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Mechanism of alkyne conversion to carbyne by 14- or 16-electron $Os(H)_2ClL_2X$ ($L = P^iPr_3$; $X = OTf$ or $B(C_6H_3(CF_3)_2)_4$)

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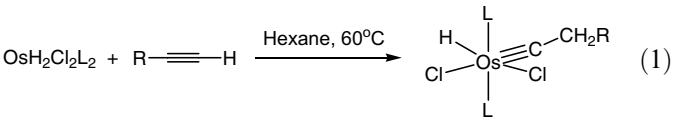
Abstract

The mechanism of conversion of terminal alkynes RC≡CH to coordinated carbyne Os≡CCH_2R by $Os(H)_2ClXL_2$ ($L = P^iPr_3$) has been studied for X = OTf and $BAr^F{}_4$ (Ar^F = 3,5-di$(CF_3)_2(C_6H_3)$. Ready loss of these X makes possible detection of η^2-RCCH (4-electron donor) and =$CH(CH_2R)$ intermediates, and D-labeling (RCCD) gives $OsDClX(CCH_2R)L_2$. The energy of various intermediates, including the only experimentally unobserved one, η^2-vinyl, was evaluated with DFT(PBE) calculations.

Keywords: Exothermic; Alkyne conversion; Carbyne; Bimetallic Os; Doubly dehalogenated; Monotriflate; Chloride-free

1. Introduction

The unusual 16-electron molecule $Os(H)_2Cl_2L_2$ ($L = P^iPr_3$) has the ability [1–3] to isomerize a terminal alkyne to a coordinated carbyne (Eq. (1)). The formation of two new C–H bonds, and the cleavage of one C–H bond are required, but establishing the mechanism of this reaction has been frustrated by the low solubility of $Os(H)_2Cl_2L_2$ in benzene or hexane, which caused previous workers to carry out the reaction at reflux temperature.



(1)

We hoped that replacement of at least one chloride by triflate would 1) increase benzene solubility and 2) provide a good leaving group, which would therefore allow observation of earlier mechanistic steps under mild conditions. We report here the results of such a study, and extend this to using $B(Ar^F)_4^-$ in order to evaluate whether triflate is weakly bound to Os *vis-à-vis* not coordinated at all. DFT calculations are used to evaluate the energy of intermediates, and also to evaluate the only intermediate which eludes direct experimental observation.

2. Results and discussion

2.1. Synthesis and characterization of $Os(H)_2ClL_2X$ ($L = P^iPr_3$, $X = OTf$ or $BAr^F{}_4$)

The reaction of $Os(H)_2Cl_2L_2$ with excess AgOTf in CH_2Cl_2 gave $Os(H)_2ClL_2(OTf)$, **1a**, in 30 min (Scheme 1). ^1H NMR (C_6D_6) shows a hydride triplet at −16.8 ppm and a ^{31}P broad singlet at 43 ppm. A triflate ^{19}F NMR singlet is seen at −78 ppm. If less than 1 equiv of AgOTf was applied, $Os(H)_2ClL_2(OTf)$ combines with unreacted $Os(H)_2Cl_2L_2$ to form $[(OsH_2L_2)_2(\mu\text{-}Cl)_3][OTf]$ and then excess AgOTf only sluggishly removes one Cl to split the bimetallic Os compound (Scheme 1) [4]. Simple use of excess AgOTf was shown earlier to form the doubly dehalogenated product, $OsH_2(OTf)_2L_2$ instead of the monotriflate [5], and we were concerned that our product might contain some of this ditriflate. To evaluate whether this chloride-free product was produced, $Os(H)_2Cl_2L_2$ was added to the product from $Os(H)_2Cl_2L_2$ and excess AgOTf (more than 2 equiv). Since this produced mainly

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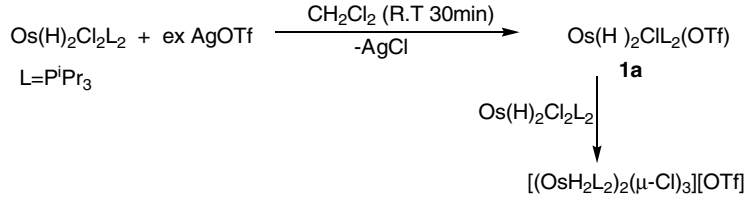


Scheme 1.

$[(OsH_2L_2)_2(\mu\text{-}Cl)_3][OTf]$, formation of this chloride bridging ($(\mu\text{-}Cl)_3$) compound confirms that the resulting product from reaction of $Os(H)_2Cl_2L_2$ with excess AgOTf at short times is $Os(H)_2ClL_2(OTf)$; $Os(H)_2L_2(OTf)_2$ cannot form the $(\mu\text{-}Cl)_3$ bridging complex with $Os(H)_2Cl_2L_2$ without an extra Cl^- source. The triflate anion in **1a** can be exchanged to the noncoordinated anion, $BAr^F{}_4$, $[Os(H)_2ClL_2][BAr^F{}_4]$, **1b**, when $NaBAr^F{}_4$ is added to a CD_2Cl_2 solution of **1a**. However, when the volatiles are removed in vacuum from a solution of **1b**, decomposition of **1b** was observed. In a solution of **1b**, a hydride triplet ($J = 32.1$ Hz) was seen at -20.1 ppm in ^1H NMR, and ^{31}P signal appears at 49.5 ppm as a broad singlet. The ^{19}F signal due to $BAr^F{}_4$ appears at -63 ppm. Attempts to crystallize **1b** led to an adduct of $Os(H)_2(OTf)_2L_2$ with $NaBAr^F{}_4$, as described in Section 6.

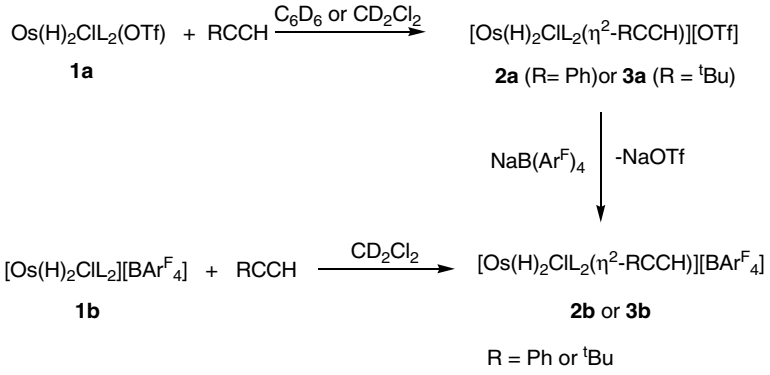
2.2. Reaction of $Os(H)_2ClL_2X$ and RCCH (R = Ph or ^{t}Bu)

2.2.1. Reaction of $Os(H)_2ClL_2X$ and PhCCH

Reaction of the Os compound **1a** with 1 equiv of PhCCH in CD_2Cl_2 gives an alkyne adduct, $[Os(H)_2ClL_2(\eta^2\text{-}PhCCH)][OTf]$, **2a**, as major product in 30 min, as confirmed by NMR spectra (Scheme 2). An alkyne proton was observed at 14.1 ppm as a triplet ($J = 2.7$ Hz) of doublets ($J = 3.3$ Hz) which couples to 2 P and to a hydride, respectively. This unusual chemical shift indicates 4-electron donation from acetylene to the metal [6–11]. One of two hydrides in the resulting adduct **2a** was observed at -0.8 ppm as a triplet of doublets of doublets, coupled to two phosphines, to the alkynyl proton and to the other hydride. The second hydride triplet of doublets coupled to two phosphines and the hydride is observed at -12.5 ppm which indicates there is no fast exchange between two hydrides. The $^{31}P\{^1H\}$ NMR spectrum showed only one chemical shift. Appearance of acetylene carbons (C(α) and C(β)) at 199.5 ppm and 185.7 ppm in ^{13}C NMR also confirms 4 electron donation from the acetylene [6–11]. Analogous carbon chemical shifts are seen for $[Os(H)_2ClL_2(\eta^2\text{-}MeCCPh)][OTf]$.

Reaction of **1a** with PhCCD produced $[Os(H)_2ClL_2(\eta^2\text{-}PhCCD)][OTf]$ and proved that the signal at 14.1 is due to the alkynyl proton in **2a**. In ^2H NMR spectra the η^2-PhCC*D* signal appeared at 14.0 ppm without deuterium scrambling (i.e., no D on Os). As well, absence of the unusual downfield resonance in reaction of **1a** with the internal alkyne MeCCPh in CD_2Cl_2, which produced $[Os(H)_2ClL_2(\eta^2\text{-}MeCCPh)][OTf]$, confirms the proton signal at 14.1 ppm in **2a** is due to the acetylene proton. ^1H NMR spectrum of this internal alkyne adduct shows one hydride signal at -0.6 ppm as a triplet of doublets coupled to 2P and another hydride at -12.6 ppm as a triplet of doublets coupled to 2P and to another hydride. Observing both hydride signals as the triplet of doublets instead of the triplet of doublets of doublets and a triplet of doublets further indicates one doublet splitting in the hydride signal at -0.8 ppm in **2a** is due to coupling to the acetylene proton. In the other words, the doublet splitting of the acetylene proton of **2a** is caused by one hydride.

