Geminal dehydrogenation of ether and amine $C(sp^3)H_2$ groups by electron-rich Ru(II) and Os†

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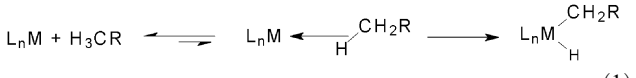
Reaction of $[RuHCl(P^iPr_3)_2]_2$ with THF or dioxolane doubly dehydrogenates the carbon α to the oxygen to yield $RuHCl(H_2)(P^iPr_3)_2$, together with the coordinated cyclic carbene, $RuHCl[=CO(CH_2)_2E](P^iPr_3)_2$, where $E = CH_2$ or O. In the presence of $CH_2{=}CH^tBu$ as hydrogen acceptor, all Ru is converted to its carbene complex. The cyclic amines $RN(CH_2)_4$ (R = H, Me) react analogously, to produce N-substituted carbene complexes by geminal dehydrogenation; a crystal structure is presented for the carbene complex with R = H, which reveals intermolecular NH···Cl hydrogen bonding. Similar chemistry is established for $Os(H)_3Cl(P^iPr_3)_2$, at 25 °C, in the presence of $H_2C{=}CH^tBu$, to give $OsHCl[=CO(CH_2)_3](P^iPr_3)_2$. Pyrrolidine reacts rapidly at 25 °C to give first a 1 : 1 *amine* adduct, then slowly the *trihydride* carbene $Os(H)_3Cl[=C(NH)(CH_2)_3](P^iPr_3)_2$, together with H_2. $Os(H)_2Cl_2(P^iPr_3)_2$ is first dehydrochlorinated by one mole of pyrrolidine, then a second mole of pyrrolidine is geminally dehydrogenated to form $Os(H)_3Cl[=C(NH)(CH_2)_3](P^iPr_3)_2$. The five-coordinated carbene $OsHCl[=CO(CH_2)_3](P^iPr_3)_2$ will add H_2, and the resulting product exists as two isomers, a trihydride with Cl *cis* to the carbene and a species with Cl *trans* to carbene and H and "2H" mutually *trans*. Isomer preferences, strength of H_2 binding, and carbene plane orientation are discussed, together with DFT calculations on the thermodynamics of ether dehydrogenation by ruthenium. The latter reveal that coordination of removed H_2 to Ru is essential to achieving favorable thermodynamics.

Attack and cleavage, by a molecular transition metal species, of $C(sp^3)$–H bonds is a continuing subject of study,[1–5] with apparently both electrophilic and nucleophilic metal complexes being able to accomplish this. Among the latter, very common is the use of an (η^3-facial ligand) ML_n moiety, where M often has a d^8 configuration. Examples include $(C_5R_5)ML$ or $[HB(C_3N_2R_4)_3]ML$ (M = Rh or Ir), where the facial η^3 constraint on metal coordination geometry precludes the normally preferred planar structure around M, and thus confers enhanced reactivity on the metal. Alternatives exist to this attack strategy,[6,7] since the "Shilov system" for attack on methane appears to involve planar L_3Pt^{II} cations, though these are also d^8.

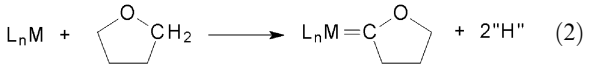
Guided speculative rationalization, as well as computational studies have shown that alkane coordination to an unsaturated metal is sufficiently weak[8–13] that the opposing $T\Delta S$ term in a bimolecular mechanism often dominates;[14] this often frustrates detection of either the adduct or its product of oxidative addition [eqn. (1)].



(1)

It is therefore productive to consider attaching to the molecule containing the $C(sp^3)$–H bond a traditional Lewis base donor D_0, whose dative bond energy $D_0 \rightarrow M$ can pay the "price" of $T\Delta S$, and bring the C–H bond in proximity to the metal, for subsequent attack. This rationalizes the observations[15–17] that cyclic ethers, mainly THF, can undergo attack at the H–C_α bond. Success with acyclic ethers [e.g., $O(C_2H_5)_2$] is less common,[18,19] presumably since acyclic ethers bind less strongly to metals than do cyclic ethers.

Ethers represent especially interesting substrates for $C(sp^3)$–H activation since the hydrido metal alkyl is only a primary product, and *double* dehydrogenation can occur [eqn. (2)],



(2)

assisted by π-donation to the resulting heteroatom-substituted carbene by the metal as well as by the heteroatom. Removal of *two* hydrogens from sp^3 carbon raises the question of the fate of those hydrogens, and the influence of that fate on the thermodynamics of the transformation. We report here[20] on the use of the 14-electron fragment $RuHClL_2$ ($L = P^iPr_3$), a potent π-base, to effect this transformation. We also generalize to other saturated heterocycles, and then show how this reaction can also be effected by an osmium analog, available from $Os(H)_3ClL_2$, and also from $Os(H)_2Cl_2L_2$.

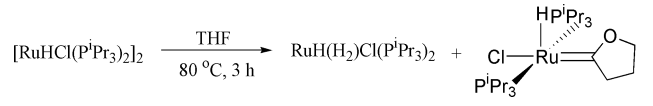
Results

Geminal dehydrogenation of ethers by $[RuHClL_2]_2$

(a) THF. Dimeric[21] $[RuHClL_2]_2$ reacts with excess THF under mild conditions to produce equimolar $RuH(H_2)$-

† Electronic supplementary information (ESI) available: crystallographic data, fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles. See http://www.rsc.org/suppdata/nj/b2/b200168n/

ClL_2[22,23] and the cyclic heteroatom-substituted carbene, $RuHClL_2(=COC_3H_6)$[24] according to eqn. (3).

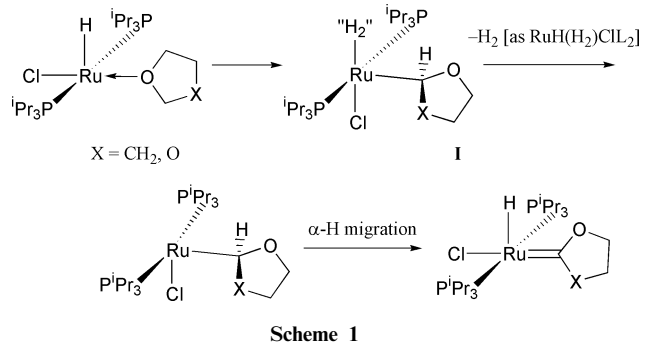


(3)

This net *double* C–H activation of THF α-protons is readily achieved by simply heating a THF solution of $[RuHClL_2]_2$ for 3 h at 80 °C. The presence of $CH_2{=}CH^tBu$ does not serve to enhance the conversion of Ru to $RuHClL_2(=COC_3H_6)$ in this reaction, because, at elevated temperatures, it induces decomposition of $[RuHClL_2]_2$. We propose this reaction is initiated by oxidative addition of a THF α-C–H to yield intermediate $Ru(H_2)ClL_2(–CHOC_3H_6)$, which can lose H_2 to unreacted $[RuHClL_2]_2$ to form the observed $RuH(H_2)ClL_2$ (Scheme 1). From this unobserved H_2 loss alkyl species, $RuClL_2(–CHOC_3H_6)$, α-H migration to Ru generates the observed carbene. Such an intermediate was proposed for the isomerization of coordinated cyclic and acyclic *vinyl* ethers to carbene using $[RuHClL_2]_2$ by Ru–H addition to CHR=CH(OR′), and confirmed by ^2H labeling studies in the generation of the observed carbene products.[24] Since $[RuHClL_2]_2$ remains dimeric at room temperature at spectroscopically detectable levels in the presence of THF,[21] mild heating is required to split the halide bridges and generate the monomeric THF adduct. If $[RuHClL_2]_2$ is *synthesized* in THF at room temperature (by dehydrohalogenation of $RuH_2Cl_2L_2$), 15–20% of the carbene, $RuHClL_2(=COC_3H_6)$, is observed since the initially formed $RuHClL_2$ monomer can be solvated by THF and form carbene in competition with its dimerization.

(b) Dioxolane. The reaction of $[RuHClL_2]_2$ with neat dioxolane results in the formation of equimolar $RuHClL_2[=C(OCH_2)_2]$, **1**, and $RuH(H_2)ClL_2$ over a period of 3 h at room temperature. No evidence for the formation of $RuHClL_2[=C(OCH_2OCH_2)]$, **2**, the product of C–H activation of dioxolane at the 4,4′ positions, was seen. In addition to illustrating the selectivity of $[RuHClL_2]_2$ in cleavage of $C(sp^3)$–H bonds, the exclusive formation of $RuHClL_2[=C(OCH_2)_2]$ supports the mechanism shown in Scheme 1. A mechanism involving β-H elimination of **I** in Scheme 1 to generate observed $RuH(H_2)ClL_2$ and free or coordinated 2,3-dihydrofuran, which is then isomerized by $[RuHClL_2]_2$ to give carbene (THF dehydrogenation), *fails* to explain the observed $RuHClL_2[=C(OCH_2)_2]$ from dioxolane, as species **I** (Scheme 1) has no β-hydrogens. Also, any α,β-dehydrogenation of dioxolane would yield 1,3-dioxol-4-ene, susceptible to isomerization by $[RuHClL_2]_2$ to give the *unobserved* $RuHClL_2[=C(OCH_2OCH_2)]$.

When excess 3,3-dimethyl-1-butene ($CH_2{=}CH^tBu$) is added to the dioxolane solution of $[RuHClL_2]_2$, *quantitative* conversion of Ru to $RuHClL_2[=C(OCH_2)_2]$ is observed at 25 °C. This occurs when the olefin reacts cleanly with $RuH(H_2)ClL_2$ at 25 °C to liberate *n*-hexane ($CH_3CH_2{}^tBu$) and regenerates the $RuHClL_2$ fragment (verified independently) for further reaction with ether (Scheme 1).



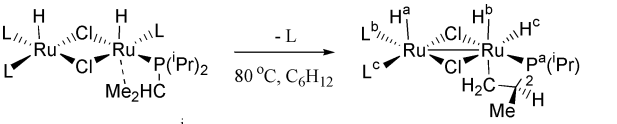
Scheme 1

(c) Other ethers. The six-membered heterocyclic ethers 1,4-dioxane and 1,3,5-trioxane *fail* to produce the corresponding carbenes upon reaction with $[RuHClL_2]_2$. Neither reagent shows reactivity toward $[RuHClL_2]_2$ at room temperature, and when heated in neat dioxane, $[RuHClL_2]_2$ forms the P^iPr_3 metallated dimer (see below), $Ru_2H_3Cl_2(L)_2[\eta^2\text{-}P(^iPr)_2C(H)\text{-}MeCH_2]$, hereby represented as $Ru_2H_3Cl_2(L)_2(\eta^2\text{-}L)$, as the major product. When $[RuHClL_2]_2$ and excess trioxane are heated in benzene at 80 °C, the resulting solution contains a mixture of $Ru_2H_3Cl_2(L)_2(\eta^2\text{-}L)$ and $(C_6H_6)RuHClL$, a new member of the class (arene)RuHClL (L = 3° phosphine), as its major constituents. The use of cyclohexane as the solvent for reaction with excess trioxane gives $Ru_2H_3Cl_2(L)_2(\eta^2\text{-}L)$ in >85% yield. However, with both six-membered heterocyclic ethers, *ca.* 5–10% of $RuHCl(CO)L_2$ was observed after 9 h at 80 °C in inert solvent. Since we find that $RuHClL_2(=COC_3H_6)$ decomposes slowly in C_6D_6 at 80 °C ($t_{1/2} = 20$ h) to yield a mixture containing $RuHCl(CO)L_2$ as the major constituent, the possibility exists that the Ru(CO) complex seen in the dioxane and trioxane cases results from the decomposition of carbene complexes (as minor products) under the reaction conditions.

Neat acyclic ether MeO^tBu gives no carbene with $[RuHClL_2]_2$ after 9 h at 80 °C, but instead only a mixture of $Ru_2H_3Cl_2(L)_2(\eta^2\text{-}L)$, $RuH(H_2)ClL_2$, and $RuHCl(CO)L_2$.

$Ru_2H_3Cl_2(L)_2[\eta^2\text{-}P(^iPr)_2C(H)MeCH_2]$

When $[RuHClL_2]_2$ is heated in alkane solvent, the P^iPr_3 metallated dimer, $Ru_2H_3Cl_2(L)_2(\eta^2\text{-}L)$ and equimolar free phosphine are formed over a period of 15 h at 80 °C. The solid-state structure of $[RuHClL_2]_2$ shows[21] a prominent agostic C–H interaction between one of the Ru centers and a CH_3 group of one P^iPr_3 ligand, illustrating how the C–H bond that is thermally activated is primed for reaction before heating [eqn. (4)].



$[RuHClL_2]_2$; L = P^iPr_3

$Ru_2H_3Cl_2L_2[\eta^2\text{-}P(^iPr)_2C(H)MeCH_2]$

$J(P^a\text{-}P^b) = 177$ Hz $J(P^a\text{-}H^a) = 36$ Hz

$J(P^a\text{-}P^c) = 111$ Hz

$J(P^b\text{-}P^c) = 14$ Hz

(4)

No back reaction of $Ru_2H_3Cl_2(L)_2(\eta^2\text{-}L)$ to $[RuHClL_2]_2$ is observed at room temperature (over 2 days) in the presence of free P^iPr_3.

