As mentioned earlier, the addition of diazomethane to the unsaturated $OsH(Cl)(CO)(PPr^i_3)_2$ unsaturated species gives the 18-electron *trans* hydrido-carbene complex and not the 16-electron methyl complex resulting from insertion of the reactive carbene group into the Os—H bond. To understand this result, the model complex $Os(CH_3)(Cl)(CO)(PH_3)_2$, **5**, was optimized (Fig. 4). Complex **5** was found to be 25.7 kcal mol^{-1} *more* stable than **4H**. Another isomer of $OsH(CH_2)(Cl)(CO)PH_3)_2$, with H and CH_2 *cis*, was found to be slightly more stable (2.5 kcal mol^{-1}) than **4H**. The magnitude of the energy preference for the unsaturated species **5** is thus surprising. The formation of **4H** is in agreement with the shape of the LUMO of $OsH(Cl)(CO)(PH_3)_2$ pointing away from the hydride.



Coordination of CH_2 *trans* to H is thus kinetically preferred. Access to a structure where H and CH_2 would be mutually *cis* is prevented by the high energy barrier for site exchange in 18-electron hexa-coordinated complexes. Recent experiments have shown that methylene transfer to the Os—H bond is made possible by the presence of bulky phosphines like PBu^t_2Me in place of PPr^i_3. Loss of PBu^t_2Me results in the production of a highly fluxional 5-coordinated species favouring close proximity of H and CH_2 and thus insertion of CH_2 into Os—H.[18]

Discussion and Conclusions

The general belief that hexa-coordinated 18-electron complexes should have a geometry close to that of an ideal octahedron has some limitations. Similar distortions, in general of lesser magnitude, have been observed in a number of complexes containing M–ligand multiple bonds.[1] Carbene groups need to be stabilized by π-electron-donor groups.[19] This donation can originate from a π-donor substituent like OR or NR_2 as in Fischer carbene complexes. The donation can also originate from the occupied metal d orbitals and efficient donation is achieved by early transition metals like Ta (Schrock carbene complexes). In the present case, the carbene does not have any significant π-donor ligands and Os^{II}, although being a 5d metal, is not by itself a strong electron donor to the carbene. It is therefore of interest that a structural deformation becomes a key factor to stabilize the carbene ligand.

The greater stability of the 16-electron unsaturated isomer with respect to the 18-electron hydrido-carbene illustrates the caution that needs to be taken in the blind use of the 18-electron rule. In $Os(X)(CH_2)(CO)(Cl)L_2$, the presence of two π-acceptor ligands (carbene and CO) in the hexacoordinated complex is an unfavourable factor. However, the leading factors responsible for the greater stability of a 16-electron *versus* an 18-electron isomeric form are still to be clearly revealed and we are currently working in this direction.

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