Opinion

Evolving approaches to integration of computational with experimental chemistry: an example from osmium hydrido (η^1/η^2-)nitrosyl/nitroxyl chemistry†

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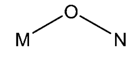
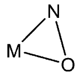
The energies and structures of less stable isomers of metal-ligand systems need to be analyzed to learn about general trends in stability; the example of H–M–NO is considered.

The nitrosyl ligand attached to one metal has long been recognized to have two structural alternatives, linear and bent; recent rapid, low temperature crystallographic studies[1] have also shown two more: O-bound (**A**) , and η^2 (**B**).



A

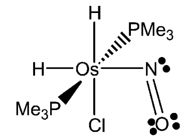


B

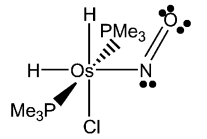
Both are high energy isomers and formed by photolysis of normal N-bound nitrosyls. The increasing accessibility of fast density functional theory (DFT) program packages offers an exceptional opportunity to learn about isomeric structures that might never reach detectable equilibrium (or even nonequilibrium) populations. We refer here not to transition states, but to authentic minima.[2–7]

Learning not only the energy, but also the bond lengths and angles in less favorable isomers by DFT geometry optimizations, permits analysis of these in terms of bonding and, ultimately, assessment (rationalization) of *why* these are less stable. For example, we reported earlier that $Os(H)_2Cl(NO)L_2$ ($L = P^iPr_3$) has a structure with the nitrosyl best described as the linear type.[8] We discuss here the results of density functional theory (DFT) computations[9] that more fully probe isomeric structures and help to understand their relative stabilities. By this example, we hope to stimulate others to draw chemically significant *general* conclusions from not only the experimentally observed, but also the experimentally unobservable, *via* DFT calculations as a companion to experimental work. This is clearly of exceptional utility when a new isomeric form of a "non-innocent" ligand like NO is discovered, and earlier examples of this strategy have appeared very recently.[1] The ligand NO is an especially appropriate vehicle for this discussion since it is so versatile and its electronic and geometric structure as a ligand are so easily misunderstood or misrepresented. Because of the importance of NO to physiological processes,[10] molecular level understanding of its numerous structural and redox forms will help to avoid potential future biochemical misinterpretations. Another example of this computational approach to isomer energy evaluation has appeared recently.[11]

Calculations (program package Priroda,[12] PBE functional,[13] SBK basis set[14]) show (Fig. 1), in addition to the linear nitrosyl structure $Os(H)_2Cl(NO)L_2$, **1**, a second stationary point: $Os(H)_2Cl(\eta^2\text{-}NO)L_2$, **2**. This is an energy minimum, although it lies 22 kcal mol^{-1} (ΔG°_{298}) higher than isomer **1**. The geometry optimization converges to structure **2** when starting from geometry **C**,



C



D

since the oxygen lone pairs are more accessible (*vs.* nitrogen) for interacting with the LUMO. Starting from geometry **D** leads *back* to geometry **1** because the nitrogen lone pair interacts with that LUMO, and leads to increasing the Os–N–O angle to near 180°. In **2**, the hydrides are *cis*, as in **1**, but the OsNO unit forms a triangle where the Os–O distance is only 0.37 Å longer than the Os–N distance. The bonding in this

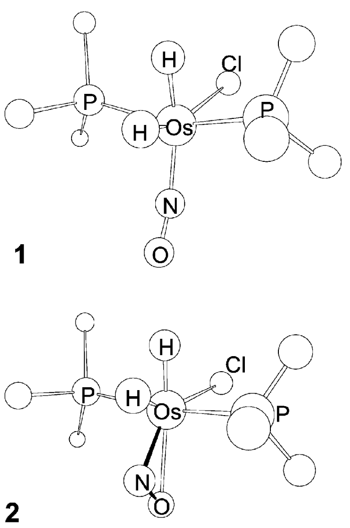


Fig. 1 DFT-optimized geometries of $Os(H)_2Cl(NO)(PMe_3)_2$, **1**, and $Os(H)_2Cl(\eta^2\text{-}NO)(PMe_3)_2$, **2**.

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† Electronic supplementary information (ESI) available: computational details. See http://www.rsc.org/suppdata/nj/b2/b205506f/.