The molecule is characterized by a well-defined AMX pattern by $^{31}P\{^1H\}$NMR in C_6D_{12} consisting of three doublets of doublets centered at δ −7.2, 61.3, and 91.7. The metallated phosphine (P^a) is assigned to the highest field resonance and displays large couplings to the other two phosphines of 177 (P^a–P^b) and 111 (P^a–P^c) Hz. A much smaller P–P coupling is observed between P^b and P^c (14 Hz), suggesting that they are *cis* disposed. Since the presence of three bulky P^iPr_3 groups on a single metal is highly unlikely, we propose that the metallated phosphine, P^a lies on one Ru, while P^b and P^c are arranged *cis* on the other Ru, and that the mechanism to strongly couple P^a with P^b and P^c results from a Ru–Ru bond. Two high-field ^1H NMR signals are seen in a 2 : 1 intensity ratio at −12.6 ppm (H^b and H^c) and −18.2 ppm (H^a); H^a is split into a doublet by coupling to one phosphine (P^a *via* the Ru–Ru bond). The coalesced signal for H^b/H^c is a broad singlet, and the two resonances show T_1 times of 170 (H^a) and 145 (H^b/H^c) ms at room temperature, thus suggesting they are all hydrides.

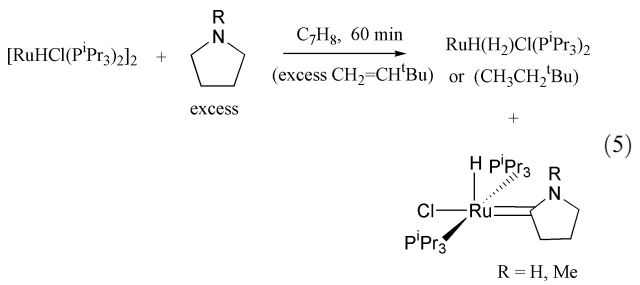
As expected from the C_1 symmetry of the molecule, by ^{13}C NMR, four ^{i}Pr methyl signals are seen for the alkyl ligands of P^b and P^c, and four additional ^{i}Pr methyls are observed with less intensity for the ^{i}Pr units of P^a, whose rotation about Ru–P is fixed by chelation. The carbons of the $CH(Me)CH_2$ chain of metallated P^a are seen as a doublet for $CH(\mathit{Me})CH_2$ [δ 39.2, $J_{P^a\text{–}C} = 24$ Hz], a doublet of apparent triplets for $\mathit{C}H(Me)CH_2$ [δ 40.7, $J_{P^a\text{–}C} = 16$ Hz, $J_{P^b/P^c\text{–}C} = 2$ Hz], and an apparent triplet for $CH(Me)\mathit{C}H_2$ [δ 46.8, $J_{P^b/P^c\text{–}C} = 4$ Hz]. By ^1H NMR, the protons of the $CH(Me)CH_2$ unit are observed as an AB pattern for $CH(Me)C\mathit{H}_2$ [δ 1.59, 2H, $^2J_{H\text{–}H} = 6$ Hz], a doublet for $CH(\mathit{Me})CH_2$ [δ 1.63, 3H, 6 Hz, and a doublet for $C\mathit{H}(Me)CH_2$ [δ 3.00, 1H, 10 Hz]. All other expected ^1H and ^{13}C resonances for the alkyl portions of the phosphines are also present.

The presence of approximately 5% (based on Ru) of $Ru_2H_3Cl_2(L)_2(\eta^2\text{-L})$ in the mixture of $RuH(H_2)ClL_2$ and $RuHClL_2(=COC_3H_6)$ generated from $[RuHClL_2]_2$ in hot THF, and the observation that it remains after further heating, suggests that it is formed concurrently and competitively with the carbene and is not an intermediate in the THF activation process.

We also considered an alternative identity, that from liberation of propylene and formation of a dimer with a bridging phosphide ligand: $RuHCl(P^iPr_3)(\mu\text{-Cl})(\mu\text{-}P^iPr_2)Ru(H)_2(P^iPr_3)$. When a solution of this molecule, together with equimolar P^iPr_3 in C_6D_{12} is subjected to excess H_2 (1 atm), the dihydrogen complex $RuH(H_2)Cl(P^iPr_3)_2$ is regenerated in quantitative yield ($t_{½} = 3$ days; 25 °C). This excludes a bridging phosphido product (which lacks the necessary C_3 fragment), but is consistent with hydrogenolysis of the metallated P^iPr_3 Ru–C bond, and re-coordination of the free phosphine, thus strengthening the assignment of the thermolysis product as $Ru_2H_3Cl(L)_2(\eta^2\text{-L})$.

Geminal dehydrogenation of amines by $[RuHClL_2]_2$

The cyclic amine pyrrolidine [eqn. (5)]



(5)

is also dehydrogenated by $[RuHClL_2]_2$, but at a dramatically faster rate than is THF.[25] A toluene solution of $[RuHClL_2]_2$ is quantitatively converted to $RuH(H_2)ClL_2$ and equimolar cyclic nitrogen-substituted carbene $RuHClL_2[=CN(H)C_3H_6]$ upon exposure to equimolar (Ru : N) or excess pyrrolidine in less than 1 h at room temperature. As with dioxolane dehydrogenation, addition of excess $CH_2{=}CH^tBu$ to the reaction mixture results in quantitative conversion of Ru to the carbene, and scavenging of the lost H_2 as $CH_3CH_2{}^tBu$ rather than $RuH(H_2)ClL_2$, when the reaction is monitored *in situ* by NMR. The molecule is characterized by ^1H NMR in THF-d_8 with a hydride signal at δ −21.8 (t, 21 Hz) and 3 CH_2 units of the five-membered ring. The $^{31}P\{^1H\}$ NMR shows a singlet, and the carbene carbon yields a signal at δ 256.3 (t, 10 Hz) by $^{13}C\{^1H\}$ NMR. The NH proton is observed by ^1H NMR as a sharp singlet at δ 8.00, whose high-field position is consistent with some hydrogen bonding equilibrium in solution.

An X-ray crystal structure determination of $RuHClL_2[=CN(H)C_3H_6]$ shows a square pyramidal coordination geometry with Cl approximately *trans* to the carbene ligand, and the hydride ligand *trans* to the empty site (Fig. 1 and Table 1).

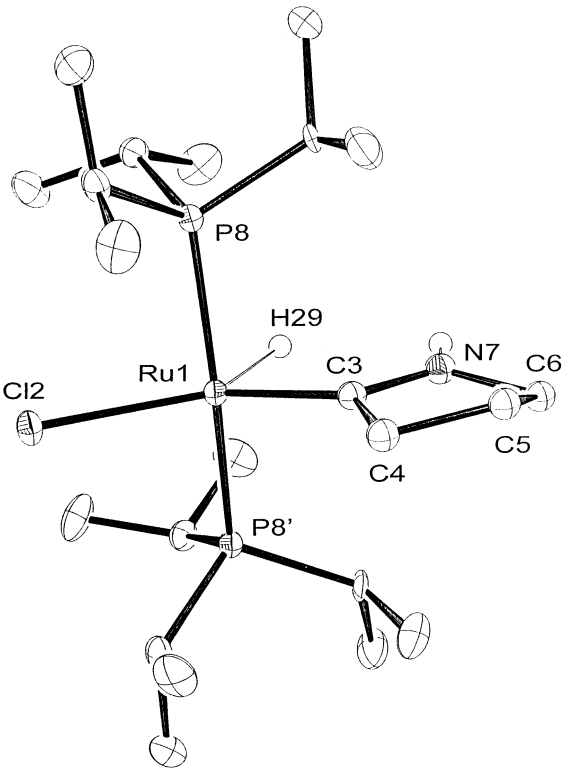


Fig. 1 ORTEP drawing of $RuHCl(P^iPr_3)_2(C_4NH_7)$, showing selected atom labeling. Only selected hydrogens are shown, as open circles.

Table 1 Selected bond distances (Å) and angles (°) for $RuHCl(C_4NH_7)(P^iPr_3)_2$

Ru(1)–Cl(2)	2.4949(16)	N(7)–C(3)	1.325(8)
Ru(1)–P(8)	2.3426(9)	N(7)–C(6)	1.484(8)
Ru(1)–C(3)	1.898(6)	Ru(1)–H(A)	1.75
Cl(2)–Ru(1)–P(8)	90.21(5)	Ru(1)–C(3)–N(7)	131.6(4)
Cl(2)–Ru(1)–C(3)	147.04(18)	Ru(1)–C(3)–C(4)	123.0(4)
P(8)–Ru(1)–P(8)′	163.66(5)	N(7)–C(3)–C(4)	105.4(5)
P(8)–Ru(1)–C(3)	94.25(5)	Cl(2)–Ru(1)–H(A)	132.4
Ru(1)–P(8)–C(9)	115.60(20)	P(8)–Ru(1)–H(A)	83.8
Ru(1)–P(8)–C(12)	115.64(22)	C(3)–Ru(1)–H(A)	80.6
Ru(1)–P(8)–C(15)	113.51(11)	C(3)–N(7)–H(7)	121.6
		C(6)–N(7)–H(7)	120.4

A crystallographic mirror plane contains Ru, H, Cl, C(α), N, and the other ring carbons, and the ^{i}Pr substituents on the two phosphines adopt identical (*i.e.*, mirror-related) positions. Since the five-membered ring is unlikely to be totally planar, some modest disorder of at least C4, C5, and C6 is indicated, but this minor point has no significant impact on our interpretations. The NH group was clearly resolved from the CH_2 groups in the diffraction data, showing that HN is *syn* to the hydride. While hydrogen positions from X-ray diffraction are subject to considerable systematic error, the (Ru)H···H(N) distance, 2.2 Å, is too long to suggest any attractive interaction. On the other hand, the (N)H···Cl distance between two molecules, 2.43 Å, is short enough[26] to qualify as a hydrogen bond. Particularly because of N → C3 donation, the amine hydrogen should have enhanced Brønsted acidity. This hydrogen bond is propagated throughout the crystal to form a polymeric chain (Fig. 2), which we suggest is the origin of the atypically low solubility of this molecule relative to the molecules $RuHCl[=C(R)(OR')](P^iPr_3)_2$. The hydrogen bonding forms a chain, rather than discrete dimers (**II**) because the RuCl and NH functionalities have a *trans* disposition around

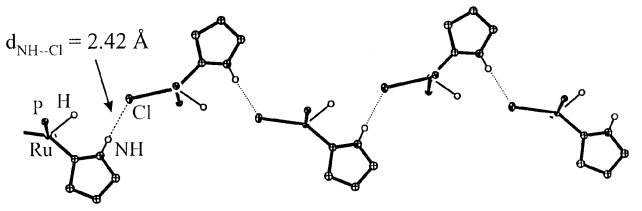
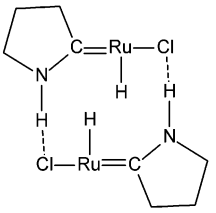


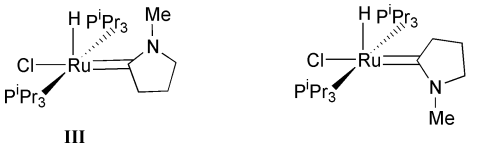
Fig. 2 Intermolecular hydrogen bonding in crystalline $RuHCl(P^iPr_3)_2(C_4NH_7)$.

the Ru=C bond; such a dimer would also suffer ^{i}Pr/^{i}Pr repulsions between the two monomer units.



II

The five-membered heterocyclic 3° amine, 1-methylpyrrolidine, is also dehydrogenated to carbene according to eqn. (5). Again, the use of sacrificial olefin to scavenge H_2 results in >80% formation of carbene, $RuHClL_2[=CN(Me)C_3H_6]$, from $[RuHClL_2]_2$ over a period of 15 h at room temperature. The NMe-substituted molecule exists in two NMR resolvable isomeric forms in a 3 : 1 ratio at ambient temperature, which we believe to result from hindered rotation about Ru=C from the presence of the *N*-methyl substituent. We have previously shown[24] the rotational barrier about Ru=C(OR)R′ to be ~10 kcal mol^{-1}, so the added bulk from an NMe substituent could easily increase this barrier to the point of slowing rotation about Ru=C on the NMR timescale at room temperature. This isomerism is evident by ^{1}H NMR in C_6D_6 in the form of two hydride signals centered at −24.1 (major) and −25.8 ppm, and two corresponding sets of signals for the NMe and outer two CH_2 units of the pyrrolidine ring (in the same ratio). The central CH_2 units of the two isomers are not well-resolved due to partial overlap with signals of the P^iPr_3 ligands. Further proof for this interpretation is seen in the $^{31}P\{^1H\}$ NMR spectrum, where two singlets at 56.8 (major) and 53.9 ppm are observed. From correlation of the hydride and phosphorus chemical shifts with those of $RuHClL_2[=CN(H)C_3H_6]$ and $RuHCl[=C(R)(OR')](P^iPr_3)_2$, where the favored orientation of the carbene places the heteroatom *syn* to Ru–H (from NOE studies), we tentatively assign the major isomer as **III**. An orientation of $Ru=C(NR_2)R'$ eclipsing the P–Ru–P vector would yield inequivalent phosphines, and is *not* observed.



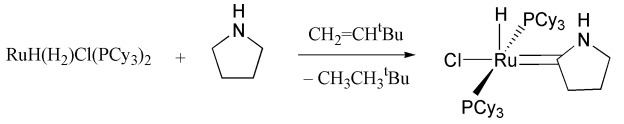
III

As with the cyclic ethers, the six-membered heterocycle, piperidine, fails to produce $RuHClL_2[=CN(H)C_4H_8]$ from $[RuHClL_2]_2$ at room or elevated temperatures.