An 18-valence electron count on the Os center in **2a** requires that OTf^- is not coordinated to the metal. This was also confirmed by reaction of triflate-free **1b** with PhCCH in CD_2Cl_2 (Scheme 2). The product, $[Os(H)_2ClL_2(\eta^2\text{-}PhCCH)][BAr^F{}_4]$, **2b**, showed signals simi-



Scheme 2.

lar to **2a**. By removing the volatiles from **2a**, PhCCH is lost from **2a** to reform **1a**; PhCCH is thus weakly bound to the Os center. The anion exchanged product, **2b** is also synthesized in reaction of **2a** with $NaBAr^F_4$ (Scheme 2).

Over one day of reaction period (with equimolar or excess PhCCH in CD_2Cl_2), the adduct **2a** disappears, with reappearance of **1a**. As well, a broad ^1H NMR signal between 6 ppm and 8 ppm was also increased due to polymerization of phenylacetylene [12].

Attempting to grow single crystals of **2a** from a benzene/CH_3I solution causes anion redistribution, resulting in $[Os(H)_2(OTf)L_2(\eta^2\text{-PhCCH})][OTf]$. The hydrides were not evident in final difference maps, and have been placed in Fig. 1 to show the relationship of the coordination geometry to an octahedron (considering the η^2-PhCCH ligand as occupying one site). The alkyne is oriented so than the C≡C vector eclipses the $Os(H)_2$ plane, which gives the cation an idealized mirror plane, consistent with the ^{31}P NMR spectrum. The alkyne substituent is *syn* to the (less bulky) hydride ligand. The lack of virtual coupling in the ^{i}Pr proton resonances, which implies $^2J_{p-p}$ which is not large, is consistent with the strong bend in ∠P–Os–P (128.981 (5)°), which rehybridizes one occupied d_π orbital for better back donation to the alkyne. In spite of the triflate oxygen being trans to a hydride, there is evidence for significant perturbation of the S/O bond for the oxygen bound to Os. This S1–O1 distance, 1.496 (4) Å, is significantly longer than those to the other two O (1.435 (5) and 1.443 (5) Å) and to the three of free triflate (1.450 (5)–1.457 (5) Å) in the lattice. The Os–O1 distance, 2.217 (4) Å, is long, however compared to those (2.13 (1)–2.15 (1) Å) in $Os(H)_2(OTf)_2L_2$. The Cl–C2 distance in the coordinated alkyne (1.299 (8) Å) is lengthened (from a free alkyne, 1.20 Å) [13] to an extent which qualifies as four electron donation towards Os. In addition, the Os/C distances are short enough to confirm this conclusion.

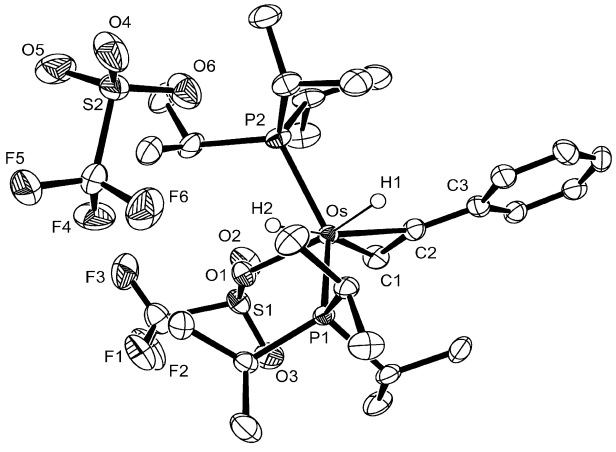


Fig. 1. ORTEP drawing (50% probability) of $[Os(H)_2(OTf)(\eta^2\text{-PhCCH})(P^iPr_3)_2][OTf]$ showing selected atom labeling. Only the hydride hydrogens are shown, and unlabeled atoms are carbon. Selected bond lengths (Å) and angles (°): Os–C1, 1.994(6); Os–C2, 2.007(5); Os–O1, 2.217(4); Os–P1, 2.3904(13); Os–P2, 2.3810(14); C1–C2, 1.299(8); S1–O1, 1.496(4); S1–O2, 1.443(5); S1–O3, 1.435(5); S2–O4, 1.457(5); S2–O5, 1.450(5); S2–O6, 1.453(4); C1–Os–O1, 89.4(2); C2–Os–O1, 110.38(15); C1–Os–P1, 175.86(10); C1–Os–P2, 116.60(18); C2–Os–P1, 111.03(15); C2–Os–P2, 110.38(15); O1–Os–P1, 88.65(10); O1–Os–P2, 89.23(11); P1–Os–P2, 128.98(5); C1–C2–C3, 143.8(5).

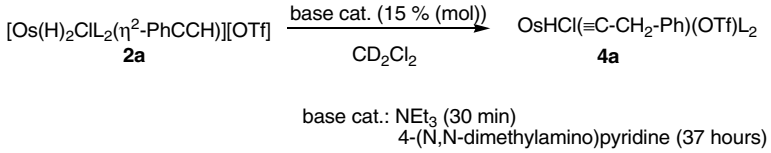
2.2.2. Reaction of $Os(H)_2ClL_2X$ and ^{t}BuCCH

Compound **1a** in CD_2Cl_2 was consumed by 1 equiv of ^{t}BuCCH in 30 min to produce the acetylene adduct, $[Os(H)_2ClL_2(\eta^2\text{-}^t\text{BuCCH})][OTf]$, **3a**, as a major product, Scheme 2. Its alkyne proton was observed at 13.4 ppm as triplet of doublets due to coupling to 2P and one hydride, respectively. This unusual chemical shift indicates 4 electron donation from acetylene to the metal compound [6–11]. The two hydrides appeared at −0.8 ppm (triplet of doublets of doublets) and −13.0 ppm (triplet of doublets). The hydride signal at −0.8 ppm was coupled to 2 P (t, $J = 34.5$ Hz), other hydride (d, $J = 4.8$ Hz) and to the alkyne proton (d, $J = 2.7$ Hz). The other hydride signal at −13.0 ppm was coupled to two P with $J = 16.6$ Hz and to the other hydride with $J = 4.8$ Hz. Coupling of the acetylene proton to only one hydride suggests one hydride is placed trans to the acetylene proton, but the other is located cis to the acetylene proton. $^{31}P\{^1H\}$ NMR spectrum showed only one chemical shift. Substitution of OTf^- by BAr^F_4 in **3a** was performed by addition of $NaBAr^F_4$ to **3a** in CD_2Cl_2 to produce $[Os(H)_2ClL_2(\eta^2\text{-}^t\text{BuCCH})][BAr^F_4]$, **3b**, in 30 min, Scheme 2. Alternatively, **3b** can be prepared when ^{t}BuCCH is added to **1b** in CD_2Cl_2. The NMR spectra are very similar to **3a** because the anions in **3a** and **3b** do not coordinate to the cationic Os.

2.3. Formation of carbyne complex from π-adduct promoted by base

2.3.1. Formation of $OsHCl(C\text{–}CH_2Ph)L_2(OTf)$

The π-adduct, **2a**, can be transformed to the carbyne compound, $OsHCl(C\text{–}CH_2Ph)L_2(OTf)$, **4a** in 30 min in CD_2Cl_2, by addition of 15 mol% of NEt_3 (Scheme 3). In C_6D_6, the reaction was completed in 4 h due to the low solubility of **1a**. Formation of **4a** was confirmed by NMR spectra. In ^1H NMR, a $-CH_2-$Ph singlet appeared at 2.6 ppm (intensity 2). The phosphorus are equivalent, and lead to a triplet hydride signal. In $^{13}C\{^1H\}$ NMR, a triplet at 279 ppm ($J = 10.6$ Hz) confirms a multiple bond between Os and C(α) (Os≡C or Os=C). This C(α) signal in ^{13}C NMR and CH_2 signal with two proton integration and the hydride signal indicate formation of **4a**; no carbene alpha proton was seen around 20 ppm in ^1H NMR. In addition, an isotope labeled experiment reacting $[Os(H)_2ClL_2(\eta^2\text{-PhCCD})][OTf]$ with NEt_3 (15 mol%/Os) was attempted; the fate of deuterium could not be confirmed because of scrambling of deuterium on ^{i}Pr groups and the hydride, by addition of the base. Instead of NEt_3, when catalytic amount (15 mol%) of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) was applied to the isotopically normal reaction, this transformation required 37 h which



Scheme 3.

might be due to strong basicity of DMAP causing weak catalytic ability.

2.3.2. Reaction of $[Os(H)_2ClL_2(\eta^2\text{-}PhCCH)][OTf]$ with NaOPh

Over 1 day, the reaction mixture of **2a** with NaOPh in C_6D_6 showed the formation of a product confirmed to be $OsHCl(CCH_2Ph)L_2(OPh)$ by NMR spectra, Scheme 4. In ^1H NMR, $-CH_2Ph$ appeared at 2.7 ppm as a broad singlet and a hydride triplet appeared at −12.1 ppm. A ^{31}P NMR singlet was observed. The different NMR parameters for this product (versus triflate) indicate binding ^-OPh to the Os center (versus ^-OTf in **2a)**.