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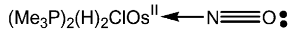
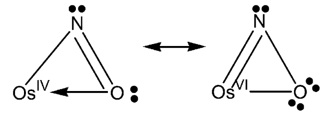
$Os(\eta^2\text{-}NO)$ isomer can be represented as **2a** and **2b**,

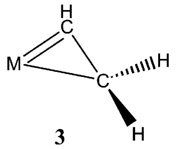


E



2a **2b**

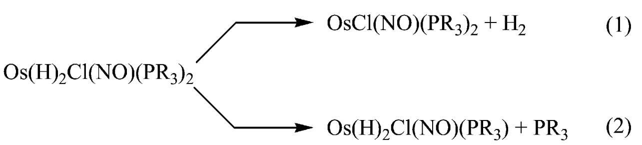
with the calculated NO distance (1.24 Å) indicating that **2a** predominates. It is interesting that conventional charges for these alternative forms (linear as NO^+ in **E**, **2a** as NO^- and **2b** as NO^{3-}) then lead to three different metal formal oxidation states, and that the relative isomer stabilities of **1** and **2** fail to reflect the general preference of the 5d metal for its *highest* oxidation state. Thus, among *three* structural options, all of which achieve an 18-electron osmium configuration, DFT calculations show that the greatest stability is achieved in structure **E** (*i.e.*, **1**). Note also that the resonance form **2b** has formal similarities to an η^2-vinyl unit, **3**.[15]



3

How can we additionally benefit from knowing this 22 kcal mol^{-1} $\Delta G°_{298}$ to form **2** from **1**? It tells us that, as an *intermediate* in a thermal reaction, the equilibrium population of **2** is at most 10^{-16} at 298 K, thus making it quite unattractive for attack by some second reagent. It is the nature of the Eyring (exponential) equation that $\Delta G^{\ddagger}$ values within a narrow *window* lead to half lives that determine the time evolution of a first-order reaction as being measurable without rapid kinetic techniques. To be monitored on the timescale of 1–5 h at 25 °C, $\Delta G^{\ddagger}$ must be in the range 22–26 kcal mol^{-1}. Above 26.5 kcal mol^{-1} there will appear to be "no reaction" ($\tau_{1/2} > 500$ h). These define the huge practical difference between activation energies of 21 and 27 kcal mol^{-1}, as well as the ability to exclude a transition state energy >27 kcal mol^{-1} as a viable mechanistic candidate at 25 °C.

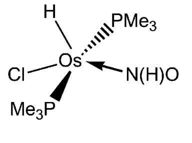
Species **2** is, however, accessible, on an energetic basis only, *via* any photon with $\lambda < 1300$ nm; thus, photoproduction of this isomer might be possible.[16] The $\Delta G°_{298}$ to form **2** from **1** can also be used, in comparison with calculation of the energies of reactions 1 and 2, to predict which of the three reactions might occur (*i.e.*, selectivity) thermally. The $\Delta G°_{298}$ of eqn. (1) ($R = CH_3$) is calculated to be 11.9 kcal mol^{-1}, which is the lowest energy process among those considered here for **1**.[17]



$$Os(H)_2Cl(NO)(PR_3)_2 \longrightarrow OsCl(NO)(PR_3)_2 + H_2 \quad (1)$$

$$Os(H)_2Cl(NO)(PR_3)_2 \longrightarrow Os(H)_2Cl(NO)(PR_3) + PR_3 \quad (2)$$

Another traditional isomeric alternative for H and NO ligands is combined into a nitroxyl ligand, HNO. Although rare, these are known.[18] A search of the potential energy surface for structure **4**, beginning from starting geometry **5** gave only the product of H migration to Os, **1**.



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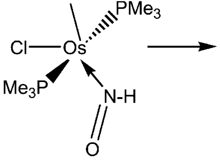
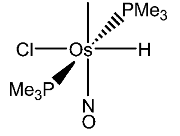


5



1

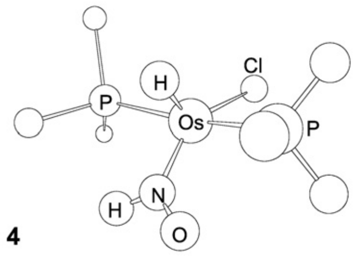


Fig. 2 DFT-optimized geometry of $OsHCl(HNO)(PMe_3)_2$, **4**.

Geometry optimization beginning from an alternative conformer of **5**, in which the HNO plane is rotated 180° (*i.e.*, O *anti* to Cl) did not lead to a *trans*-dihydrido nitrosyl complex due to unfavorable *trans*-destabilization of the two hydrides (large *trans*-effect). Instead, it gave a nitroxyl complex (**4**, Fig. 2), at an energy 23 kcal mol^{-1} higher than **1**, as a square pyramidal species with HNO binding to Os only through nitrogen. In spite of the different starting orientation of the HNO plane, the geometry-optimized rotational conformation around the Os–N bond has the HNO plane *perpendicular* to the HOsCl plane. The Os–N bond is short (1.886 Å) compared to that in the linear nitrosyl **1** (1.811 Å) and the N–O bond is long (1.267 Å) compared to that in the linear nitrosyl in Fig. 1 (1.185 Å).