$RuH(H_2)Cl(PCy_3)_2$ as a source of "$RuHCl(PCy_3)_2$"

The above observation that equimolar mixtures of $RuH(H_2)ClL_2$ and carbene complex (in the presence of excess ether or amine) yielded the heterocyclic carbenes quantitatively when treated with olefin led us to investigate the use of $RuH(H_2)ClL_2$ as an *in situ* source of "$RuHClL_2$". To date, a reliable preparation of $[RuHClL_2]_2$ with $L \neq P^iPr_3$ has not been found, presumably because the use of bulkier phosphines prohibits dimerization, leading to decomposition. The use of smaller phosphines frustrates the synthesis of $RuH_2Cl_2L_2$ or $RuH(H_2)ClL_2$, our precursors to $[RuHClL_2]_2$, by contamination with RuL_3 species.

Treatment of $RuH(H_2)Cl(PCy_3)_2$ (Cy = cyclohexyl) with excess pyrrolidine in the presence of $CH_2=CH^tBu$ gives carbenes $RuHCl(PCy_3)_2[=CN(H)C_3H_6]$ [eqn. (6)].



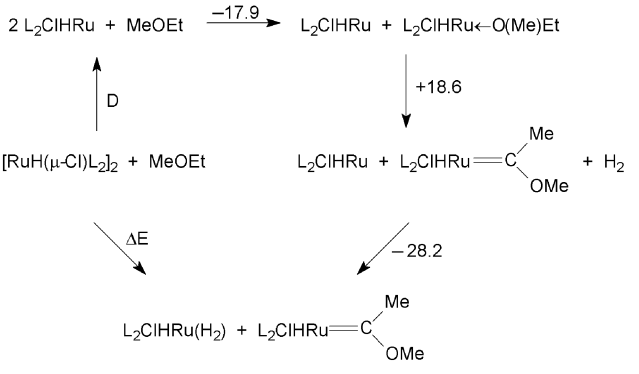
(6)

This molecule is characterized by a high-field triplet ^{1}H signal and well-resolved outer ring CH_2 protons; the central CH_2 signal is obscured by those of the PCy_3 ligands. Again, the $^{31}P\{^1H\}$ NMR shows only a singlet, indicating that the plane of the carbene is perpendicular to the P–Ru–P axis.

This *in situ* generation of "$RuHCl(PCy_3)_2$" has limitations, however, as evidenced by the failure of $RuH(H_2)Cl(PCy_3)_2$ and $CH_2=CH^tBu$ to yield $RuHClL_2[=C(X)C_2H_4(Y)]$ in the presence of excess *N*-methylpyrrolidine (X = NMe, Y = CH_2) or dioxolane (X = O, Y = O) at room or elevated temperatures (80 °C, 3 days). Instead, $RuCl(PCy_3)(\eta^4\text{-}C_6H_8PCy_2)$ is formed in nearly quantitative yield, a product resulting from metallation and dehydrogenation of one phosphine to give an allylic ligand. The identity of $RuCl(PCy_3)(\eta^4\text{-}C_6H_8PCy_2)$ was confirmed by comparison to an authentic sample obtained by independent literature synthesis.[27] The most diagnostic spectroscopic features of this molecule in C_6D_6 are an AX pattern seen by $^{31}P\{^1H\}$ NMR, the *lack* of a ^{1}H NMR high-field signal (Ru–H_n), and the presence of two allylic C–H signals in the ^{1}H NMR spectrum. Thus, effective use of $RuH(H_2)Cl(PCy_3)_2$ and $CH_2=CH^tBu$ as a source of "$RuHCl(PCy_3)_2$" requires that any "trapping" substrate must react more readily than an intramolecular phosphine C–H bond. This is clearly seen in the contrasting reactivity toward HNC_4H_8 and $MeNC_4H_8$ described above; note that the *N*-methyl substituted pyrrolidine was shown to react slower than pyrrolidine with $[RuHClL_2]_2$ in the previous section.

Computational study of dehydrogenation thermodynamics

DFT (B3PW91) calculations were carried out on a number of the fundamental steps in the ether dehydrogenation. These are summarized in Scheme 2. The overall ΔE, for two molecules forming two molecules (thus small $T\Delta S$ is expected) is [D − 27.5] kcal mol^{-1}, where D is the energy of dissociating the halide-bridged dimer $[RuH(\mu\text{-}Cl)(P^iPr_3)_2]_2$ into monomers. This dimer scission reaction energy was not calculated since the idealized phosphine model employed, PH_3, would significantly overestimate the relevant value for bulky P^iPr_3.



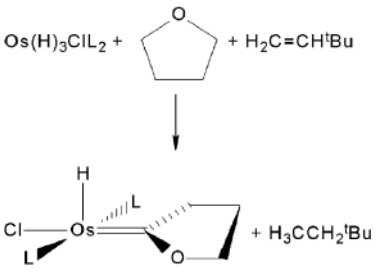
Scheme 2

This is accentuated since the phosphines are *cis* in the dimer, but *trans* in the monomer.[28] The essential point of the thermodynamic cycle in Scheme 2 is that the energy of dehydrogenation of coordinated or free ether by the "prepared" fragment $RuHCl(PH_3)_2$ to form *free* H_2 is endergonic, and it becomes even more endergonic when the dimer scission energy D is added to it. Thus, the -28.2 kcal mol^{-1} gained from binding free H_2 to the fragment $RuHCl(PH_3)_2$ is essential to the thermodynamic viability of ether dehydrogenation observed here.

Generalizing to Os

Because the dimer $[OsHCl(P^iPr_3)_2]_2$, or any simple adduct of general formula $OsHClL'(P^iPr_3)_2$, is unknown, the 14-e$^-$ transient $OsHCl(P^iPr_3)_2$ or its functional equivalent must be generated *in situ*. The available reagents[29–32] are $OsH_{4-x}Cl_x(P^iPr_3)_2$ ($x=1$ or 2), from which the desired '$OsHClL_2$' might be accessible by scavenging either H_2 ($x=1$) or HCl ($x=2$).

(a) Use of $Os(H)_3ClL_2$. Reactive removal of 2H from $Os(H)_3ClL_2$ can be accomplished with ^{t}BuHC=CH$_2$. After 4.5 h at 25 °C in C_6D_6, olefin adduct $OsHCl(H_2C{=}CH^tBu)L_2$ is produced in 50% yield, together with <10% yield each of $Os(H)_2Cl_2L_2$, OsH_5ClL_2 and free L. However, the isolated olefin complex is itself unreactive to neat THF after 5.5 h at 25 °C as is OsH_3ClL_2 in neat THF over 48 h at 25 °C. Nevertheless, a reactive transient formed from $Os(H)_3ClL_2$ and ^{t}BuHC=CH$_2$ (1 : 2 molar ratio) in neat THF gives, within 2 h at 25 °C, a 55% yield of the carbene in eqn. (7),



(7)

a 30% yield of $OsHCl(H_2C{=}CH^tBu)L_2$, and 5% yield of OsH_5ClL_2. While trapping by THF is thus not complete, it is relatively efficient; no effort was made to optimize the yield of the carbene by manipulation of the olefin : Os ratio or by dilution.

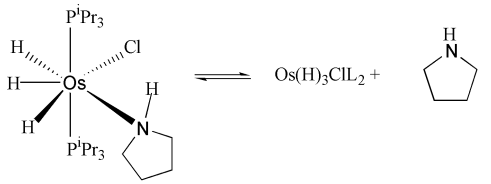
The competitive nature of this trapping is also evident by reaction of $Os(H)_3ClL_2$ with equimolar *tert*-butyl ethylene in neat Et_2O at 20 °C. After 38 h, a 5% yield of the acyclic carbene complex $OsHCl[C(Me)(OEt)]L_2$ was obtained, together with a 50% yield of $OsHCl(H_2C{=}CH^tBu)L_2$ and unreacted $Os(H)_3ClL_2$. Also detected (10% of Os-containing products) are $OsHCl(CCH_2)L_2$ and $OsHCl(CO)L_2$, the known[33] products of the secondary reaction of $OsHCl[C(Me)(OEt)]L_2$. Thus, an acyclic ether is less effectively dehydrogenated than is its cyclic analog.

Reaction of pyrrolidine with $Os(H)_3ClL_2$: mechanism of dehydrogenation

(a) Adduct formation. For reference, it was shown earlier[29] that $Os(H)_3ClL_2$ binds MeCN or NH_3 with a large K, and an "off" rate of $\sim$5 s^{-1}, while acetone, MeOH and THF are only bound weakly (K of 10^{-1} to 10^{-3}).

In benzene-d$_6$ at room temperature, $Os(H)_3Cl(P^iPr_3)_2$ reacts rapidly with excess (5 equiv) pyrrolidine to form an 18-electron adduct, which is the only species present 15 min after mixing the reagents. This adduct is characterized by its broad hydride signal at -13.49 ppm in the ^{1}H NMR spectrum and a sharp singlet in the ^{31}P $\{^1$H$\}$ NMR spectrum. Signals due to the N–H proton are not observed at 20 °C for either coordinated or free pyrrolidine, and the signals due to the methylene groups of coordinated and of free pyrrolidine are coalesced and somewhat broad at room temperature. The phosphine methyl region deceptively displays only *one* doublet of virtual triplets (apparent quartet), indicating that both phosphines are *trans* to each other, but more importantly it suggests that the methyl groups are not diastereotopic. It has been shown that the LUMO for $Os(H)_3Cl(P^iPr_3)_2$ lies between the chloride and the hydride ligands in the basal plane of the molecule.[29] Therefore, in adduct structure **IV**, the methyl groups of the phosphines should show diastereotopicity.

A process that renders both methyl groups equivalent on the NMR timescale is the dynamic equilibrium between the coordinated and free pyrrolidine [eqn. (8)].

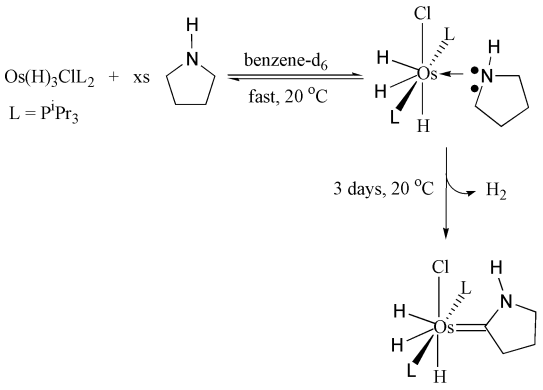


IV (8)

Such a process also explains the absence of any of the N–H signals. Interestingly, upon vacuum removal of the volatiles from a solution containing **IV** and dissolution of the resulting solid in benzene-d$_6$, the adduct **IV** persists. Nevertheless, in the absence of excess pyrrolidine in solution, a fraction of the adduct releases pyrrolidine over time and some $Os(H)_3Cl(P^iPr_3)_2$ is observed at 20 °C (^{1}H and ^{31}P NMR evidence). Further proof of an *equilibrium* process comes from low temperature NMR experiments. Upon cooling a toluene-d$_8$ solution of the adduct to -40 °C, the N–H proton due to free pyrrolidine is observed, as well as the NH signal due to coordinated pyrrolidine at 3.54 ppm. At this temperature, the phosphine methyl region displays two overlapping doublets of virtual triplets. At -70 °C the diastereotopic methyl signals of the adduct are completely decoalesced. Thus, at -40 °C the equilibrium process is frozen on the NMR timescale. This low-temperature NMR experiment is also informative as to the nature and disposition of the hydride ligands. At -20 °C the broad hydride signal at -13.49 ppm decoalesces and two signals of relative intensity 1 : 2 are observed at -12.65 and -13.71 ppm, respectively. These signals sharpen upon cooling to -70 °C. At this temperature their T_1 values are 93 and 73 ms, respectively, indicating that all three hydrogen atoms can be described as classical hydride ligands, but with ∠H–Os–H smaller than 90°. The ^{31}P $\{^1$H$\}$ NMR spectrum does not experience any change at low temperatures. This spectroscopic behavior (including *partial* hydride decoalescence) is analogous to that displayed[29] by the compound $Os(H)_3Cl(NH_3)(P^iPr_3)_2$, further supporting our assignment for structure **IV**.

(b) Dehydrogenation. Over a period of 3 days the 18-electron pyrrolidine adduct $Os(H)_3Cl[N(H)C_4H_8](P^iPr_3)_2$ releases H_2. The resulting 16-electron intermediate of formula $OsHCl[N(H)C_4H_8](P^iPr_3)_2$ cleaves both of the α-C–H bonds of the bound pyrrolidine to form the heterosubstituted carbene $Os(H)_3Cl[{=}CN(H)C_3H_6](P^iPr_3)_2$ (Scheme 3).

This double α-C–H activation occurs at room temperature and without any H_2 scavenger such as *t*-butyl ethylene and it differs from Ru in giving a saturated (OsH_3) product, not a monohydride. The resulting broad hydride signal at -10.9 (20 °C) decoalesces by -80 °C. Three new peaks appear at -8.51 ($T_1=111$ ms), -9.77 ($T_1=86$ ms) and -14.47 ($T_1=97$ ms) ppm with equal intensities. The fact that such low temperatures are required to decoalesce the three signals indicates that they are arranged in a *cis* disposition (*vide infra*), and their



Scheme 3

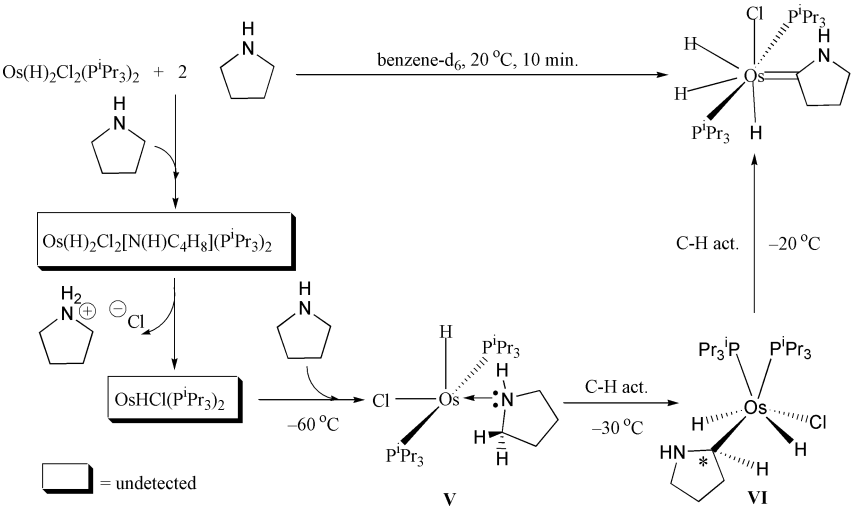
T_1 values are large enough to indicate classical hydride nature. The $^{31}P\{^1H\}$ NMR spectrum does not experience any significant change, even at −80 °C. Such information implies that the carbene substituents are oriented perpendicular to the P–Os–P vector (otherwise an AB pattern should result).