2.3.3. Reaction of $[Os(H)_2ClL_2(\eta^2\text{-}PhCCH)][OTf]$ with $^nBu_4NCl$

Compound **2a** in C_6D_6 was completely consumed by a nucleophile, $^nBu_4NCl$, in 1 day; slow reaction leads to other products, but a major one was characterized by NMR spectra (Scheme 5) to be $OsHCl_2(CCH_2Ph)L_2$ [3]. A hydride triplet at −6.6 ppm in ^1H NMR and 20.3 ppm in ^{31}P NMR agreed well with published data [3]. This reaction also indicates that the stronger nucleophile, Cl^- (versus OTf^-) promotes conversion to the carbyne. Trapping of the alkyne adduct **2a** depends on the weak nucleophile OTf^-, since then the 4-electron donor potential of alkyne can be exploited.

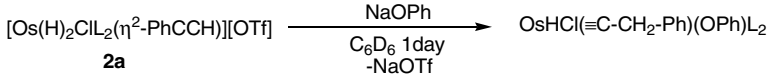
2.4. Reaction of $Os(H)_2Cl(OTf)L_2$ with HCCH

2.4.1. Formation of $OsHCl(CMe)L_2(OTf)$

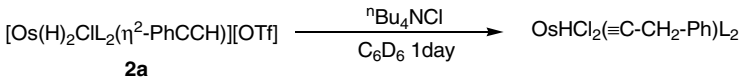
Reaction of **1a** with excess acetylene (300 mmHg) in C_6D_6 showed complete consumption of the Os reagent in less than 20 min at 23 °C, to produce $OsHCl(CMe)L_2(OTf)$, **5a**, Scheme 6. By isotope labeling experiment with $H^{13}C^{13}CH$ in CD_2Cl_2, formation of Os≡C was confirmed. A doublet of triplets at 279.1 ppm in $^{13}C\{^1H\}$ NMR corresponded to carbyne C(α) which coupled to C(β) and two P. C(β), coupled to C(α), appeared at 40.8 ppm as a doublet. A hydride triplet in **5a** appeared at −10.3 ppm. A singlet at 0.6 ppm corresponds to the carbyne methyl group.

However, some broadening in the methine CH signal (at 2.7 ppm) and two virtual quartet Me groups (at 1.22 and 1.14 ppm) in ^{i}PrP groups as well as one ^{31}P strong singlet at 42 ppm with two small broad ^{31}P signals at 41 and 43 ppm indicates that there is some equilibrium in the reaction mixture, all in C_6D_6. In addition, there is also a small broad signal at −8.9 ppm in ^1H NMR. In CD_2Cl_2, the hydride triplet at −10.3 ppm was broader, but the intensity of the small broad singlet at −8.9 ppm was increased. As well, intensity of the ^{31}P NMR signal at 42 ppm was decreased but two broad signals at 41 and 43 ppm were slightly increased. This complicated behavior could be due to two possible equilibria, Scheme 7. One is equilibrium of binding OTf^- group to the Os compound, k_1 or k_1'. Another is site exchange of ^-Cl and ^-OTf groups, k_2. These possibilities were also confirmed by observing two sharp singlets at −77.4 and −77.6 ppm and one weak broad signal at −78.5 ppm in ^{19}F NMR spectra in CD_2Cl_2. DFT calculation on these isomers (**a** and **b**) shows them to have electronic energies separated by 6 kcal/mol.

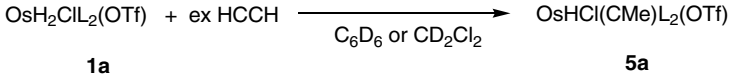
The X-ray structure determination (Fig. 2) shows that the crystals, which grew in toluene at −60 °C, are the result of a $^-Cl/^-O_3SCF_3$ disproportionation process, with the result that two triflate ligands are in one molecule. We base



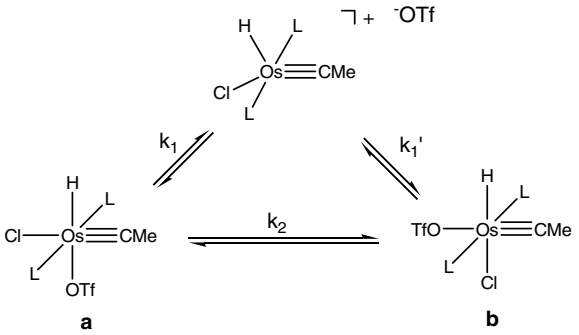
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

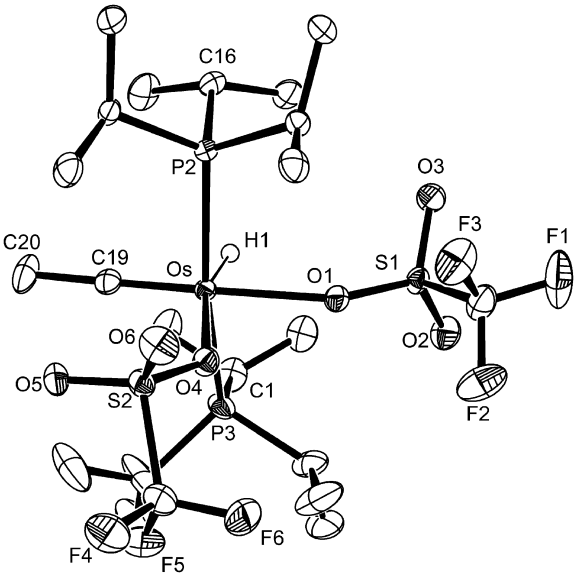
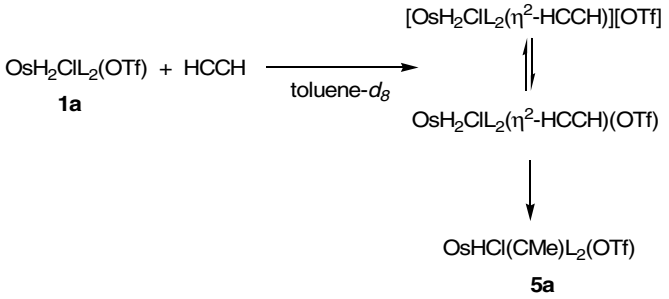


Fig. 2. ORTEP drawing (50% probability) of $OsH(OTf)_2(CCH_3)(PiPr_3)_2$ showing selected atom labeling. Only the hydride hydrogen is shown, and unlabeled atoms are carbon. Selected bond lengths (Å) and angles (°): Os–C19, 1.702(3); Os–O1, 2.2305(18); Os–O4, 2.2575(17); Os–P1, 2.4511(7); Os–P2, 2.4464(6); S1–O1, 1.4665(19); S1–O2, 1.4292(19); S1–O3, 1.4346(19); S2–O4, 1.4710(18); S2–O5, 1.4297(19); S2–O6, 1.431(2); C19–Os–O1, 177.77(10); C17–Os–O4, 103.32(10); O1–Os–O4, 79.90(6), C19–Os–P1, 93.42(8); C19–Os–P2, 90.28(8); O1–Os–P1, 86.17(5); O1–Os–P2, 89.58(5); P1–Os–P2, 165.29(2); O4–Os–P1, 93.07(5); O4–Os–P2, 99.92(5); S1–O1–Os 150.03(12); S2–O4–Os, 135.51(11).

our claim of only one triflate in the yellow species $OsHCl(CMe)(OTf)L_2$ on the fact that it is benzene-soluble but that red $OsH(CMe)(OTf)_2L_2$, once it forms and crystallizes from toluene at low temperature, is insoluble in benzene. The coordination geometry at Os in the bis-triflate is approximately octahedral, with the bulky phosphines mutually *trans* and the two triflates mutually *cis*. The species is molecular and saturated (18 valence electrons), not an ionic salt with one lattice triflate and a five coordinate $Os(H)(CMe)(OTf)(P^iPr_3)_2^+$. The Os≡C distance, 1.702 (3) Å, is consistent with a triple bond and both Os–O distances are quite long (2.23 and 2.25 Å) compared to those [5] (2.13 (1) and 2.15 (1) Å) in $OsH_2(OTf)_2L_2$. The triflate *trans* to hydride has a slightly longer Os–O bond length and it is significantly distorted angularly (∠C19–Os–O4 = 103.32(10)°), as if to avoid being exactly trans to hydride. The P–Os–P angle is also bent: 165.29(2)°. The S/O bond lengths internal to a given triflate show lengthening for the coordinated O (1.4665 (19) and 1.4710 (18) Å) relative to the pendant O (1.4292 (19), 1.4346 (19), 1.4297 (19) and 1.431 (2) Å); the binding to Os is thus strong enough to lengthen those S/O bonds. The Os–O–S bond angles are very different: 150.03 (12)° for O1 and 135.51 (11)° for O4. The conformation of the ^{i}Pr groups puts the bulkier, "inwardly directed" groups (on C1 and C16) towards the smallest ligand, hydride.