Together, these suggest significant back donation (Scheme 1) from Os to the HNO π system.[19] In this way, unsaturated **4** can achieve stability no worse than saturated **2**, a conclusion that follows since these two are essentially isoenergetic.

Thus, this system demonstrates forcefully the influence of the choice of initial structure on geometry optimizations, as well as how that initial choice leads *predictably* to one isomeric minimum.

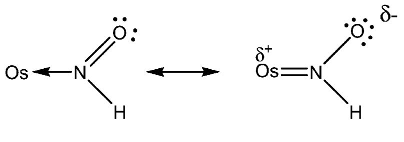
The calculated isomerization energy from **1** to **4** sets a lower limit for the half-life of any adduct-forming reaction [eqn. (3)] *via* a pre-equilibrium isomerization mechanism.

$$Os(H)_2Cl(NO)(PR_3)_2 \rightleftharpoons OsHCl(HNO)(PR_3)_2 \xrightarrow{L'} OsHCl(HNO)L'(PR_3)_2 \quad (3)$$

These are numbers that a kineticist would generally benefit from knowing.

Consider also a reaction whose rate law is established to be first-order in species A and which kinetic and labeling experiments have shown to be nondissociative. The mechanism thus involves rate-determining "isomerization" of A to some higher energy but structurally ill-defined A*. The identity of A* might be established if (say) three proposed structures of A* are shown by DFT calculations to have two structures with much higher calculated energies than the third.

The much diminished stability of the nitroxyl *vs.* the hydrido nitrosyl species cannot be rationalized on the basis of metal formal oxidation states as can[20–22] the carbene *vs.* hydrido carbyne alternative (Scheme 2), because the observed linear NO is properly considered as a monocation (**E**). The isomer preference must therefore rest more on the higher reducing power of a 5d metal (better suited to the higher π acidity of NO^+ than



Scheme 1

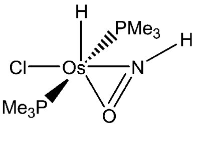
$L_2HClOs^{II}(HNO)$ *vs.* $L_2H_2ClOs^{II}(NO^+)$

$L_2HClOs^{IV}(CHR^{2-})$ *vs.* $L_2H_2ClOs^{VI}(CR^{3-})$

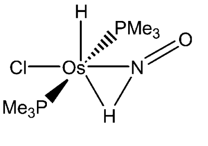
Scheme 2

to HNO), together with the 18-valence-electron count for the nitrosyl alternative.

Another question of interest is the possibility of isomeric forms of binding the nitroxyl ligand to osmium, in particular η^2 versions, which would then utilize the otherwise empty orbital in structure **4**. We considered an η^2-N/O structure, **F**, as well as an η^2-H/N structure, **G**.



F



G

Geometry optimization from each of these starting geometries showed that neither is an energy minimum. **F** leads to Os–O dissociation and **G** leads to Os–H dissociation. Concurrently, during geometry optimization, the HNO plane rotates, so that the energy minimum achieved both from **F** and from **G** is exactly that of **4**. The preference for η^1-HNO *vs.* these η^2 forms suggests that the π acidity of η^1-HNO is more important for overall stability than is achieving an 18-valence-electron count. The absence of a minimum for a given structural type must be interpreted with caution, since, in unfavorable cases, a *shallow* minimum may appear or disappear depending on the computational method used. However, these results can be conservatively interpreted to conclude that an experimental search for these isomeric structures **F** and **G** may be fruitless. Here again, knowing the energy, or the character of the energy surface describing high energy isomers that nevertheless have acceptable *Lewis structures* (as exemplified here by **2**, **4**, **F** and **G**), can be a very useful contribution of DFT calculations.

The energy and the structure of less stable isomers of structures accessible at equilibrium can be analyzed to learn much about general trends in stability, which is essential to moving from the empirical to the rational in molecular transition metal chemistry. Dramatic *experimental* advances[23] in establishing the geometric structure of transients can contribute here, as can computational studies. Although publishing computational studies *without* accompanying experimental work is being discouraged[24] by editorial policy, experimentalists today are citing computational results to identify transients, and their structure.[25–27]

On the cautionary side, computational work, exemplified here by different optimized structures resulting from different starting geometries, sometimes demands exceptional care in the search of the potential energy surface.

Acknowledgements

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