Can the H_2 loss be accelerated? Upon addition of *tert*-butyl ethylene (2 moles per mole Os) 1 h after mixing pyrrolidine with $Os(H)_3ClL_2$, at which time $Os(H)_3Cl[N(H)C_4H_8](P^iPr_3)_2$ is the major species, no side reactions are observed and the reaction proceeds cleanly to the final carbene *without* any rate acceleration. These results imply that (a) neither the adduct nor the final carbene are dehydrogenated by *tert*-butyl ethylene, presumably since they are saturated compounds and cannot bind the olefin, and (b) the adduct with pyrrolidine is much stronger than any adduct formed with *t*-butyl ethylene.

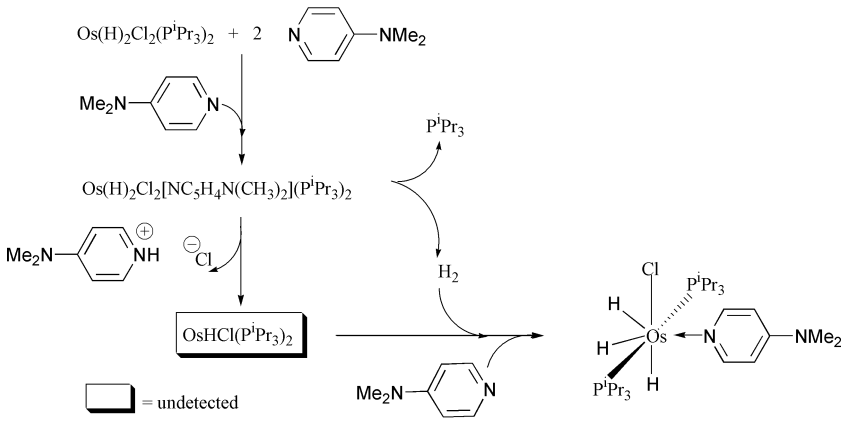
(c) Reaction of pyrrolidine with $Os(H)_2Cl_2L_2$. At this point we attempted to generate the 14-electron fragment $OsHClL_2$ by dehydrohalogenation, using the basic character of the amine reagent to scavenge HCl from $Os(H)_2Cl_2(P^iPr_3)_2$ by a fast Brønsted acid-base reaction. That fragment might then react with a second mole of amine, to form the carbene $Os(H)_3Cl[=CN(H)C_3H_6](P^iPr_3)_2$. Amine thus performs two very different roles in this attempt. Indeed (Scheme 4), the reaction (4 : 1 amine : Os) proceeds to completion in 10 min at room temperature in benzene-d_6 and the carbene is obtained, together with a white precipitate that was identified as pyrrolidinium chloride. To identify any intermediate species, the reagents were mixed at −78 °C in THF-d_8 and the reaction monitored by ^1H and $^{31}P\{^1H\}$ NMR. We observed the formation of two new species (**V** and **VI**, Scheme 4) already at −70 °C, along with unreacted $Os(H)_2Cl_2(P^iPr_3)_2$. These species display characteristic peaks in the hydride region at −9.79 (**VI**) and at −26.11 (**V**) ppm. The multiplicity of both peaks can be resolved, the former being a doublet of doublets with $J_{H-P} = 47.1$ Hz and $J_{H-P'} = 35.1$ Hz, indicating inequivalent phosphines, and the latter being a triplet with $J_{H-P} = 17.0$ Hz. Associated with these hydrides are two new peaks in the $^{31}P\{^1H\}$ NMR, a singlet at 55.0 ppm (**V**), and an AB pattern with $J_{P-P'} = 101$ Hz (**VI**). The structure of **VI** is based on that of $Os(H)_2Cl_2L_2$.[29–32] The chiral carbon (*) accounts for the inequivalence of the phosphines in **VI**, and the small $J_{PP'}$ indicates considerable bending from a strictly mutual *trans* disposition, as is true in $Os(H)_2Cl_2L_2$ itself and consistent with an Os^{IV} (d^4) intermediate. The signals in the hydride region broaden upon warming the solution, making it difficult to follow the population of these species by ^1H NMR; however, the $^{31}P\{^1H\}$ NMR signals remain visible, and can be monitored. The final carbene is initially observed at −60 °C and becomes the major product at −30 °C. Intermediate **V** disappears at −30 °C, while at this temperature, a significant amount of the species corresponding to the AB pattern (**VI**) persists in solution, and can still be observed in small amounts at room temperature, where the carbene is the major product. The AB pattern then disappears and the only product observed is the carbene. Thus, starting from $Os(H)_2Cl_2L_2$ (Scheme 4), it is possible to see each of the two C–H scission steps.

The fact that we are not able to observe an amine adduct of $Os(H)_2Cl_2(P^iPr_3)_2$ is consistent with an initial fast acid-base reaction, therefore rendering the C–H activation as the rate-determining step. It has been proposed[34] that HCl loss from $Os(H)_2Cl_2(P^iPr_3)_2$ is stimulated by adduct formation. This is different from the THF system, where $OsHCl(P^iPr_3)_2$ forms by hydrogenation of *t*-butyl ethylene by $Os(H)_3Cl(P^iPr_3)_2$, a much slower process than HCl loss; thus, the rate-determining step occurs prior to C–H bond activation.

Because piperidine, a six-membered cyclic amine, is not dehydrogenated by $[RuHClL_2]_2$, we therefore investigated its reaction with $Os(H)_2Cl_2(P^iPr_3)_2$ in benzene-d_6 at room temperature. The goal was to halt the reaction at an analog of **V** for possible isolation. However, over a period of 12 h, the reaction proceeds cleanly to the analogous carbene $Os(H)_3Cl[=CN(H)C_4H_8](P^iPr_3)_2$ with no intermediates detected and a white precipitate (piperidinium chloride) as a coproduct. In another attempt to detect a $OsHCl(amine)(P^iPr_3)_2$ species, we tested the reactivity of $Os(H)_2Cl_2(P^iPr_3)_2$ with a sterically compact tertiary amine (quinuclidine). However, when these two reagents are mixed in benzene-d_6,



Scheme 4



Scheme 5

no reaction is observed after 24 h at room temperature. The crowding observed in the structure of $Os(H)_2Cl_2(P^iPr_3)_2$ (∠P–Os–P = 112°),[29–32,35] added to the steric impact of the tertiary amine, apparently makes the quinuclidine adduct thermodynamically unviable. We tested this point by reacting $Os(H)_2Cl_2(P^iPr_3)_2$ with 4-dimethylaminopyridine in benzene-d_6 at room temperature (Scheme 5). This amine is a stronger base than a secondary alkyl amine and with no possibility of further α-C–H double activation. In this case, a fast reaction occurs to form the initial 18-electron adduct, $Os(H)_2Cl_2[NC_5H_4N(CH_3)_2](P^iPr_3)_2$, which is the only product present in the reaction after 15 min. This adduct displays a triplet hydride signal at −6.68 ppm with a $J_{H-P} = 10$ Hz, new signals due to bound base (through the pyridine nitrogen) and a singlet in the $^{31}P\{^1H\}$ NMR spectrum.

This adduct is metastable and, over a period of 17 h, signs of unselective reactivity are observed, giving several products. The main product is identified as $Os(H)_3Cl[NC_5H_4N(CH_3)_2](P^iPr_3)_2$ by comparison with an authentic sample.[33] The other main product is free phosphine, which confirms that the initial adduct is crowded and releases a phosphine to reduce steric interactions. The fate of the lost chloride is the amine hydrochloride, seen as a colorless precipitate.

Competition experiment

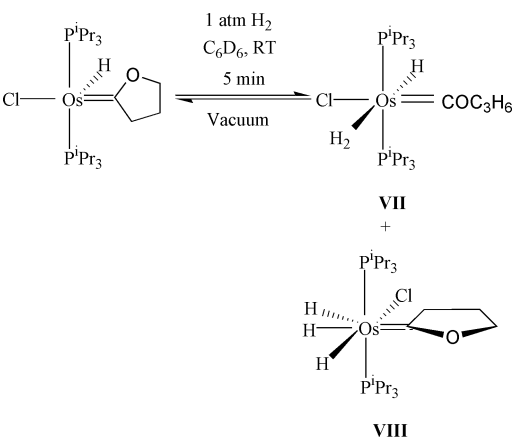
A competition experiment between THF and pyrrolidine could prove that the binding capacity of the substrate to OsH_3ClL_2 is the determining factor that allows for a fast or slow C–H activation. Therefore, the compound $Os(H)_2Cl_2(P^iPr_3)_2$ was dissolved in THF and equimolar pyrrolidine (1 : 1 Os : pyrrolidine, dissolved in THF) was added dropwise to the solution. The only carbene obtained is the pyrrolidine-derived $OsH_3Cl[=CN(H)C_3H_6](P^iPr_3)_2$, along with unreacted $Os(H)_2Cl_2(P^iPr_3)_2$. None of the THF-derived carbene $OsHCl(=COC_3H_6)(P^iPr_3)_2$ was detected. This is a surprising result if we take into account that at any given time there is an overwhelming excess of THF surrounding the 14-electron transient $OsHCl(P^iPr_3)_2$, but instead the transient reacts with the added pyrrolidine. Thus, it is clear that the binding capacity of the substrate (pyrrolidine *vs.* THF) is a determining factor in the C–H activation process.

Thermodynamics of binding H_2 (2H)

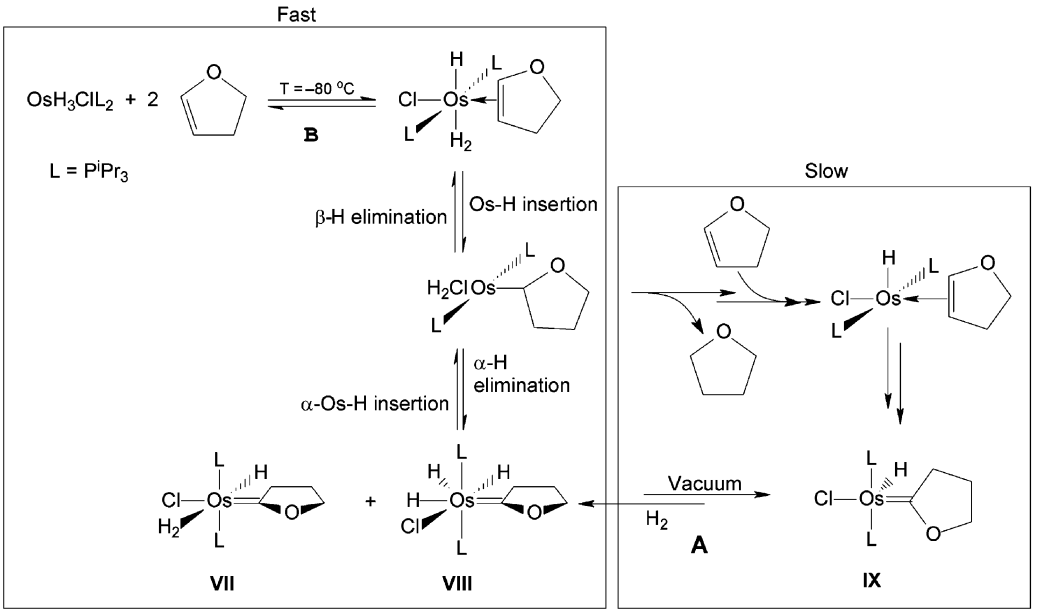
It is noteworthy that the final carbene products of general formula $MH_xCl(=CEC_3H_6)(P^iPr_3)_2$ (M = Ru, Os; E = O, NH) differ in the number of hydride ligands present in the molecule when changing from E = O ($x = 1$) to E = NH ($x = 3$) in the case of M = Os. Why? To answer this question, we tested whether $OsHCl[=C(O)C_3H_6](P^iPr_3)_2$ will bind H_2 and, if so, what is the structure of the adduct?