2.4.2. Mechanistic studies

Since no intermediate was seen in the reaction of Scheme 6 at room temperature, variable temperature NMR experiments were performed by combining the reagents at low temperature, then recording spectra followed by warming in 10 °C increments; these observations are consistent with Scheme 8. In the NMR experiments, reaction of **1a** with HCCH in toluene showed an acetylene adduct with 4 electron donation as a primary product at −60 °C. Two inequivalent hydride signals appeared at −1.5 ppm (double of triplets) coupled to the hydride and two P, and −13.0 ppm (doublet of triplets of triplets) coupled to the hydride, 2P and two acetylene protons. Two acetylene proton signals at 13.9 (br s) and 13 ppm (br s) confirmed 4 electron donation from acetylene. This adduct completely converted to the hydride/carbyne complex, **5a** by +10 °C. In addition, already at −60 °C, two proton signals were observed at 6.0 and 6.1 ppm consistent with two electron instead of 4 electron alkyne donation; this would be consistent with triflate remaining attached in this kinetic product. This compound disappeared above about −35 °C, consistent with it being in equilibrium with the 4e donor alkyne cation complex, by triflate gain/loss. In addition, variable temperature ^{2}H NMR experiments of **1a** with DCCD in CH_2Cl_2 (with 1 μL of C_6D_6 for reference) also proved formation of a η^2-DCCD adduct (broad singlet at 13.7 and 12.8 ppm in ^{2}H NMR) which was observed from −60 °C and completely disappeared at +10 °C. In ^{2}H NMR, a methyl group (1.2 ppm) signal in the carbyne complex **5a** began to be evident from -20 °C and its hydride was observed from −10 °C. The ^{2}H NMR ratio of the methyl



Scheme 8.

and the hydride was 1:1 due to one D migration from acetylene to Os. This ratio is consistent with the double H migration, Scheme 9, when the acetylene adduct converted to the carbyne complex via a hypothetical carbene intermediate.

Since study of reaction of **1a** with HCCH showed no detectable carbene (cf. Scheme 9) the possibly less reactive $Os(H)_2Cl_2L_2$ was next studied. Reaction of $Os(H)_2Cl_2L_2$ with excess HCCH in C_6D_6 was complete in 2 h at room temperature to produce a carbyne complex. However, in short reaction period (10 min), a new species was observed which was confirmed to be a carbene complex. One unique quartet proton signal at 25.5 ppm corresponds to a carbene proton coupled to a Me group (which appeared at 1.5 ppm as a doublet coupled to carbene proton). The absence of a new hydride signal in this intermediate confirms the double hydride migration to the acetylene (Scheme 9). This carbene complex in C_6D_6 solution begins to transform to the known carbyne, $OsHCl_2(CMe)L_2$,[3] in 2 h.

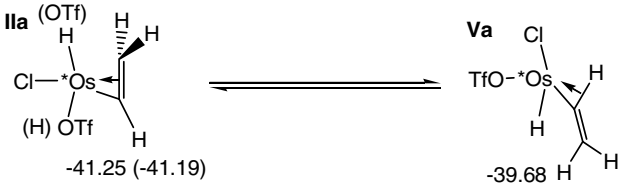
3. DFT calculations

Because we were unable to observe a vinyl intermediate from the η^2-alkyne involving a single hydride migration from the adduct, DFT calculations were carried out to evaluate various mechanisms. We calculated two alternatives: neutral molecule (OTf^- coordinated to Os) and cation (OTf^- not coordinated to Os). Scheme 10 shows triflate coordinated throughout, while Scheme 12 considers a cationic Os complex; the triflate was wholly absent in this latter calculation. In Scheme 10, the primary product could be $[Os(H)_2ClL_2(\eta^2\text{-HCCH})OTf]$, **Ia** whose HCCH donates two, not four electrons. By one hydride migration to acetylene, η^2-vinyl complex **IIa** is formed. **IIa** has two possible isomers differing by only 0.06 kcal/mol (based on the location of triflate and the hydride).

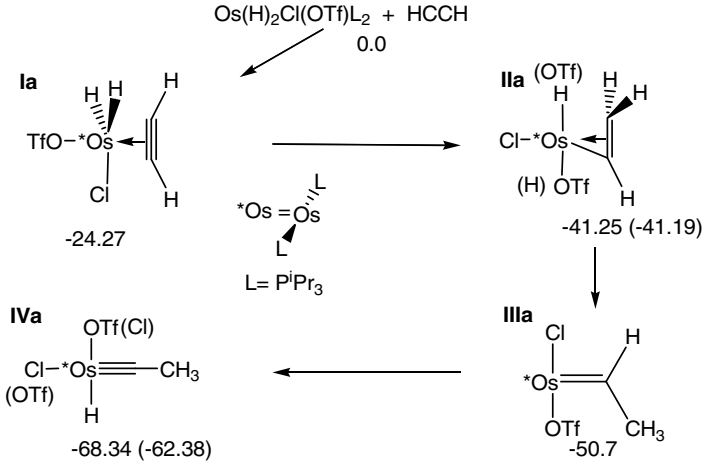
At this step, Scheme 11, η^2-vinyl ligand could convert to an η^1-vinyl ligand, **Va** whose energy is 1.5 kcal/mol higher than the η^2 isomer [14–16]. In this equilibrium, the second hydride migration ($Os \rightarrow C_\beta$) could involve **IIa** forming the carbene compound, **IIIa**. A carbene proton migration to the Os center finally produces a carbyne complex, **IVa**, which has two possible isomers, with triflate trans to the strong σ donor hydride ligand being more stable.

Scheme 12 describes the mechanism of formation of the carbyne complex with a cationic Os complex. As a primary product, $[Os(H)_2Cl(\eta^2\text{-HCCH})L_2]$ **Ib**, which was experimentally seen, is formed. By hydride migration, η^2-vinyl complex **IIb** is formed. Because of two possibilities of location of Cl and H, **IIb** has two isomers with $\Delta E = -3.3$ kcal/mol. In addition, the η^2-vinyl ligand in **IIb** could be converted to the η^1-vinyl Os complex which also has two isomers, Scheme 13. Next, the second hydride migration produces carbene complex, **IIIb**, which is found to be

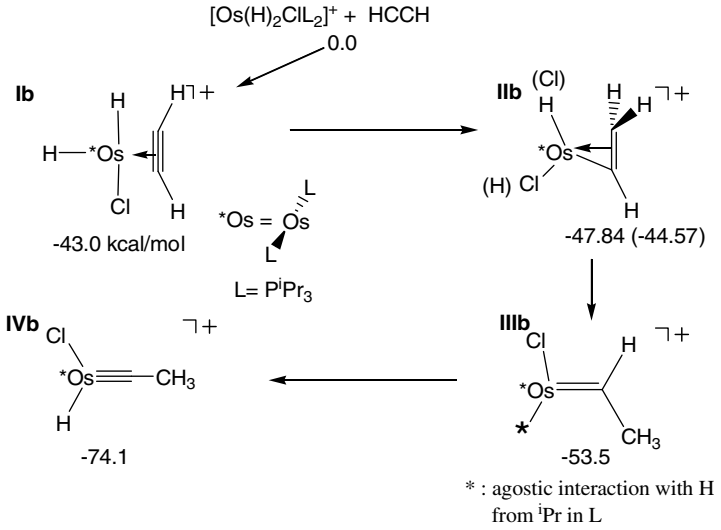
Scheme 9.



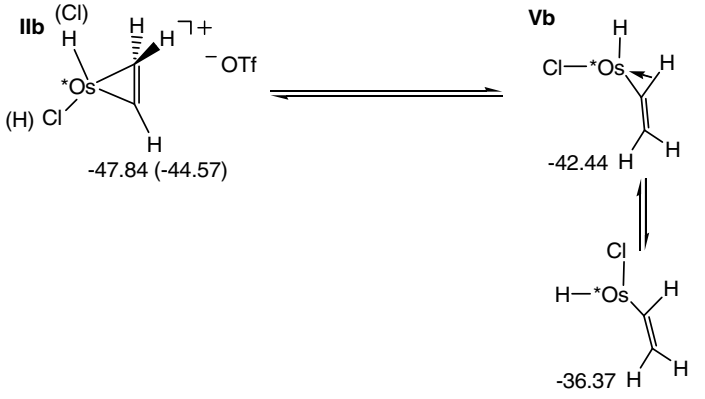
Scheme 11.



Scheme 10. $\Delta(E + \text{ZPE})$, kcal/mol.



Scheme 12.



Scheme 13.

stabilized by agostic interaction with one methyl in the $^{i}Pr_3P$ group. This is the unique consequence which differentiates it from Scheme 10. A cationic carbyne, **IVb**, is finally produced by migration of the carbene proton to the metal.

4. Summary

The mechanisms proposed in Scheme 10 and 12 show the same pathway through the π adduct, the η^2-vinyl adduct, and the carbene to the carbyne. The first step, formation of the adducts, **Ia** or **Ib** is favorable because of the low valence electron count (16 ($Os(H)_2ClL_2(OTf)$) or 14 ($[Os(H)_2ClL_2]^+$). Energetically, ΔE is larger to form **Ib** versus **Ia** because the valence electron changes from 14 to 18 in Scheme 12 but 16 to 18 in Scheme 10. In addition, the Os coordination number changes might indicate **Ia** ($6 \rightarrow 7$) being less favorable ΔE than **Ib** ($5 \rightarrow 6$). However, ΔE from **Ia** to **IIa** is larger than **Ib** to **IIb**. Due to crowding of the Os center by the η^2-acetylene binding mode, isomerization to the carbene (**IIIa** or **IIIb**) by hydride migration is favorable. In the case of **IIIb**, since it produces low coordination and valence electron counts, **IIb** is stabilized by an agostic interaction with a Me group in $^{i}Pr_3P$. Due to the characteristics of a 5d metal [17], which prefers the most π acidic ligand, the carbene ligand is finally isomerized to the hydride carbyne.