(a) Reaction of $OsHCl[=C(O)C_3H_6]L_2$ with H_2. Two products formed. Scheme 6 shows that two *isomeric* products are observed. The ^1H NMR spectrum (in C_6D_6) of the *trans*-hydride/dihydrogen isomer **VII** displays characteristic broad signals at −2.16 and −8.31 ppm with intensity 2 : 1, whereas the *cis*-trihydride **VIII** displays a broad peak at −9.98 ppm. The relative population of these species (95 : 5) at 20 °C indicates a thermodynamic preference for the *trans*-hydride/dihydrogen redox isomer. The $^{31}P\{^1H\}$ NMR spectrum also displays two broad peaks for these species centered at 33.5 and 30.9 ppm, indicative of an equilibrium relating both isomers. One hour after mixing the reagents (under H_2 atm), some 2,3-dihydrofuran is observed; no THF is observed. Vacuum removal of the volatiles effects loss of H_2 by these species and the monohydride cyclic carbene is regenerated, along with some $Os(H)_3Cl(P^iPr_3)_2$. Notably, the two 18-e$^-$ cyclic carbene products have been detected to be intermediates in our previously reported[33] synthesis of $OsHCl[=C(O)C_3H_6](P^iPr_3)_2$ from $Os(H)_3Cl(P^iPr_3)_2$ and 2,3-dihydrofuran in benzene-d_6. Thus, the appearance of 2,3-dihydrofuran and $Os(H)_3Cl(P^iPr_3)_2$ upon hydrogenation of $OsHCl[=C(O)C_3H_6](P^iPr_3)_2$ indicates that all the steps involved in the synthesis of $OsHCl[=C(O)C_3H_6](P^iPr_3)_2$ are reversible (Scheme 7).

It is possible to further verify this reaction scheme by entering from a different direction (*i.e.*, Scheme 7, at **B**, not **A**) and working under conditions of kinetic control. Combining $OsH_3Cl(P^iPr_3)_2$ with 2,3-dihydrofuran (1 : 2 molar ratio) in toluene-d_8 at −80 °C shows essentially complete consumption of $OsH_3Cl(P^iPr_3)_2$ to form ∼20% of the olefin adduct $OsHCl(H_2)(\eta^2\text{-}2,3\text{-dihydrofuran})(P^iPr_3)_2$, identified by comparison of its ^1H and ^{31}P NMR parameters to those of the $\eta^2\text{-}H_2C{=}CH(OPh)$ analog. The hydride region of the spectrum



Scheme 6

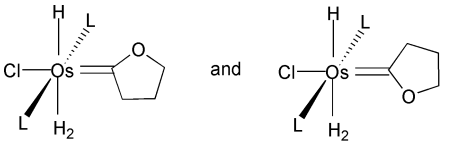


Scheme 7

at −80 °C shows two signals, in a 1 : 2 intensity ratio, each a triplet; the decoalescence of the signal of intensity 2 from the single hydride at −80 °C suggests the H and the H_2 are mutually *trans*, and thus have a higher barrier to site exchange than when all three are *cis*.

The major (~70%) product at −80 °C is the *carbene* complex **VII**; its dominance already at −80 °C indicates a very low activation energy for this hydrogen migration isomerization from coordinated olefin to coordinated carbene. Also detected are low (<5%) levels of the isomeric carbene complex **VIII**, and the dehydrogenated carbene **IX**. Already at −70 °C, this reaction mixture has evolved so that >90% of the osmium is in complex **VII**; the η^2-olefin complex has been consumed, but the *trans*-H/H_2 carbene has not transformed further into the *cis*-$(H)_3$ carbene.

(b) Dihydride *vs.* dihydrogen: influence of metal stereochemistry. We studied a THF-d_8 solution containing both 18-electron "OsH_3" carbene compounds at low temperature by ^1H NMR and $^{31}P\{^1H\}$ NMR and measured their T_1 values in the absence of added H_2. Upon cooling, the minor (at 20 °C) species *cis*-trihydride (**VIII**) decreases in population, showing that the *trans*-hydride/hydrogen species (**VII**) is thermodynamically favored. At −10 °C the hydride signal due to the isomer **VIII** resolves into a triplet with $J_{H-P} = 15$ Hz. At this temperature, the hydride signal at −8.9 ppm ($T_1 = 697$ ms), corresponding to the single hydride in structure **VII**, is resolved into a triplet with $J_{H-P} = 21$ Hz, whereas the signal due to the dihydrogen still appears as a broad singlet ($T_1 = 18.5$ ms). At −70 °C, the dihydrogen signal begins to decoalesce and the single hydride signal broadens. At this temperature, two decoalesced signals in a 1 : 1 intensity ratio at 31.6 and 34.2 ppm are observed for species **VII** in the $^{31}P\{^1H\}$ NMR spectrum, in addition to a trace of **VIII**. At −100 °C the signal due to the dihydrogen ligand has decoalesced into two signals of equal intensity at −1.97 ($T_1 = 7.9$ ms) and −2.58 ($T_1 = 8.6$ ms) ppm, whereas the signal due to the single hydride consists of *two overlapping triplets* at −8.29 ($T_1 = 243$ ms) and −8.47 ($T_1 = 243$ ms) ppm. The $^{31}P\{^1H\}$ NMR spectrum displays two sharp singlets at this temperature. The measured T_1 values for the decoalesced signals around −2 ppm establish their dihydrogen nature, indicating that each of these decoalesced species still possesses a *trans*-hydride/dihydrogen conformation. We propose these observations result from slow rotation around the Os=C bond. The singlet character of the two $^{31}P\{^1H\}$ NMR signals indicate that the rotamers have their carbene planes aligned perpendicular to the P–Os–P vector (**VIIa** and **VIIb**).



VIIa **VIIb**

(c) Origin of different isomer structures for E = O *vs.* NH: *N*-methylpyrrolidine as substrate. When comparing the structures displayed by the compounds of general formula $OsH_3Cl[=C(E)C_nH_{2n}](P^iPr_3)_2$ (E = O, NH; $n = 3, 4$), we observe that a *trans*-hydride/dihydrogen redox isomer, which allows for a push-pull interaction between the mutually *trans* chloride and carbene ligands, is absent for E = NH and is thermodynamically preferred with the heteroatom E = O, a weaker π-donor than NH. On the other hand, the *cis*-trihydride isomer observed for E = NH (Scheme 4) might be dictated by a wholly different factor: an intramolecular hydrogen bond between the chloride and the NH proton, a possibility absent when E = O. In an attempt to determine which effect is dominant, we investigated the reactivity of $Os(H)_2Cl_2(P^iPr_3)_2$ and $Os(H)_3Cl(P^iPr_3)_2$ with an excess of a tertiary cyclic amine, *N*-methylpyrrolidine, where hydrogen bonding is precluded. The reaction of this amine with $Os(H)_2Cl_2(P^iPr_3)_2$ was carried out in 5 : 1 mole ratio in benzene-d_6 at room temperature. The reaction is slower than the reaction with pyrrolidine and after 36 h gives several *N*-methylpyrrolidine containing products, one of which can be identified as the corresponding carbene $Os(H)_3Cl\{=C[N(Me)]C_3H_6\}(P^iPr_3)_2$. The carbene displays a broad peak in the ^1H NMR spectrum near −11 ppm, indicative of a *cis*-trihydride conformation. Only the signals due to the two methylene groups adjacent to the carbene carbon and to the nitrogen atom can be identified since the signal due to the central methylene is obscured by the ^{i}Pr groups. The methyl group on nitrogen resonates as a sharp singlet at 3.03 ppm. The $^{31}P\{^1H\}$ NMR spectrum of this compound shows a sharp singlet, indicating that the carbene substituents are

perpendicular to the P–Os–P vector, analogous to the pyrrolidine carbene $Os(H)_3Cl[=C(NH)C_3H_6](P^iPr_3)_2$ (*vide supra*). The same product is obtained when the reagent employed is $Os(H)_3Cl(P^iPr_3)_2$. In this case, the formation of the N-adduct $Os(H)_3Cl[N(Me)C_4H_8](P^iPr_3)_2$ is fast, characterized by a broad peak in the ^1H NMR spectrum at −19.22 ppm and a broad peak in the $^{31}P\{^1H\}$ NMR spectrum at 52.4 ppm, both slightly different from those of the starting material. The signals due to free *N*-methylpyrrolidine are somewhat broad, again showing that the adduct is weak and in equilibrium with the free amine. The subsequent reaction, formation of the carbene, is very slow and proceeds only 10% toward completion after 44 h at room temperature. Upon heating for 5 h at 60 °C, the peaks corresponding to the carbene species *decrease* in intensity whereas the peaks corresponding to the adduct increase in intensity and move closer to the chemical shift of $Os(H)_3Cl(P^iPr_3)_2$, indicating the existing equilibrium between the carbene species $Os(H)_3Cl\{=C[N(Me)]C_3H_6\}(P^iPr_3)_2$, the adduct $Os(H)_3Cl[N(Me)C_4H_8](P^iPr_3)_2$, and $Os(H)_3Cl(P^iPr_3)_2$ plus *free* amine.

In summary, in answering the question of isomer preference, the carbene $Os(H)_3Cl\{=C[N(Me)]C_3H_6\}(P^iPr_3)_2$ displays a *cis*-trihydride conformation, even though there is no possible hydrogen bond stabilizing it. Therefore, we conclude that the π-donor ability of the α-heteroatom is the isomer-determining characteristic. The greater the heteroatom π-donation to the empty p orbital of the carbene carbon, the less stabilizing a Cl → Os push-pull interaction will be, hence the chloride is less "required" as a π-donor in the position *trans* to the carbene.

Discussion

By systematic study of the cyclic amine and ether substrates, this work has made it possible to directly observe the crucial event(s) in the more widely observed ether dehydrogenations: C–H bond cleavage. Specifically, we have observed: (a) pre-equilibrium formation of an adduct of the unsaturated metal reagent with the N lone pair; (b) one product of the initial C_α–H oxidative addition, to give an α-aminoalkyl ligand; and (c) α-H migration from this ligand to form the carbene complex, the final product of geminal dehydrogenation.

The theme of the subsequent steps, which are detectable equilibria, involves the fate of the two removed hydrogens. This is primarily under the influence of the metal, with Ru not strongly retaining these H on the carbene complex, but surrendering them to another molecule of reagent $RuHClL_2$, and subsequently to hydrogenate $H_2C{=}CH^tBu$; the more reducing Os retains the removed H as hydride ligands, an oxidative event that consequently diminishes back-donation to the carbene carbon.

We attribute the necessity for a scavenger in dehydrogenation of THF by $OsH_3Cl(P^iPr_3)_2$ to the fact that the two reagents [$Os(H)_3Cl(P^iPr_3)_2$ and THF] do not form a strong adduct.[29] Indeed, such an adduct is only detectable at low temperatures, where α-C–H bond activation was not observed. In contrast, all adducts formed with N-based ligands (NH_3, MeCN) are stronger, therefore more abundant at room temperature. We believe this capacity to form a strong adduct is necessary for the C–H activation process.

Analogous to our earlier report,[36] the ability to bind H_2 and the ability to reduce it to two separate hydride ligands, are both diagnostic of the π-basicity of an ML_n fragment. In another example,[29] addition to $Os(H)_3ClL_2$ of PEt_3 gives the trihydride $Os(H)_3Cl(PEt_3)L_2$, which does not lose H_2, while addition of CO gives $OsHCl(H_2)(CO)L_2$, which readily loses H_2. Thus, in $OsH_3ClL'L_2$, if L′ is electron-withdrawing (the π-acid CO), the metal is inadequately electron-rich to keep "$2H^-$" from being oxidized to H_2, and back-donation to that H_2 is insufficient to keep it from being lost to bulk solution. A less electron-withdrawing L′ (*e.g.*, PEt_3) leaves the metal sufficiently reducing (π-donating) to keep "$2H^-$" and Os(IV).

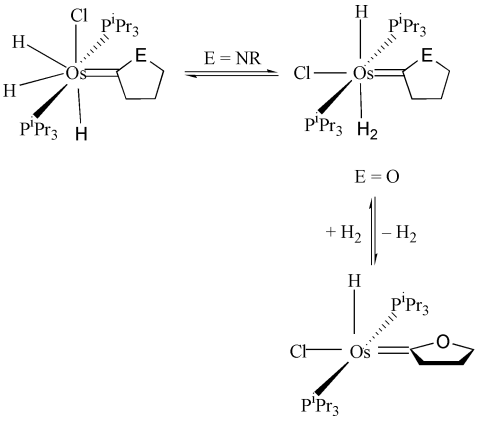
This work has also shown the application of $C(sp^3)$–H activation to produce N-heterocyclic carbenes in high yields and in one pot. Previous syntheses of N-substituted carbenes involved first multi-step routes to O-substituted carbenes, followed by amination with HNR_2 and loss of water or alcohol.[37]

In the present heteroatom-substituted carbene examples, the lower electronegativity of NR (R = H or Me) than O means that the NR carbenes are less π-electrophilic (π-acidic) towards Os. Since the NR carbenes are thus weaker π-acids, Os is more electron-rich in their carbenes; these thus resist loss of H_2 and they moreover exist wholly as tri*hydrides*. The O carbenes, because they drain more π-electron density from Os, lead to near thermoneutrality of the $Os^{IV}(H)_3$ and $Os^{II}H(H_2)$ redox isomeric forms, and moreover bind H_2 weakly, so that entropy leads to loss of H_2 [eqn. (9)].