The absence of a vinylidene intermediate implied by the results in Scheme 9 is suggested to be due to the 4-electron alkyne donation and the η^2-vinyl binding.

5. Conclusion

This work has demonstrated that replacement of chloride by triflate lowers the barrier for the first substrate coordination in the reaction between the $L_2Os^{IV}(H)_2$ moiety and alkynes, not limited to terminal alkynes but also including MeCCPh. Thus, in spite of $Os(H)_2Cl_2L_2$ being unsaturated, its previous reaction with PhCCH was carried out at 60 °C and only $Os(H)Cl_2(CCH_2Ph)L_2$ was reported. The good leaving group character of triflate makes a 4-elec-

tron donor alkyne species detectable here, as $Os(H)_2(RCCH)ClL_2^+$ although there is some evidence for triflate coordinating to this Os at low temperature, giving molecular $Os(H)_2(RCCH)Cl(OTf)$, as an equilibrium participant with 2e donor alkyne. Hydrogenation of alkyne, to yield observable $Os(H)Cl(OTf)(CCH_2Ph)L_2$, can require base catalysis, since it is well established [18–22] that an apparently simple 1,2-H migration can have a large barrier for intramolecular conversion. Isotope label studies here show that the terminal alkyne proton finally resides on Os in the product. Detecting a carbene intermediate was possible by returning to the $OsCl_2$ reagent but working at 23 °C, since the accelerating effect of triflate ligand promotes rapid conversion of the carbene species to the carbyne and thus keeps the carbene concentration below detectable limits. While DFT calculations show continuously exothermic steps beginning both from 16-electron $Os(H)_2ClL_2(OTf)$ and from 14-electron $Os(H)_2ClL_2^+$, the fact that both the spectroscopic data (e.g. 4-e donor alkyne) and the crystal structure of the primary product $Os(H)_2Cl(PhCCH)L_2^+$ show triflate to not bind, makes us favor the absence of coordinated triflate until the final carbyne-forming step.

6. Experimental

6.1. General considerations

All manipulations were performed using standard Schlenk techniques or in an argon filled glovebox unless otherwise noted. Solvents were distilled from Na, Na/benzophenone, or CaH_2, degassed prior to use, and stored over 4 Å molecular sieves in air-tight vessels. All NMR solvents were also dried, vacuum transferred and stored in the glovebox under argon. $OsH_2Cl_2(P^iPr_3)_2$ was synthesized according to a published procedure [1]. Before HCCH was added in the evacuated headspace of the NMR tube, the top of the frozen solvent in the NMR tube was melted by hand to avoid condensing HCCH while the bottom of the tube was submerged in liquid N_2. All other reagents were used as received from commercial vendors. ^1H NMR chemical shifts are reported in ppm relative to protio impurities in the deutero solvents. ^{19}F NMR spectra are referenced to external standard CF_3CO_2H. ^{31}P NMR or ^{13}C NMR spectra are referenced to external standards of H_3PO_4or natural abundance ^{13}C peak of the solvent respectively. NMR spectra were recorded with a Varian Gemini 2000 (300 MHz ^1H; 121 MHz ^{31}P; 75 MHz ^{13}C, 282 MHz ^{19}F) or a Varian Unity INOVA instrument (400 MHz ^1H; 162 MHz ^{31}P; 101 MHz ^{13}C, 376 MHz ^{19}F).

6.2. Reaction of $Os(H)_2Cl_2L_2$ with AgOTf; forming $Os(H)_2ClL_2(OTf)$ 1a

$Os(H)_2Cl_2L_2$ (0.5 g, 85.8 mmol) was dissolved into 20 mL of CH_2Cl_2. AgOTf (0.66 g, 257.4 mmol) was added into the solution and the reaction mixture was stirred 30 min, then filtered through a 1.5 cm tall Celite column to removed salts. Solvent was then removed in vacuo. ^1H NMR (C_6D_6, 25 °C): −16.75 ppm (t, $J_{HP} = 35.4$ Hz, 2 H, OsH_2), 0.98 (dd, $J_{HP} = 15.6$ Hz, $J_{HP} = 7.2$ Hz, 36H, $P(CHMe_2)_3$), 1.97 (m, 6H, $P(CHMe_2)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 43 (br s) ppm. ^{19}F NMR (C_6D_6, 25 °C): −78 (s) ppm.

If less than 1 equiv of AgOTf was applied, $[(OsH_2L_2)_2(\mu\text{-}Cl)_3][OTf]$ [4] was formed. Addition of more than 2 equiv of AgOTf to the reaction mixture produced $Os(H)_2ClL_2(OTf)$.

6.3. Reaction of $Os(H)_2ClL_2(OTf)$ with $NaBAr^F{}_4$; formation of $[Os(H)_2ClL_2][BAr^F{}_4]$ 1b

$Os(H)_2ClL_2(OTf)$ (10 mg, 14.3 μmol) was dissolved in 0.5 mL CD_2Cl_2. $NaBAr^F{}_4$ (12.7 mg, 14.3 μmol) was added in the solution. The complete anion exchange was finished in 30 min; NaOTf was removed by a Celite column. ^1H NMR (CD_2Cl_2, 25 °C): −20.07 ppm (t, $J_{HP} = 32.1$, 2H, OsH_2), 1.36 (dd, $J_{HP} = 15.6$ Hz, $J_{HP} = 6.9$ Hz, 36H, $P(CHMe_2)_3$), 2.24 (m, 6H, $P(CHMe_2)_3$), 7.55 (s, 4H, $BAr^F{}_4$), 7.72 (s, 8H, $BAr^F{}_4$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): 49.5 (bs) ppm. ^{19}F NMR (CD_2Cl_2, 25 °C): −63 (s) ppm.

Attempting to grow single crystals of **1b** through slow solvent diffusion (by Et_2O/CH_2Cl_2 layering) gave $[Os(H)_2(OTf)_2L_2\ NaOEt_2]_2[BAr^F{}_4]_2$, Fig. 3 and Table 1, in which two $OsH_2(OTf)_2L_2$ moieties were held together by $2Na(Et_2O)^+$. Thus, this shows replacement of both chloride in this least soluble material. The nature of the "dimeric" structure is that each Na^+ binds to one oxygen of two triflates on each neutral $Os(H)_2(OTf)_2L_2$ molecule, with an overall center of symmetry relating the two halves in the $[Os(H)_2(OTf)_2L_2Na(OEt_2)]_2^{2+}$ dication. The $BAr^F{}_4$ anions show no interaction with the dication. In short, although Na^+ has not totally removed triflate from osmium, it is poised to pull these off, showing the active mechanistic role for an alkali metal ion electrophile in triflate removal. One Et_2O molecule completes a square pyramidal geometry around each Na^+. The S/O distances

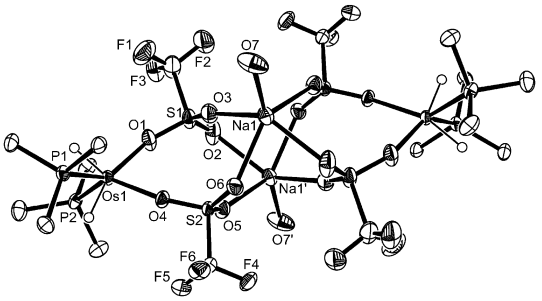


Fig. 3. ORTEP drawing (50% probability) of $[Os_2H_4Na_2(OTf)_4L_4]\ [BAr^F{}_4]_2(Et_2O)_2$ showing selected atom labeling. Only the hydride hydrogens are shown, and unlabeled atoms are carbon. Only methine carbons in *i*Pr groups are shown and ethyl groups have been deleted. The species here has a center of symmetry between Na1 and Na1′.

Table 1
Selected bond lengths (Å) and angles (°)

Os1–O1	2.103(3)	Os1–O4	2.155(2)
Os1–P2	2.2744(9)	Os1–P1	2.2748(9)
Os1–H1OS	1.52(4)	Os1–H2OS	1.44(4)
S1–O2	1.416(3)	S1–O3	1.436(3)
S1–O1	1.477(3)	S1–C19	1.843(5)
S1–Na1	3.3426(18)	S2–O6	1.428(3)
S2–O5	1.434(3)	S2–O4	1.464(2)
Na1–O7	2.313(6)	Na1–O6	2.379(3)
Na1′–O5	2.399(3)	Na1′–O2	2.420(3)
Na1–O3	2.435(3)	Na1–Na1′	4.176(3)
O1–Os1–O4	87.34(9)	O1–Os1–P2	94.05(8)
O4–Os1–P2	134.25(7)	O1–Os1–P1	138.78(9)
O4–Os1–P1	93.73(7)	P2–Os1–P1	113.38(3)
O1–Os1–H1Os	85.0(14)	O4–Os1–H1Os	157.6(14)
P2–Os1–H1Os	67.5(14)	P1–Os1–H1Os	78.5(14)
O1–Os1–H2Os	154.6(16)	O4–Os1–H2Os	84.6(16)
P2–Os1–H2Os	75.0(17)	P1–Os1–H2Os	66.0(16)
H1Os–Os1–H2Os	111(2)		

involving Os are longer than those involving Na^+, and the Na/O distances to ether are shorter than to triflate.

6.4. Reaction of $Os(H)_2ClL_2(OTf)$ with PhCCH; formation of $[Os(H)_2ClL(\eta^2\text{-PhCCH})][OTf]$, **2a**

The CD_2Cl_2 solution (0.5 mL) of 14.3 μmol $Os(H)_2ClL_2(OTf)$ (10 mg) was prepared in J. Young tube. PhCCH (1.6 μL, 14.3 μmol) was added to the NMR tube. The pale orange solution color changed to red in 30 min. Complete formation of $[Os(H)_2ClL(\eta^2\text{-PhCCH})][OTf]$ was observed by NMR. ^1H NMR (CD_2Cl_2, 25 °C): −12.50 ppm (dt, $J_{HH} = 4.5$ Hz, $J_{HP} = 17.1$ Hz, 1 H, Os*H*), −0.76 (ddt, $J_{HH} = 3.3$ Hz, $J_{HH} = 4.2$ Hz, $J_{HP} = 33$ Hz, 1H, Os*H*), 1.14 (dd, $J_{HP} = 17.1$ Hz, $J_{HP} = 6.6$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.28 (dd, $J_{HP} = 17.1$ Hz, $J_{HP} = 6.6$ Hz, 18H, P(CH*Me*$_2$)$_3$), 2.64 (m, 6H, P(C*H*Me$_2$)$_3$), 7.72 (t, $J_{HH} = 7.2$ Hz, 2H, *Ph*), 7.83 (t, $J_{HH} = 7.2$ Hz, 1 H, *Ph*), 8.08 (d, $J_{HH} = 7.2$ Hz, 2H, *Ph*), 14.13 (dt, $J_{HH} = 3.3$ Hz, $J_{HP} = 2.7$ Hz, 1H, PhCC*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): 84.6 (s) ppm. ^{19}F NMR (CD_2Cl_2, 25 °C): −78.3 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): 199.5 ppm (br s), 185.7 (s), 136.3, (s), 135.3 (s), 131.0 (s), 129.9 (s).

6.5. Reaction of $[Os(H)_2ClL_2][BAr^F{}_4]$ with PhCCH; formation of $[Os(H)_2ClL_2(\eta^2\text{-PhCCH})][BAr^F{}_4]$, **2b**

Compound **A**: 1.6 μL (14.3 μmol) of PhCCH was added to 14.3 μmol $[Os(H)_2ClL_2][BAr^F{}_4]$ dissolved in 0.5 ml of CD_2Cl_2in a J. Young tube. Formation of the adduct, $[Os(H)_2ClL_2(\eta^2\text{-PhCCH})][BAr^F{}_4]$ was complete in 30 min.

Compound **B**: 14.3 μmol of $[Os(H)_2ClL_2(\eta^2\text{-PhCCH})][OTf]$ in 0.5 mL CD_2Cl_2 was prepared in a J. Young tube. $NaBAr^F{}_4$ (12.7 mg, 14.3 μmol) was added to the solution. The anion exchange was complete in 30 min. ^1H NMR (CD_2Cl_2, 25 °C): −12.56 ppm (dt, $J_{HH} = 4.5$ Hz, $J_{HP} = 16.8$ Hz, 1H, Os*H*), −0.89 (ddt, $J_{HH} = 3.3$ Hz, $J_{HH} = 4.2$ Hz, $J_{HP} = 32.7$ Hz, 1H, Os*H*), 1.11 (dd, $J_{HP} = 17.1$ Hz, $J_{HP} = 6.9$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.26 (dd, $J_{HP} = 17.1$ Hz, $J_{HP} = 6.6$ Hz, 18H, P(CH*Me*$_2$)$_3$), 2.56 (m, 6H, P(C*H*Me$_2$)$_3$), 7.56 (s, 4H, $BAr^F{}_4$), 7.66 (t, $J_{HH} = 7.5$ Hz, 2H, *Ph*), 7.72 (s, 8H, $BAr^F{}_4$), 7.80 (t, $J_{HH} = 7.2$ Hz, 1H, *Ph*), 7.99 (d, $J_{HH} = 7.5$ Hz, 2H, *Ph*), 14.22 (dt, $J_{HH} = 3.3$ Hz, $J_{HP} = 2.7$ Hz, 1 H, PhCC*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): 83.8 (s) ppm. ^{19}F NMR (CD_2Cl_2, 25 °C): −63.8 (s) ppm.

6.6. Reaction of $Os(H)_2ClL_2(OTf)$ with MeCCPh, forming $[Os(H)_2ClL_2(\eta^2\text{-MeCCPh})][OTf]$

$Os(H)_2ClL_2(OTf)$ (10 mg, 14.3 μmol) in 0.5 mL CD_2Cl_2 was prepared in a J. Young tube. MeCCPh (18 μL, 14.3 μmol) was added to the solution. Formation of the adduct, $[Os(H)_2ClL_2(\eta^2\text{-MeCCPh})][OTf]$ was complete in 30 min. ^1H NMR (CD_2Cl_2, 25 °C): −12.57 ppm (dt, $J_{HH} = 3.3$ Hz, $J_{HP} = 17.1$ Hz, 1H, Os*H*), −0.55 (ddt, $J_{HH} = 3.3$ Hz, $J_{HP} = 32.1$ Hz, 1H, Os*H*), 1.10 (dd, $J_{HP} = 17.1$ Hz, $J_{HP} = 7.2$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.17 (dd, $J_{HP} = 16.5$ Hz, $J_{HP} = 6.9$ Hz, 18H, P(CH*Me*$_2$)$_3$), 2.63 (m, 6H, P(C*H*Me$_2$)$_3$), 4.36 (s, 3H, PhCC*Me*), 7.74 (t, $J_{HH} = 7.8$ Hz, 2 H, *Ph*), 7.84 (t, $J_{HH} = 7.5$ Hz, 1H, *Ph*), 8.00 (d, $J_{HH} = 6.9$ Hz, 2H, *Ph*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): 83.8 (s) ppm. ^{19}F NMR (CD_2Cl_2, 25 °C): −78.5 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): 225.6 ppm (s), 193.4 (s), 135.8, (s), 132.2 (s), 131.0 (s), 128.2 (s).

6.7. Reaction of $Os(H)_2ClL_2(OTf)$ with ^{t}BuCCH; formation of $[Os(H)_2ClL_2(\eta^2\text{-}^t\text{BuCCH})][OTf]$ (**3a**)

$Os(H)_2ClL_2(OTf)$ (10 mg, 14.3 μmol) was dissolved in 0.5 mL of CD_2Cl_2 in a J. Young tube. ^{t}BuCCH (1.8 μL, 14.3 μmol) was added to the solution. Reaction was complete in 30 min to form $[Os(H)_2ClL_2(\eta^2\text{-}^t\text{BuCCH})][OTf]$. ^1H NMR (CD_2Cl_2, 25 °C): −13.00 ppm (dt, $J_{HH} = 4.8$ Hz, $J_{HP} = 16.6$ Hz, 1H, Os*H*), −0.76 (ddt, $J_{HH} = 2.7$ Hz, $J_{HH} = 4.8$ Hz, $J_{HP} = 34.5$ Hz, 1H, Os*H*), 1.25 (dd, $J_{HP} = 16.4$ Hz, $J_{HP} = 6.0$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.33 (dd, $J_{HP} = 16.0$ Hz, $J_{HP} = 6.0$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.40 (s, 9H, HCC^t*Bu*), 2.53 (m, 6H, P(C*H*Me$_2$)$_3$), 13.40 (dt, $J_{HH} = 2.7$ Hz, triplet was not completely resolved, 1H, ^{t}BuCC*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): 85.3 (s) ppm. ^{19}F NMR (CD_2Cl_2, 25 °C): −78.5 (s) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −40 °C): 199.1 ppm (s), 192.2 (s).

6.8. Reaction of $[Os(H)_2ClL_2][BAr^F{}_4]$ with ^{t}BuCCH; formation of $[Os(H)_2ClL(\eta^2\text{-}^t\text{BuCCH})][BAr^F{}_4]$ (**3b**)

Compound **A**: 1.8 μL (14.3 μmol) of ^{t}BuCCH was added to 14.3 μmol $[Os(H)_2ClL_2][BAr^F{}_4]$ dissolved in 0.5 ml of CD_2Cl_2in J. Young tube. Formation of the adduct, $[Os(H)_2ClL_2(\eta^2\text{-}^t\text{BuCCH})][BAr^F{}_4]$ was complete in 30 min.