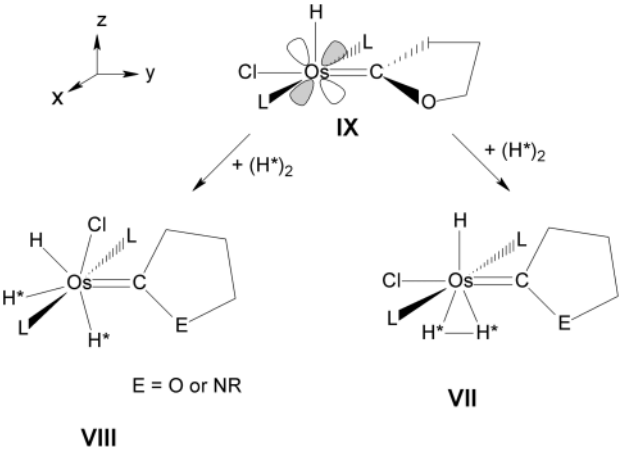
$$OsHCl(H_2)(=COC_3H_6)L_2 \rightleftharpoons OsHCl(=COC_3H_6)L_2 + H_2 \quad (9)$$

Orientation of the carbene plane

The orientation of the carbene substituents (*i.e.*, "the carbene plane") is variable in the compounds reported here. In the *mono*hydride $Os(H)Cl[=C(O)C_3H_6](P^iPr_3)_2$, the substituents on the carbene carbon are aligned parallel to the P–Os–P vector, whereas for the *tri*hydride $Os(H)_3Cl[=C(NH)C_3H_6](P^iPr_3)_2$, the carbene substituents are perpendicular to the P–Os–P vector (Scheme 8). If we take structure **IX** (Scheme 9) as indicating that the d orbital drawn (d_{yz}) is the more potent d_π



Scheme 8



Scheme 9

donor orbital to the more π-acidic oxygen carbene, then the carbene must rotate on *oxidative addition* of $(H^*)_2$ since the two OsH* bonds are formed by the electron density of that d_{yz} orbital. Even the binding of intact $(H^*)_2$ in the more stable redox isomer (**VII**) should cause rotation of the carbene plane to avoid competition of the $(H^*)_2$ and carbene back-bonding orbitals for the same (d_{yz}) orbital. Finally, the different conformation for RuHCl(carbene)L_2 (*i.e.*, equivalent L) than for its Os analogs is attributed to the weaker π-basicity of Ru (*vs.* Os), enabling steric repulsion by the bulky phosphines to dictate the carbene plane conformation for Ru.

Experimental

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, P_2O_5, or CaH_2, degassed prior to use, and stored over 4 Å molecular sieves in air-tight vessels. All reagents were used as received from commercial vendors after drying and degassing when necessary. *In situ* NMR identification of RuHCl(CO)-$(P^iPr_3)_2$,[38,39] and $RuH(H_2)Cl(P^iPr_3)_2$,[22,23] was made by comparison to literature data and/or authentic samples. $[RuHCl(P^iPr_3)_2]$ and $RuH(H_2)Cl(PCy_3)_2$ were prepared as described.[24] ^{1}H NMR chemical shifts are reported in ppm relative to protio impurities in the deutero solvents. ^{31}P NMR spectra are referenced to an external standard of 85% H_3PO_4 (0 ppm). NMR spectra were recorded with either a Varian Gemini 2000 (300 MHz ^{1}H; 121 MHz ^{31}P; 75 MHz ^{13}C), a Varian Unity Inova instrument (400 MHz ^{1}H; 162 MHz ^{31}P; 101 MHz ^{13}C), or a Varian VXR instrument (400 MHz ^{1}H; 101 MHz ^{13}C). The following abbreviations are used: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets, q = quartet, vt = virtual triplet, dvt = doublet of virtual triplets, m = multiplet, br = broad, ap = apparent. Infrared spectra were recorded using a Nicolet 510P FT-IR spectrometer.

Syntheses and reactions

$RuHCl(P^iPr_3)_2(=COC_3H_6)$. *Method 1.* 2,3-Dihydrofuran (1.00 mL, 13.2 mmol) was added *via* syringe at room temperature to a stirred solution of 200 mg (0.218 mmol) of $[RuHCl(P^iPr_3)_2]_2$ in 20 mL of toluene. The mixture was allowed to react overnight before removal of the volatiles *in vacuo*. The oily red residue was found to be of >95% purity by ^{1}H and ^{31}P NMR and can be harvested in quantitative yield and used without further purification if desired. Analytically pure material can be obtained by washing the residue with 10 mL of pre-cooled pentane (−78 °C) and drying the resulting orange powder *in vacuo*. Isolated yield (washed): 185 mg (80%).

Method 2. $[RuHCl(P^iPr_3)_2]_2$ (15.0 mg, 0.016 mmol) was dissolved in 0.5 mL of THF and added to an NMR tube equipped with a Teflon closure. The sample was heated for 3 h at 80 °C and the volatiles were removed *in vacuo*. ^{1}H and ^{31}P NMR measurements taken upon re-dissolving the residue in C_6D_6 showed complete consumption of starting material and >90% conversion to equimolar $RuHCl(P^iPr_3)_2(=COC_3H_6)$ and $RuH(H_2)Cl(P^iPr_3)_2$.[1]H and ^{31}P{^{1}H} NMR data has been reported previously.[24]

Thermolysis of $RuHCl(P^iPr_3)_2(=COC_3H_6)$ in C_6D_6. $RuHCl(P^iPr_3)_2(=COC_3H_6)$ (10.0 mg, 0.019 mmol) was dissolved in 0.5 mL of C_6D_6 and added to an NMR tube equipped with a Teflon closure. Hexamethyldisiloxane (1.0 μL) was added as an internal standard and the tube was sealed. The sample was heated at 80 °C and monitored periodically by ^{1}H and ^{31}P NMR as the sample decomposed to $RuHCl(CO)(P^iPr_3)_2$. The approximate $t_{1/2}$ for this decomposition was found to be 20 h.

$RuHCl(P^iPr_3)_2[=C(OCH_2)_2]$. 3,3-Dimethyl-1-butene (17.5 μL, 0.135 mmol) and 25 mg (0.027 mmol) of $[RuHCl(P^iPr_3)_2]_2$were combined in 0.5 mL dioxolane in an NMR tube equipped with a Teflon closure. After tumbling for 2 h at room temperature all material from the initially heterogeneous mixture was dissolved, and assay of the solution by ^{31}P NMR showed complete conversion to a single product. The volatiles were removed *in vacuo* and the red–orange residue was re-dissolved in C_6D_6.[1]H,^{31}P and ^{13}C NMR spectra show quantitative conversion to the title compound.[1]H NMR (300 MHz, C_6D_6, 20 °C): δ −27.9 (t,$^2J_{P-H}$ = 20 Hz, 1H, Ru*H*), 1.31 [dvt, $J_{P-H} = {}^3J_{H-H} = 7$ Hz, 18H, $P(CH\mathit{Me}_2)_3$], 1.33 [dvt, $J_{P-H} = {}^3J_{H-H} = 7$ Hz, 18H, $P(CH\mathit{Me}_2)_3$], 2.51 [m, 6H, $P(C\mathit{H}Me_2)_3$], 3.32 [s, 4H, $Ru{=}C(OC\mathit{H}_2)_2$].^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 20 °C): δ 57.7 (s).^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 °C): δ 20.4 [s, $P(CH\mathit{Me}_2)_3$], 20.8 [s, $P(CH\mathit{Me}_2)_3$], 25.7 [vt, J_{P-C} = 11 Hz, $P(\mathit{C}HMe_2)_3$], 66.3 [s, $Ru{=}C(O\mathit{C}H_2)_2$], 237.2 [t,$^2J_{P-C}$ = 13 Hz, $Ru = \mathit{C}(OCH_2)_2$].

$Ru_2H_3Cl_2(P^iPr_3)_2[\eta^2\text{-}P(^iPr)_2C(H)MeCH_2]$. $[RuHCl(P^iPr_3)_2]_2$ (150 mg, 0.164 mmol) was dissolved in 15 mL of cyclohexane and heated at 80 °C for 12 h. The volatiles were removed *in vacuo*, and a portion of the oily orange–brown residue dissolved in C_6D_{12} showed quantitative conversion to the title compound and equimolar free P^iPr_3 by ^{1}H,^{31}P, and ^{13}C NMR. The liberated phosphine can be removed by prolonged drying *in vacuo* at 50 °C, or by chromatography through a short column of dry (250 °C, 0.003 torr, 48 h) Al_2O_3 (neutral, activity I, 60–325 mesh) with hexane–EtOAc, to yield a pasty orange–brown solid.[1]H NMR (400 MHz, C_6D_{12}, 20 °C): δ −18.21 (d, J_{P-H} = 36 Hz, 1H, Ru*H*, T_1 = 170 ms), −12.57 [s, 2H, $Ru(\mathit{H})_2$, T_1 = 145 ms], 1.21, 1.28, 1.33, 1.39 [m, 48H total, all $P(CH\mathit{Me}_2)_n$], 1.59 [AB pattern, J_{H-H} = 6 Hz, 2H, $RuC\mathit{H}_2CH(Me)P^iPr_2$], 1.63 [d, J_{Pa-H} = 6 Hz, 3H, $RuCH_2CH(\mathit{Me})P^iPr_2$], 1.66 (m, 1H $PC\mathit{H}Me_2$), 2.23 [m, 3H, $P(C\mathit{H}Me_2)_3$], 2.28 [m, 3H, $P(C\mathit{H}Me_2)_3$], 2.55 (m, 1H, $PC\mathit{H}Me_2$), 3.00 [d, J_{Pa-H} = 10 Hz, 1H, $RuCH_2C\mathit{H}(Me)P^iPr_2$]. ^{31}P{^{1}H} NMR (162 MHz, C_6D_{12}, 20 °C): δ −7.2 (dd, J_{Pa-Pc} = 111 Hz, J_{Pa-Pb} = 177 Hz, 1P, RuP_a), 61.3 (dd, J_{Pb-Pa} = 177 Hz, J_{Pb-Pc} = 14 Hz, 1P, RuP_b), 91.7 (dd, J_{Pc-Pa} = 111 Hz, J_{Pc-Pb} = 14 Hz, 1P, RuP_c). ^{13}C{^{1}H} NMR (101 MHz, C_6D_{12}, 20 °C): δ 18.3 (s, $PCH\mathit{Me}_2$), 19.4 [s, $P(CH\mathit{Me}_2)_3$], 20.1 (s, $PCH\mathit{Me}_2$), 20.2 [(s, $P(CH\mathit{Me}_2)_3$], 20.5 [s, $P(CH\mathit{Me}_2)_3$], 20.6 [s, $P(CH\mathit{Me}_2)_3$], 20.7 (s, $PCH\mathit{Me}_2$), 22.5 (s, $PCH\mathit{Me}_2$), 23.8 (d, J_{Pa-C} = 31 Hz, $P\mathit{C}HMe_2$), ~26 (obscured by solvent, expected d, $P\mathit{C}HMe_2$), 26.9 [d, $J_{Pb/c-C}$ = 24 Hz, $P(\mathit{C}HMe_2)_3$], 28.6 [d, $J_{Pb/c-C}$ = 24 Hz, $P(\mathit{C}HMe_2)_3$], 39.2 [d, J_{Pa-C} = 24 Hz, $RuCH_2CH(\mathit{Me})P^iPr_2$], 40.8 [d of ap t, J_{Pa-C} = 16 Hz, $J_{Pb/c-C}$ = 2 Hz, $RuCH_2\mathit{C}H(Me)P^iPr_2$], 46.8 [ap t, $J_{Pb/c-C}$ = 4 Hz, $RuCH_2CH(Me)P^iPr_2$].

Thermolysis of $[RuHCl(P^iPr_3)_2]_2$in C_6H_6. $[RuHCl(P^iPr_3)_2]_2$ (15.0 mg, 0.016 mmol) was dissolved in 0.5 mL of benzene and added to an NMR tube equipped with a Teflon closure. The sample was heated for 9 h at 80 °C and the volatiles were removed *in vacuo*. ^{1}H and ^{31}P NMR measurements taken upon re-dissolving the residue in C_6D_6 showed complete consumption of starting material and 63% molar conversion of ruthenium to $Ru_2H_3Cl_2L_2(\eta^2\text{-L})$ and 31% production of $(\eta^6\text{-}C_6H_6)RuHCl(P^iPr_3)$. An appropriate quantity of free P^iPr_3 was also observed. Selected NMR data for $(\eta^6\text{-}C_6H_6)RuHCl(P^iPr_3)$: ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ −7.15 (d,$^2J_{P-H}$ = 50 Hz, 1H, Ru*H*), 4.91 (s, 6H, C_6H_6).^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 72.3 (s).

Thermolysis of $[RuHCl(P^iPr_3)_2]_2$ in 1,4-dioxane. $[RuHCl(P^iPr_3)_2]_2$ (15.0 mg, 0.016 mmol) was dissolved in 0.5 mL of

1,4-dioxane and added to an NMR tube equipped with a Teflon closure. The sample was heated for 9 h at 80 °C and the volatiles were removed *in vacuo*. ^{1}H and ^{31}P NMR measurements taken upon re-dissolving the residue in C_6D_6 showed complete consumption of starting material and 69% molar conversion of ruthenium to $Ru_2H_3Cl_2L_2(\eta^2$-L) and equimolar free P^iPr_3, 24% to $RuH(H_2)Cl(P^iPr_3)_2$, and 8% conversion to $RuHCl(CO)(P^iPr_3)_2$.

Thermolysis of $[RuHCl(P^iPr_3)_2]_2$ and excess 1,3,5-trioxane. $[RuHCl(P^iPr_3)_2]_2$ (15.0 mg, 0.016 mmol) and 10.0 mg (0.111 mmol) of 1,3,5-trioxane were dissolved in 0.5 mL of benzene and added to an NMR tube equipped with a Teflon closure. The sample was heated for 15 h at 80 °C and the volatiles were removed *in vacuo*.^{1}H and ^{31}P NMR measurements taken upon re-dissolving the residue in C_6D_6 showed full consumption of starting material and 29% molar conversion of ruthenium to $(\eta^6$-$C_6H_6)RuHCl(P^iPr_3)$, 57% to $Ru_2H_3Cl_2L_2(\eta^2$-L), 7% to $RuH(H_2)Cl(P^iPr_3)_2$, and 7% conversion to $RuHCl(CO)(P^iPr_3)_2$. An appropriate quantity of free P^iPr_3 was also observed.