Compound **B**: 14.3 μmol of $[Os(H)_2ClL_2(\eta^2\text{-}^t\text{BuCCH})][OTf]$ in 0.5 mL CD_2Cl_2 was prepared in a J. Young tube. $NaBAr^F{}_4$ (12.7 mg, 14.3 μmol) was added to the solution. The anion exchange was complete in 30 min. ^1H

NMR (CD_2Cl_2, 25 °C): −12.98 ppm (dt, $J_{HH} = 4.8$ Hz, $J_{HP} = 16.2$ Hz, 1H, Os*H*), −1.30 (ddt, $J_{HH} = 1.8$ Hz, $J_{HH} = 5.1$ Hz, $J_{HP} = 33.9$ Hz, 1H, Os*H*), 1.23 (dd, $J_{HP} = 17.1$ Hz, $J_{HP} = 6.9$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.31 (dd, $J_{HP} = 16.5$ Hz, $J_{HP} = 7.2$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.47 (s, 9H, HCC^t*Bu*), 2.50 (m, 6H, P(C*H*Me$_2$)$_3$), 7.57 (s, 4H, B*Ar*$^F_4$), 7.72 (s, 8H, BAr$^F_4$), 13.40 (dt, $J_{HH} = 2.1$ Hz, triplet was not completely resolved, 1H, ^{t}BuCC*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): 85.2 (s) ppm.

6.9. Isomerization of [Os(H)$_2$ ClL$_2$(η^2-PhCCH)][OTf] to OsHCl(C–CH$_2$Ph)L$_2$ (OTf) with base catalyst (NEt$_3$ or DMAP)

The 0.5 mL solution of CD_2Cl_2 with 1.43 μmol of [Os(H)$_2$ClL$_2$(η^2-PhCCH)][OTf] was prepared in a J. Young tube. 15 mol% of base (NEt_3 (0.3 μL) or 0.3 mg of DMAP) was added to the tube. Isomerization was complete in 30 min using NEt_3 (in 37 h using DMAP). [*OsHCl(C–CH$_2$Ph)L$_2$(OTf)*] ^{1}H NMR (C_6D_6, 25 °C): −9.88 ppm (t, $J_{HP} = 16.5$ Hz, 1H, Os*H*), 1.12 (dd, $J_{HP} = 9.9$ Hz, $J_{HP} = 4.5$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.26 (dd, $J_{HP} = 11.1$ Hz, $J_{HP} = 5.4$ Hz, 18H, P(CH*Me*$_2$)$_3$), 2.46 (m, 6H, P(C*H*Me$_2$)$_3$), 2.59 (s, 2H, –C*H*$_2$–Ph), 6.92–7.09 (m, 5H, *Ph*). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 42.5 (s) ppm. ^{19}F NMR (C_6D_6, 25 °C): −78.3 (s) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): 279.1 ppm (t, $J_{CP} = 10.7$ Hz, Os≡*C*), 129.8, (s), 129.4 (s), 128.7 (s), 127.3 (s).

6.10. Reaction of [Os(H)$_2$ClL(η^2-PhCCH)][OTf] with NaOPh; formation of OsHCl(C–CH$_2$ Ph)L$_2$(OPh)

[Os(H)$_2$ClL$_2$(η^2-PhCCH)][OTf] (14.3 μmol) in 0.5 mL C_6D_6 was prepared in a J. Young tube. NaOPh (2 mg, 14.3 μmol) was added to the solution and the mixture was shaken 1 day. Reaction was completed in 1 day. The volatiles were removed in vacuo. The solid was redissolved in pentane and the salts were removed through a Celite column. The filtrate was dried in vacuum. [*OsHCl(C–CH$_2$Ph)L$_2$(OPh)*] ^{1}H NMR (C_6D_6, 25 °C): −12.05 ppm (t, $J_{HP} = 16.5$ Hz, 1H, Os*H*), 1.08 (dd, $J_{HP} = 13.8$ Hz, $J_{HP} = 7.2$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.13 (dd, $J_{HP} = 15.0$ Hz, $J_{HP} = 7.2$ Hz, 18H, P(CH*Me*$_2$)$_3$), 2.15 (m, 6H, P(C*H*Me$_2$)$_3$), 2.74 (s, 2H, –C*H*$_2$–Ph), 6.6–7.3 (m, 10H, *Ph*). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 38.6 (s) ppm.

6.11. Reaction of [Os(H)$_2$ClL(η^2-PhCCH)][OTf] with ^{n}Bu$_4$ NCl, formation of OsHCl$_2$ (C–CH$_2$ Ph)L$_2$

^{n}Bu$_4$NCl (4 mg, 14.3 μmol) was added to the 0.5 mL C_6D_6 solution in a J. Young tube which contained 14.3 μmol of [Os(H)$_2$ClL$_2$(η^2-PhCCH)][OTf]. Reaction was completed by shaking 1 day. The volatiles were removed in vacuo. The solid was redissolved in pentane and the precipitates were removed through a Celite column. The filtrate was dried in vacuum. NMR data agreed with known values [3].

6.12. Reaction of Os(H)$_2$ ClL$_2$ (OTf) with HCCH; formation of OsHCl(CMe)L$_2$(OTf)

Os(H)$_2$ClL$_2$(OTf) (10 mg, 14.3 μmol) and 0.5 mL of C_6D_6 were placed in a J. Young NMR tube. This solution was freeze–pump–thaw–degassed 3 times in liquid N_2 and the headspace evacuated. HCCH (300 mmHg) was added to the NMR tube. The pale orange color of Os(H)$_2$ClL$_2$(OTf) changed to pale yellow during shaking 2 h. The same reaction, but in CD_2Cl_2, is complete in 10 min. ^{1}H NMR (C_6D_6, 25 °C): −10.3 ppm (t, $J_{HP} = 16$ Hz, 1H, Os*H*), 0.605 (s, 3H, CC*H*$_3$), 1.08 (dvt, 18H, P(CH*Me*$_2$)$_3$), 1.19 (dvt, 18H, P(CH*Me*$_2$)$_3$), 2.63 (m, 6H, P(C*H*Me$_2$)$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 42 (s) ppm.

6.13. Variable temperature NMR experiments of Os(H)$_2$ClL$_2$ (OTf) with HCCH

Os(H)$_2$ClL$_2$(OTf) (14.3 μmol) was dissolved in 0.5 mL of CD_2Cl_2 in a J. Young tube and was degassed through 3 freeze–pump–thaw cycles using liquid N_2. HCCH (0.2 atm) was added into the evacuated head space of solution in the tube which was pre-cooled to −78 °C. After 5 min, the NMR tube is placed into the NMR probe which is pre-cooled to −60 °C. NMR spectra was collected at −60, −50, −35, −25 −15, −10, 0, +10 and +20 °C with 5 min interval. Os(H)$_2$ClL$_2$(OTf) was completely consumed at −60 °C.

At −60 °C, formation of the η^2-HCCH adducts, [Os(H)$_2$ClL$_2$(η^2-HCCH)][OTf] and Os(H)$_2$ClL$_2$(η^2-HCCH)(OTf) ($^-$OTf coordinates to Os) were observed. When the reaction temperature was increased to −35 °C, no new signal appeared. However, the signals corresponding to molecular Os(H)$_2$ClL$_2$(η^2-HCCH)(OTf) increased. These two compounds were completely consumed at +10 °C. Above −35 °C, the carbyne compound began to be observed. *[Os(H)$_2$ClL$_2$(η^2-HCCH)][OTf]* ^{1}H NMR (CD_2Cl_2, −35 °C): 13.87 ppm (d, $J_{HH} = 10.8$ Hz, 1H, η^2 − *H*CCH), 13.00 (d, $J_{HH} = 2.4$ Hz, 1H, η^2-HCC*H*), −1.46 (ddt, $J_{HH} = 1.2$ Hz, $J_{HH} = 2.4$ Hz, $J_{HP} = 30.3$ Hz, 1H, Os–*H*), −13.02 (ddt, $J_{HH} = 6$ Hz, $J_{HH} = 16.8$ Hz, $J_{HP} = 17.2$ Hz, 1H, Os–*H*), $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −35 °C): 91.9 ppm (s). *Os(H)$_2$ClL$_2$(η^2-HCCH)(OTf)* ^{1}H NMR (CD_2Cl_2, −35 °C): 6.09 ppm (s, 1H, η^2-*H*CCH), 5.95 (s, 1H, η^2-HCC*H*), −9.98 (t, $J_{HP} = 16$ Hz, 2H, Os–*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −35 °C): 37.3 ppm (s).

6.14. Reaction of Os(H)$_2$Cl$_2$L$_2$ with HCCH; formation of OsHCl$_2$(CMe)L$_2$

Os(H)$_2$Cl$_2$L$_2$ (10 mg, 17.3 μmol) was placed with 0.5 mL of CD_2Cl_2 or C_6D_6 in a J. Young tube. This solution was freeze–pump–thaw-degassed 3 times in liquid N_2 and the headspace evacuated. HCCH (400 mmHg) was added. The red solution color changed to pale yellow in less than 2 h. In 10 min, the reaction mixture in C_6D_6 shows formation of the carbene compound, which was confirmed by

NMR spectra, $OsCl_2(=C(H)Me)L_2$ (^1H NMR (C_6D_6, 25 °C): 1.47 ppm (d, $J_{HH} = 6$ Hz, 3H, Os=C(H)*Me*), 25.45 (q, $J_{HH} = 6$ Hz, 1H, Os=C(*H*)Me), $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 27.2 ppm (s)). $[OsHCl_2(CMe)L_2]$ ^1H NMR (C_6D_6, 25 °C): −7.23 ppm (t, $J_{HP} = 15.6$ Hz, 1H, Os*H*), 0.198 (s, 3H, CCH_3), 1.25 (dvt, $J = 7.2$ Hz, $J = 14.8$ Hz, 18H, P(CHMe_2)$_3$), 1.44 (dvt, $J = 7.2$ Hz, $J = 14.8$ Hz, 18H, P(CHMe_2)$_3$), 2.69 (m, 6H, P(C*H*Me$_2$)$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 21.5 ppm (s).