Thermolysis of $[RuHCl(P^iPr_3)_2]_2$ in MeO^{t}Bu. $[RuHCl(P^iPr_3)_2]_2$ (15.0 mg, 0.016 mmol) was dissolved in 0.5 mL of methyl *tert*-buyl ether and added to an NMR tube equipped with a Teflon closure. The sample was heated for 9 h at 80 °C and the volatiles were removed *in vacuo*. ^{1}H and ^{31}P NMR measurements taken upon re-dissolving the residue in C_6D_6 showed full consumption of starting material and 85% molar conversion of ruthenium to $Ru_2H_3Cl_2L_2(\eta$-L) and equimolar free P^iPr_3, 8% to $RuH(H_2)Cl(P^iPr_3)_2$, and 7% conversition to $RuHCl(CO)(P^iPr_3)_2$.

$RuHCl(P^iPr_3)_2$[=CN(H)C_3H_6]. Pyrrolidine (182.3 μL, 2.18 mmol) and 281.4 μL (2.18 mmol) 3,3-dimethyl-1-butene were added *via* syringe to a stirred solution of 200 mg (0.218 mmol) $[RuHCl(P^iPr_3)_2]_2$ in 20 mL of toluene at room temperature. The mixture was allowed to react for 2 h with precipitation of a red solid before removal of the volatiles *in vacuo*. The solid was washed with pentane (2 × 15 mL) and the resulting red-orange powder was dried *in vacuo*. Yield: 125 mg (54%). The reaction yield is quantitative by ^{31}P NMR when monitored *in situ*. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ −21.8 (t, $^2J_{P-H}$ = 21 Hz, 1H, Ru*H*), 1.20 [dvt, $J_{P-H} = {}^3J_{H-H} = 7$ Hz, 18H, P(CH*Me*$_2$)$_3$], 1.24 [dvt, $J_{P-H} = {}^3J_{H-H} = 7$ Hz, 18H, P(CH*Me*$_2$)$_3$], 1.77 [ap. quintet, $^3J_{H-H}$ = 8 Hz, 2H, Ru=CN(H)C_3H_6], 2.37 [m, 6H, P(C*H*Me$_2$)$_3$], 2.98 [t, $^3J_{H-H}$ = 8 Hz, 2H, Ru=CN(H)C_3H_6], 3.27 [t, $^3J_{H-H}$ = 7 Hz, 2H, Ru=CN(H)C_3H_6], 8.00 [s, 1H, Ru=CN(*H*)C_3H_6]. ^{31}P{^{1}H} NMR (121 MHz, THF-d_8, 20 °C): δ 59.8 (s). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8, 20 °C): δ 20.4 (s, P[CH*Me*$_2$)$_3$], 20.7 [s, P(CH*Me*$_2$)$_3$], 23.2 [s, Ru=CN(H)*C*$_3$H$_6$], 26.2 [vt, J_{P-C} = 9 Hz, P(*C*HMe$_2$)$_3$], 49.5 [s, Ru=CN(H)*C*$_3$H$_6$], 51.5 [s, Ru=CN(H)-*C*$_3$H$_6$], 256.3 [t, $^2J_{P-C}$ = 10 Hz, Ru=*C*N(H)C$_3$H$_6$].

$RuHCl(P^iPr_3)_2$[=CN(Me)C_3H_6]. $[RuHCl(P^iPr_3)_2]_2$ (20.0 mg, 0.022 mmol) 22.7 μL (0.218 mmol) of 1-methyl pyrrolidine, and 28.1 μL (0.218 mmol) of *tert*-butylethylene were dissolved in 0.5 mL of benzene and added to an NMR tube equipped with a Teflon closure. After 15 h, the volatiles were removed *in vacuo* and the sample was redissolved in C_6D_6. ^{1}H and ^{31}P NMR showed >80% conversion to the title compound as a (3 : 1) mixture of isomers that differ 180° in orientation about Ru=C. Selected NMR data follows. *Major isomer*: ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ −24.13 (t, $^2J_{P-H}$ = 22 Hz, 1H, Ru*H*), 2.79 [t, $^3J_{H-H}$ = 8 Hz, 2H, Ru=CN(Me)C_3H_6], 2.88 [s, 3H, Ru=CN(*Me*)C_3H_6], 3.43 [t, $^3J_{H-H}$ = 6 Hz, 2H, Ru=CN-(Me)C_3H_6]. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 56.8 (s). *Minor isomer*: ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ −25.48 (t, $^2J_{P-H}$ = 21 Hz, 1H, Ru*H*), 2.28 [t, $^3J_{H-H}$ = 8 Hz, 2H, Ru=CN(Me)C_3H_6], 2.60 [s, 3H, Ru=CN(*Me*)C_3H_6], 2.72 (t, $^3J_{H-H}$ = 6 Hz, 2H, Ru=CN(Me)C_3H_6]. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 53.9 (s).

$RuHCl(PCy_3)_2$[=CN(H)C_3H_6]. Under argon, 15.0 mg (0.021 mmol) of $RuH(H_2)Cl(PCy_3)_2$ and 41.7 μL (0.535 mmol) of pyrrolidine were dissolved in 0.5 mL of C_6H_6 and added to an NMR tube equipped with a Teflon seal. *tert*-Butylethylene (5.5 μL, 0.021 mmol) was added *via* syringe and the tube was sealed. After 90 min of agitation at 25 °C, the volatiles were removed *in vacuo* and the residue was dissolved in C_6D_6. Analysis of the sample by NMR showed >70% conversion to the title compound. The signal of the central CH_2 of the carbene ring was obscured by the PCy_3 resonances. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −20.11 (br s, $^2J_{P-H}$ is not resolved, 1H, Ru*H*), 1.30, 1.71, 2.23, 1.67 [m, 66H, P(C_6H_{11})$_3$], 2.76 $^3J_{H-H}$ = 8 Hz, 2H, Ru=CN(H)C_3H_6], 2.82 [$^3J_{H-H}$ = 8 Hz, 2H, Ru=CN(H)C_3H_6], 8.00 [br s, 1H, Ru=CN(*H*)C_3H_6]. ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 20 °C): δ 44.1 (s).

Reaction of $OsH_3Cl(P^iPr_3)_2$ with *t*-butylethylene in benzene. In an NMR tube, the complex $OsH_3Cl(P^iPr_3)_2$[32] (0.010 g, 0.018 mmol) was dissolved in 0.8 ml of benzene-d_6 and *t*-butylethylene (4.7 μl, 0.036 mmol) was added to the solution. The reaction was followed by ^{1}H and ^{31}P {^{1}H} NMR. After 4.5 h at room temperature the main product (50% yield) by ^{31}P {^{1}H} NMR is $OsHCl[\eta^2$-H_2C=CH(*t*-Bu)$](P^iPr_3)_2$. Also evident by ^{31}P {^{1}H} NMR are 10% $OsH_2Cl_2L_2$, 3% OsH_5ClL_2 and 10% free P^iPr_3. Upon vacuum removal of the volatiles the products decompose. Diagnostic data are provided for $OsHCl[\eta^2$-H_2C=CH(*t*-Bu)$](P^iPr_3)_2$. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −41.1 (t, J_{H-P} = 24 Hz, Os–H), 4.77 {d, J_{H-H} = 11 Hz, Os[η^2-*H*$_2$C=CH(*t*-Bu)]}. ^{31}P {^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): 5.9, 2.4 (δ_A and δ_B of an AB pattern, $J_{P-P'}$ = 312 Hz).

Reaction of $OsH_3Cl(P^iPr_3)_2$ with *t*-butylethylene in THF. In an NMR tube, $OsH_3Cl(P^iPr_3)_2$ (0.010 g, 0.018 mmol) was dissolved in 0.8 ml of THF and *t*-butylethylene (4.7 μl, 0.036 mmol) was added to the solution. The reaction was followed by ^{31}P {^{1}H} NMR. After 4.5 h at room temperature the solution contains 5% $OsH_2Cl_2L_2$, 3% OsH_5ClL_2, 8% free P^iPr_3, 30% $OsHCl[\eta^2$-H_2C=CH(*t*-Bu)$]L_2$ but the main product (55% yield) is the cyclic carbene $OsHCl[$=CO(CH$_2$)$_3$]-$(P^iPr_3)_2$. Upon vacuum removal of the volatiles, the brown residue is redissolved in benzene-d_6. Only diagnostic data are provided. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −21.90 (t, J_{H-P} = 17.4 Hz, Os–*H*), 1.41 {dvt, J_{H-H} = 7.2 Hz, *N* = 12.8 Hz, Os–P[CH(C*H*$_3$)$_2$]}, 1.44 {dvt, J_{H-H} = 7.2 Hz, *N* = 12.8 Hz, Os–P[CH(C*H*$_3$)$_2$]}, 1.46 {m, Os[=C(CH$_2$–C*H*$_2$–CH$_2$–O)]}, 1.99 {t, J_{H-H} = 7.5 Hz, Os[=C(C*H*$_2$–CH$_2$–CH$_2$–O)]}, 2.53 {m, Os–P[C*H*(CH$_3$)$_2$]}, 3.46 {t, J_{H-H} = 7.5 Hz, Os[=C(CH$_2$–CH$_2$–C*H*$_2$–O)]}. ^{31}P {^{1}H} NMR (121.4 MHz, C_6D_6, 20 °C): 44.9.

Reaction of $OsH_3Cl[$=C(O)$C_3H_6](P^iPr_3)_2$ with H_2 at low temperature. In an NMR tube, $OsHCl[$=C(O)$C_3H_6](P^iPr_3)_2$ (0.017 g, 0.027 mmol) was dissolved in 0.5 mL of THF-d_8. The solution was degassed and the head-space evacuated and charged with H_2 (460 mm Hg, 0.055 mmol). Spectra were recorded as the solution was progressively cooled from 20 °C to −110 °C. The only compound present is a 1 : 1 adduct in its two isomeric conformations (*cis*-trihydride as minor isomer and *trans*-hydride/dihydrogen as major isomer). Only diagnostic data are provided. Data for *trans*-$OsH(H_2)$-Cl-[=C(O)C_3H_6]$(P^iPr_3)_2$: ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ −2.16 [br, Os–(H_2), T_1 = 25 ms, 2H], −8.31 (vbr, Os–*H*, T_1 = 750 ms, 1H). ^{31}P {^{1}H} NMR (121.4 MHz, THF-d_8, 20 °C): 33.6. ^{1}H NMR (300 MHz, THF-d_8, −100 °C): δ −1.97

[br, Os–(H_2), $T_1 = 7.9$ ms, 2H, A], −2.58 [br, Os–(H_2), $T_1 = 8.6$ ms, 2H, B], −8.29 − 8.47 (t, $J_{H-P} = 21$ Hz, Os–*H*, $T_1 = 243$ ms, $T_1 = 243$ ms, 1H, A + B overlapping). ^{31}P {^1H} NMR (121.4 MHz, THF-d_8, −100 °C): 34.4 and 31.2. Data for *cis*-$OsH_3Cl[=C(O)C_3H_6](P^iPr_3)_2$: ^1H NMR (300 MHz, THF-d_8, 20 °C): δ −9.98 (t, $J_{H-P} = 15$ Hz, Os–H_3, 3H). ^{31}P {^1H} NMR (121.4 MHz, THF-d_8, 20 °C): 30.9. ^1H NMR (300 MHz, THF-d_8, −100 °C): δ −10.46 (t, $J_{H-P} = 15$ Hz, Os–H_3, 3H). ^{31}P {^1H} NMR (121.4 MHz, THF-d_8, −100 °C): 28.7.

Synthesis of $Os(H)_3Cl[=CN(H)C_3H_6](P^iPr_3)_2$. *Method A*. In an NMR tube, $Os(H)_2Cl_2(P^iPr_3)_2$[40] (0.01 g, 0.018 mmol) was dissolved in 0.5 ml of benzene-d_6 and pyrrolidine (7.2 μL, 0.09 mmol) was added to the solution *via* syringe. The reaction is instantaneous upon shaking the NMR tube as the fairly insoluble $Os(H)_2Cl_2(P^iPr_3)_2$ is immediately dissolved and the solution turns light yellow. A white precipitate (the corresponding ammonium chloride from pyrrolidine) forms within 2 h. The solution was decanted and the volatiles removed *in vacuo*. The yellow–orange residue was dissolved in benzene-d_6. ^1H NMR (300 MHz, C_6D_6, 20 °C): −10.92 (br, Os–*H*, 3H), 1.11 {dvt, $N = 20.1$ Hz, Os–P[CH(CH_3)$_2$]}, 1.25 {dvt, $N = 19.2$ Hz, Os–P[CH(CH_3)$_2$]}, 1.38 {tt, $J_{H-H} = 7.8$ Hz, $J_{H-H} = 7.2$ Hz, Os[=C(CH_2–CH_2–CH_2–NH)]}, 2.10 {m, Os–P[CH(CH_3)$_2$]}, 2.83 {t, $J_{H-H} = 7.2$ Hz, Os[=C(CH_2–CH_2–CH_2–NH)]}, 2.98 {t, $J_{H-H} = 7.8$ Hz, Os[=C(CH_2–CH_2–CH_2–NH)]}, 10.64 {s, Os[=C(CH_2–CH_2–CH_2–NH)]}. ^{31}P {^1H} NMR (121.4 MHz, C_6D_6, 20 °C): 26.8. ^{13}C {^1H} NMR (100 MHz, C_6D_6, 20 °C): 20.1 {s, Os–P[CH(CH_3)$_2$]}, 20.4 {s, Os–P[CH(CH_3)$_2$]}, 23.6 {s, Os[=C(CH_2–CH_2–CH_2–NH)]}, 26.9 {vt, $N = 24.6$ Hz, Os–P[CH(CH_3)$_2$]}, 51.8 {s, Os[=C(CH_2–CH_2–CH_2–NH)]}, 56.6 {s, Os[=C(CH_2–CH_2–CH_2–NH)]}, 243.7 (t, $J_{H-P} = 5.4$ Hz, Os=*C*). ^1H NMR (300 MHz, C_7D_8, −80 °C): −8.51 (br, Os–H, 1H, $T_1 = 111$ ms), −9.77 (br, Os–*H*, 1H, $T_1 = 86$ ms), −14.47 (br, Os–*H*, 1H, $T_1 = 97$ ms).

Method B. In an NMR tube, pyrrolidine (31 μL, 0.36 mmol) was added to a stirred solution of $Os(H)_3Cl(P^iPr_3)_2$ (0.01 g, 0.018 mmol) in 0.5 ml of benzene-d_6. After 3 days at room temperature, the product in solution is the carbene described above. Vacuum removal of the volatiles leaves an orange residue displaying the same spectroscopic features described above.

Synthesis of $Os(H)_3Cl[=CN(H)C_4H_8](P^iPr_3)_2$. The procedure is analogous to method A described above but using piperidine (3.4 μL, 0.036 mmol). The solution was allowed to react for 12 h at room temperature and formation of a white precipitate was observed. After this time, the reaction mixture was allowed to sit for 2 h and the yellowish solution was decanted. The volatiles were dried *in vacuo* and the yellowish residue dissolved in benzene-d_6. ^1H NMR (300 MHz, C_6D_6, 20 °C): −11.31 (br, Os–*H*, 3H), 1.13 {dvt, $N = 19.2$ Hz, Os–P[CH(CH_3)$_2$]}, 1.27 {dvt, $N = 19.2$ Hz, Os–P{CH(CH_3)$_2$]}, 1.21 {m, Os[=C(CH_2–CH_2–CH_2–CH_2–NH)]}, 1.36 {m, Os[=C(CH_2–CH_2–CH_2–CH_2–NH)]}, 2.18 {m, Os–P[CH-(CH_3)$_2$]}, 2.65 {br, Os[=C(CH_2–CH_2–CH_2–CH_2–NH)]}, 3.16 {br, Os[=C(CH_2–CH_2–CH_2–CH_2–NH)]}, 11.4 {s, Os[=C(CH_2–CH_2–CH_2–CH_2–N*H*)]}. ^{31}P {^1H} NMR (121.4 MHz, C_6D_6, 20 °C): 26.1. ^{13}C {^1H} NMR (100 MHz, C_6D_6, 20 °C): 19.3 {s, Os[=C(CH_2–CH_2–CH_2–CH_2–NH)]}, 20.2 {s, Os–P[CH-(CH_3)$_2$]}, 20.5 {s, Os–P[CH(CH_3)$_2$]}, 21.6 {s, Os[=C(CH_2–CH_2–CH_2–CH_2–NH)]}, 26.9 {vt, $N = 24.6$ Hz, Os–P[CH-(CH_3)$_2$]}, 46.2 {s, Os[=C(CH_2–CH_2–CH_2–CH_2–NH)]}, 51.9 {s, Os[=C(CH_2–CH_2–CH_2–CH_2–NH)]}, 242.6 (t, $J_{H-P} = 5.4$ Hz, Os=*C*).

$Os(H)_3Cl[N(H)C_4H_8](P^iPr_3)_2$. The procedure is analogous to that describe above in method B but using 10 : 1 mol ratio of pyrrolidine (15.4 μL, 0.18 mmol) and stopping the reaction within 15 min. The reaction is instantaneous judging from the color change from brown to pale brown and after 15 min the main product is $Os(H)_3Cl[N(H)C_4H_8](P^iPr_3)_2$. At this stage the volatiles were removed *in vacuo* and the brownish residue dissolved in toluene-d_8. ^1H NMR (300 MHz, C_7D_8, 20 °C): −13.49 (br, Os–*H*, 3H, $T_1 = 244$ ms), 1.23 {dvt, $N = 19.2$ Hz, Os–P[CH(CH_3)$_2$]}, 2.14 {m, Os–P[CH(CH_3)$_2$]}. ^{31}P {^1H} NMR (121.4 MHz, C_7D_8, 20 °C): 22.5. ^1H NMR (300 MHz, C_7D_8, −70 °C): −12.65 (br, Os–*H*, 1H, $T_1 = 93$ ms), −13.71 (br, Os–*H*, 2H, $T_1 = 73$ ms), 1.20 {dvt, $N = 19.2$ Hz, Os–P[CH(CH_3)$_2$]}, 1.26 {dvt, $N = 19.2$ Hz, Os–P[CH(CH_3)$_2$]}, 3.54 [br, Os–N(*H*)C_4H_8]. ^{31}P {^1H} NMR (121.4 MHz, C_7D_8, −70 °C): 22.5.

Reaction of $Os(H)_2Cl_2(P^iPr_3)_2$ with 4-dimethylaminopyridine. The procedure is analogous to the one described above in method A but using 4-dimethylaminopyridine (0.0042 g, 0.036 mmol). The reaction was instantaneous judging from the color change from brownish to orange. NMR spectra recorded after 15 min confirm that the main compound at this time is the adduct $Os(H)_2Cl_2[NC_5H_4N(Me)_2](P^iPr_3)_2$. ^1H NMR (300 MHz, C_6D_6, 20 °C): −6.68 (t, $J_{H-H} = 10$ Hz, Os–*H*, 2H), 1.25 (dvt, $N = 14.7$ Hz, Os–P[CH(CH_3)$_2$]}, 2.05 {s, Os–[NC_5H_4 $N(CH_3)_2$]}, 2.80 {m, Os–P[CH(CH_3)$_2$]}, 6.03 {d, $J_{H-H} = 5.7$ Hz, Os–[N(CH)$_2$–CH_2–N(CH_3)$_2$], 2H}, 10.29 {d, $J_{H-H} = 5.7$ Hz, Os–[N(CH)$_2$–CH_2–N(CH_3)$_2$], 2H}. ^{31}P {^1H} NMR (121.4 MHz, C_6D_6, 20 °C): −2.4.

Reaction of $Os(H)_2Cl_2(P^iPr_3)_2$ with pyrrolidine at low temperatures. A solution of pyrrolidine (2.9 μL, 0.036 mmol) in 0.5 mL of THF-d_8 was vacuum transferred to an NMR tube containing $Os(H)_2Cl_2(P^iPr_3)_2$ (0.01 g, 0.018 mmol). The solution was placed in an ^{i}PrOH–CO_2 bath (−78 °C) and inserted into a pre-cooled probe at −80 °C. The reaction was carefully monitored by ^1H and ^{31}P {^1H} NMR by increasing the temperature in 10 °C steps and allowing the reaction to proceed for 5 min at each step prior to acquiring the spectra. Only diagnostic data is provided for the 16e$^-$ pyrrolidine adduct $OsHCl[N(H)C_4H_8](P^iPr_3)_2$ (**V**) and the alkyl $OsH_2Cl[CHN(H)C_3H_6](P^iPr_3)_2$ (**VI**). ^1H NMR (300 MHz, THF-d_8, −70 °C): −9.79 (dd, $J_{H-P} = 47.1$ Hz, $J_{H-P'} = 35.1$ Hz, Os–*H*, **VI**), 4.48 [br, Os–CHN(*H*)C_2H_4, **VI**], −26.11 (t, $J_{H-P} = 17.0$ Hz, Os–*H*, **V**), 4.84 [br, Os–N(*H*)C_3H_6, **V**]. ^{31}P {^1H} NMR (121.4 MHz, THF-d_8, −70 °C): 28.4, 26.4 (AB pattern, $J_{P-P'} = 101$ Hz, **VI**), 55.0 (s, **V**).

Reaction of $Os(H)_2Cl_2(P^iPr_3)_2$ with *N*-methylpyrrolidine. In an NMR tube, *N*-methylpyrrolidine (8.9 μl, 0.085 mmol) was added to a solution of $Os(H)_2Cl_2(P^iPr_3)_2$ (0.01 g, 0.017 mmol) in 0.5 ml of benzene-d_6. After 3 h at room temperature, the main product in solution is the carbene $OsH_3Cl[=CN(Me)C_3H_6](P^iPr_3)_2$ in approximately 20% conversion, along with several other unidentified products. Only diagnostic data is given. ^1H NMR (300 MHz, C_6D_6, 20 °C): −11.15 (br, Os–*H*, 3H), 1.26 {dvt, $N = 19.2$ Hz, Os–P[CH(CH_3)$_2$]}, 1.38 {dvt, $N =$ 19.2 Hz, Os–P[CH(CH_3]$_2$]}, 1.45 {m, Os[=C(CH_2–CH_2–CH_2–NMe)]}, 2.94 {t, $J_{H-P} = 7.2$ Hz, Os[=C(CH_2–CH_2–CH_2–NMe)]}, 3.88 {t, $J_{H-P} = 7.8$ Hz, Os[=C(CH_2–CH_2–CH_2–N Me)]}, 3.03 {s, Os[=C(CH_2–CH_2–CH_2–NCH_3)]}. ^{31}P {^1H} NMR (121.4 MHz, C_6D_6, 20 °C): 28.8.

Reaction of $Os(H)_3Cl(P^iPr_3)_2$ with *N*-methylpyrrolidine. In an NMR tube, *N*-methylpyrrolidine (9.5 μl, 0.090 mmol) was added to a solution of $Os(H)_3Cl(P^iPr_3)_2$ (0.01 g, 0.018 mmol) in 0.5 ml of benzene-d_6. After 20 min at room temperature, the main product in solution is the adduct $OsH_3Cl[N(Me)C_4H_8](P^iPr_3)_2$. After 20 h at room temperature, 20% of the carbene $OsH_3Cl[=CN(Me)C_3H_6](P^iPr_3)_2$ has been formed, along with several other unidentified products. Only diagnostic

data is given for the adduct $OsH_3Cl[N(Me)C_4H_8](P^iPr_3)_2$. ^1H NMR (300 MHz, C_6D_6, 20 °C): −19.22 (br, Os–*H*, 3H), 1.61 {br m, Os[N(Me)(CH_2–CH_2)$_2$]}, 2.31 {br m, Os[N(Me)(CH_2–CH_2)$_2$]}, 2.25 {br s, Os[N(CH_3)(CH_2–CH_2)$_2$]}. ^{31}P {^1H} NMR (121.4 MHz, C_6D_6, 20 °C): 53.9.

Reaction of $Os(H)_2Cl_2(P^iPr_3)_2$ with pyrrolidine in the presence of THF. In a round bottom flask, $Os(H)_2Cl_2(P^iPr_3)_2$ (0.01 g, 0.017 mmol) was dissolved in 10 ml of THF. The solution was constantly stirred while a solution of pyrrolidine (1.78 μL, 0.017 mmol) in 5 ml of THF was added dropwise over a period of 10 min. The solution was allowed to react for 30 min at room temperature prior to vacuum removal of the volatiles. The solid residue, redissolved in C_6D_6, showed ^1H and $^{31}P\{^1H\}$ NMR evidence for a 1 : 1 mixture of $Os(H)_2Cl_2L_2$ and $OsH_3Cl[=C(NH)C_3H_6)L_2$.

X-Ray structure determination of $RuHCl(C_4NH_7)(P^iPr_3)_2$

A well-formed typical plate, grown from C_6D_6, was cleaved to form a nearly equidimensional sample and was then affixed to a glass fiber using silicone grease and transferred to the goniostat where it was cooled to −145 °C using standard inert atmosphere handling techniques. The data were collected on a Bruker SMART 6000 diffractometer using 5 s frames with an omega scan of 0.30 degrees. Data were corrected for Lorentz and polarization effects and equivalent reflections averaged using the Bruker SAINT software as well as utility programs from the XTEL library. An absorption correction was performed using the SADABS program supplied by Bruker AXS. The structure was solved using SHELXTL and Fourier techniques. Selected data are given in Table 2. As shown in the figures, the molecule lies with the Ru atom on a crystallographic mirror plane around which the C_4H_7N lies. Several models were examined with various combinations of atoms lying out of the mirror plane. The final model has two atoms in the ligand [C(5) and C(6)] lying out of the mirror plane and the others in the plane. When all ligand hydrogen atoms were placed in idealized positions, the hydride was visible in a difference Fourier map. Attempts to refine the hydrogen atoms were unsuccessful. A final difference Fourier map was essentially featureless.

CCDC reference number 182817. See http://www.rsc.org/suppdata/nj/b2/b200168n/ for crystallographic data in CIF or other electronic format.

Computational details

Ab initio calculations were carried out with the Gaussian 98[41] set of programs within the framework of DFT at the B3PW91 level.[42] The Hay–Wadt effective core potential (quasi-relativistic for the metal centers) was used to replace the 28 innermost electrons of Ru[43] and the 10 core electrons of P and Cl.[44] The associated double ζ basis sets were used. They were augmented by d polarization functions for P and Cl.[45] H, C, O and N were represented by a 6-31G(d,p) basis set.[46] Full geometry optimization was performed without symmetry restrictions.

Table 2 Selected crystallographic data for $RuHCl(C_4NH_7)(P^iPr_3)_2$

Formula	$C_{22}H_{50}ClNP_2Ru$
Formula weight	527.12
Crystal system	Orthorhombic
Space group	$Cmc2_1$
T/°C	–145
μ(Mo-Kα)/cm^{-1}	8.5
a/Å	21.475(1)
b/Å	8.842(0)
c/Å	13.469(0)
U/Å^3	2557.35
Z	4
Total reflections	12198
Unique reflections	3094
R_{int}	0.049
R^a [$I > 2.33\sigma(I)$]	0.0276
$R_w{}^b$ [$I > 2.33\sigma(I)$]	0.0261

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(|F_o|)$.

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