6.15. Isotope labeled experiments

6.15.1. Reaction of $Os(H)_2ClL_2(OTf)$ with PhCCD, formation of $[Os(H)_2ClL_2(\eta^2\text{-}PhCCD)][OTf]$

The CH_2Cl_2 solution (0.5 mL) (containing 1 μL of C_6D_6 for reference) of 14.3 μmol $Os(H)_2ClL_2(OTf)$ (10 mg) was prepared in a J. Young tube. PhCCD (1.6 μL, 14.3 μmol) was added to the NMR tube. The pale orange solution changed to red in 30 min. Complete formation of $[Os(H)_2ClL(\eta^2\text{-}PhCCD)][OTf]$ was observed by NMR. ^2H NMR (CH_2Cl_2 with 1 μL C_6D_6 for reference, 25 °C): 13.98 ppm (s, 1D, PhCC*D*).

6.15.2. Reaction of $Os(H)_2ClL_2(OTf)$ with $H\,^{13}C^{13}CH$; formation of $OsHCl(^{13}C^{13}CH_3)L_2(OTf)$

$Os(H)_2ClL_2(OTf)$ (10 mg, 14.3 μmol) and 0.5 mL of CD_2Cl_2 were placed in a J. Young NMR tube. This solution was freeze–pump–thaw-degassed 3 times in liquid N_2 and the headspace evacuated. $H^{13}C^{13}CH$ (300 mmHg) was added to the NMR tube. The pale orange color of $Os(H)_2ClL_2(OTf)$ changed to pale yellow after shaking 10 min. ^1H NMR (CD_2Cl_2, 25 °C): −10.41 ppm (dt, $J_{HC} = 9.2$ Hz, $J_{HP} = 16$ Hz, 1H, Os*H*), CCH_3 was not observed due to overlapping with other resonances, 1.08 (dvt, 18H, P(CHMe_2)$_3$), 1.19 (dvt, 18H, P(CHMe_2)$_3$), 2.63 (m, 6H, P(C*H*Me$_2$)$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): 43.1 ppm (d, $J_{CP} = 11.3$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): 279.1 ppm (dt, $J_{CC} = 30.4$ Hz, $J_{CP} = 10.7$ Hz, Os≡*C*), 40.8 (d, $J_{CC} = 31.8$ Hz, Os≡C–*C*H$_3$). ^{19}F NMR (C_6D_6, 25 °C): −78.6 (s) ppm.

6.15.3. Reaction of $Os(H)_2ClL_2(OTf)$ with DCCD; formation of $OsDCl(CCH_2D)L_2(OTf)$

The CH_2Cl_2 solution (0.5 mL) (containing 1 μL of C_6D_6 for reference) of 14.3 μmol $Os(H)_2ClL_2(OTf)$ (10 mg) was prepared in a J. Young tube. This solution was freeze–pump–thaw-degassed 3 times in liquid N_2 and the headspace evacuated. DCCD (300 mmHg) was added to the NMR tube. The pale orange solution was changed to pale yellow in 30 min at 23 °C. In 30 min complete formation of $OsDCl(CCH_2D)L_2(OTf)$ was observed by NMR. ^2H NMR (CH_2Cl_2 with 1 μL C_6D_6 for reference, 25 °C): −10.42 ppm (s, 1D, Os-*D*), 1.23 (s, 1D, Os≡C–CH_2D). Os≡C–CH_3 signal in CD_2Cl_2 solution of $Os(H)_2ClL_2(OTf)$ and HCCH was not observed due to overlapping with other resonances in ^1H NMR but in the C_6D_6 solution it appeared at 0.605 ppm.

6.15.4. Variable temperature NMR experiments of $Os(H)_2ClL_2(OTf)$ with DCCD

$Os(H)_2ClL_2(OTf)$ (10 mg, 14.3 μmol) and 0.5 mL of CH_2Cl_2 solution (0.5 mL) (containing 1 μL of C_6D_6 for reference) were placed in a J. Young NMR tube. This solution was freeze–pump–thaw-degassed 3 times in liquid N_2 and the headspace evacuated. DCCD (0.2 atm) was added into the evacuated head space in the tube which was pre-cooled to −78 °C. After 5 min, the NMR tube was placed into an NMR probe pre-cooled to −60 °C. ^2H NMR spectra was collected every 10 °C increment with a 5 min interval for temperature stabilization.

At −60 °C, two broad signals at 12.7 and 13.5 ppm were observed which indicates formation of η^2-DCCD adduct, $[Os(H)_2ClL_2(\eta^2\text{-}DCCD)][OTf]$. These signals disappeared at +10 °C. Below −40 °C, no new signal appeared. At −40 °C, one singlet at 1.2 ppm due to Os≡C–CH_2D appeared. The carbyne hydride singlet at −10.48 ppm was observed beginning at −30 °C.

6.16. $[Os(H)_2ClL_2(\eta^2\text{-}DCCD)][OTf]$

^2H NMR (CH_2Cl_2 with 1 μL C_6D_6 for reference, −30 °C): 13.72 ppm (s, 1D, $\eta^2 - D$CCD), 12.83 (s, 1D, η^2-DCC*D*). $OsDCl(C\text{-}CH_2D)L_2(OTf)$ ^2H NMR (CH_2Cl_2 with 1 μL C_6D_6 for reference, 25 °C): −10.45 ppm (s, D, Os-*D*), 1.2 (s, 1D, Os≡C–CH_2D).

6.17. X-ray structure determinations

6.17.1. $[OsH_2(OTf)L_2(\eta^2\text{-}PhCCH)][OTf]$

A red crystal (approximate dimensions $0.12 \times 0.10 \times 0.09$ mm^3) was grown from a mixture of CH_2Cl_2 and MeI. The final full matrix least squares refinement converged to $R_1 = 0.0412$ and $wR_2 = 0.1105$ (F^2, all data). The highest remaining electron density peak (6.5 electrons) is located at a distance of 0.8 Å of Os. It is assumed that this is indicating a core disorder and the peak is a second site of Os1. In an alternative refinement the second site of Os refines to an occupancy of 3.2%, the R_1-value decreases by 1% and most of the difference peaks (0.5 electrons) are then located in the vicinity of both Os sites. In the final refinement, the disorder remained unmodeled. Osmium is coordinated to phenylacetylene, two tri-*i*-propyl phosphines, triflate, and two hydrides. The hydrides were placed based on DFT calculations and their displacement parameters but their positions were not refined.

6.17.2. $[Os_2H_4Na_2(OTf)_4L_4][BAr^F{}_4]_2(Et_2O)_2$

A crystal was grown from toluene at −60 °C. An orange crystal was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a SMART6000 (Bruker) at 120(2) K. The space group $P2_1/n$ was determined based on intensity statistics and systematic absences. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed

in ideal positions and refined as riding atoms with relative isotropic displacement parameters, except for the hydrides bound to osmium, which were refined for all parameters. The final full matrix least squares refinement converged to $R_1 = 0.0306$ and $wR_2 = 0.0801$ (F^2, all data). The remaining electron density is rather large and located 0.83 Å from the osmium atom . Disorder was modeled for several CF_3 groups and the ether molecule connected to sodium.

6.17.3. $OsH(CMe)(OTf)_2L_2$

A crystal (approximate dimensions $0.15 \times 0.12 \times 0.05$ mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a SMART6000 (Bruker) at 120(2) K. The space group $P2_12_12_1$ was determined based on intensity statistics and systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters with the exception of the hydride bound to osmium, which was refined for all parameters. The final full matrix least squares refinement converged to $R_1 = 0.0153$ and $wR_2 = 0.0360$ (F^2, all data). The remaining electron density is located around the osmium.

7. Computational details

Theoretical calculations in this work have been performed using density functional theory [23], with the PBE [24] functional, implemented in an original program package "Priroda" authored by Dr. D. N. Laikov [25,26]. Relativistic Stevens–Basch–Krauss (SBK) effective core potential (ECP) [27–29] optimized for DFT-calculations has been used. A Gaussian-type triple zeta basis set was used: Os [5111] C,N,P,Cl [3,1,1/3,1,1/1,1] H [3,1,1/1]. Full geometry optimizations have been performed without symmetry constraint. For all species under investigation, frequency analysis has been carried out, and zero-point vibration energy corrections made. Second derivatives were evaluated analytically. All minima have been checked for the absence of imaginary frequencies.

Alternative starting structures for geometry optimization, differing by the conformations of the $MP(CHMe_2)_3$ single bonds, sometimes led to different minima (all separated by only fractions of 1 kcal/mol). These minima differed by the orientation of the P^{i}Pr group which furnished the agostic H in **IIIb**. Bond lengths and angles in the inner coordination sphere were essentially invariant (±0.02 Å and ±0.5 °) among these alternative minima. This proves the robustness of the core geometrical parameters discussed here to these structural differences, and thus, in reality, the robustness of the metal/ligand bonds to the details of the (weak) agostic interaction.

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Appendix A. Supplementary material

CCDC 638578, 638579 and 638580 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.07.031.

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