Mechanistic and thermodynamic aspects of methylene transfer from CH_2N_2 to $MHCl(CO)L_2$ (M = Ru, Os; L = tertiary phosphine): non-least motion behavior and extreme dependence on phosphine identity

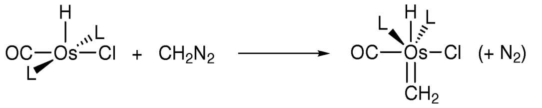
Letter

Dejian Huang, Greg J. Spivak and Kenneth G. Caulton*

Department of Chemistry, Indiana University, Bloomington, IN 47405-4001, USA

Reaction of $MHCl(CO)(PBu^t_2Me)_2$ (M = Ru and Os) with CH_2N_2 was studied from −78 to 25 °C, revealing first the formation of $MHCl(CH_2)(CO)(PBu^t_2Me)_2$, where the carbene ligand CH_2 occupies what was the open coordination site of $MHCl(CO)(PBu^t_2Me)_2$, which lies *trans* to the hydride. This intermediate then isomerizes to $M(CH_3)Cl(CO)(PBu^t_2Me)_2$, below 25 °C for each metal. The analogous reaction of $MHCl(CO)(PPr^i_3)_2$ with CH_2N_2 does indeed give $MHCl(CH_2)(CO)(PPr^i_3)_2$, which then 'decomposes' unselectively; when M = Os, C_2H_4 and $OsHCl(CO)(PPr^i_3)_2$ are among the products. This *extreme* phosphine dependence is attributed to the $H{-}M{=}CH_2$ to $M(CH_3)$ isomerization requiring phosphine dissociation; the smaller PPr^i_3 fails to dissociate at a rate competitive with alternative decomposition reactions.

It was recently reported[1] that an apparently straightforward and logical attempt to insert CH_2 into the Os—H bond of $OsHCl(CO)L_2$ ($L = PPr^i_3$) gave instead the product of 'addition' of CH_2 to osmium [eqn. (1)].



(1)

One might argue that the mutually *trans* location of H and CH_2 was responsible for the lack of $Os(CH_3)Cl(CO)L_2$ as the product; this logic thus says that the observed product forms under kinetic control and implies that $Os(CH_3)Cl(CO)L_2$ might (with patience) still be accessible as the thermodynamic product. The earlier report[1] of the reaction of CH_2N_2 with $OsHCl(CO)L_2$ sought to establish if the '. . . 16-electron alkylosmium(II) compounds of general composition $Os(CH_2R)Cl(CO)(PPr^i_3)_2$ would be accessible . . .' and commented that these 'are still unknown.' We report evidence that these target alkyls are the more stable isomeric structure for osmium, as they are also for ruthenium.

We first report results on the PBu^t_2Me analog of eqn. (1). Reaction of CH_2N_2 with $OsHCl(CO)L_2'$ ($L' = PBu^t_2Me$) in toluene at 25 °C gives only $Os(CH_3)Cl(CO)L_2'$[2] within minutes. If the reaction is executed at −78 °C and all volatiles, including solvent, removed while still cold, NMR spectra recorded within 15 min of reaction show ≈ 10% of the corresponding carbene complex $OsHCl(CH_2)(CO)(PBu^t_2Me)_2$,[3] in addition to predominantly $Os(CH_3)Cl(CO)(PBu^t_2Me)_2$. The carbene in this solution then rapidly isomerizes completely to the methyl complex in benzene solution at 25 °C; the carbene complex is thus an intermediate in forming the unsaturated methyl complex.

We next report results on the ruthenium analog. Reaction of $RuHCl(CO)L_2'$ ($L' = PBu^t_2Me$) with CH_2N_2 in Et_2O at −20 °C for 12 h gives a 90% yield of $Ru(CH_3)Cl(CO)L_2'$. This product in solution shows no hydride or carbene ^1H NMR signals, and it does show diasterotopic Bu^t methyl groups. The triplet at 0.92 ppm for $Ru(CH_3)Cl(CO)L_2'$ has an intensity consistent with three hydrogens and the chemical shift and J_{PH} values exclude this being due to an acetyl group. The ^{13}C NMR signal of this Ru-methyl carbon is a triplet ($J_{PC} = 6$ Hz) at −11.0 ppm. The ν(CO) value, 1898 cm^{-1}, is lower than that of $OsHCl(CO)(CH_2)L_2$ (1910 cm^{-1} in KBr), in agreement with a lower oxidation state for the ruthenium species. This molecule [$\delta(^{31}P) = 34.4$] is thus analogous to $Ru(Ph)(Cl)(CO)(PBu^t_2Me)_2$,[4] even by comparison of the ν(CO) (1902 cm^{-1}) and $\delta(^{31}P)$ 34.0) values of the latter.

Monitoring of this reaction beginning at −75 °C reveals visible gas evolution and $^{31}P\{^1H\}$ NMR signals of an intermediate, as well as a small amount of $Ru(CH_3)Cl(CO)(PBu^t_2Me)_2$. At −75 °C, the intermediate appears as a $^{31}P\{^1H\}$ AB spin system (δ = 81.1 and 72.6) due to hindered rotation of the phosphines in this crowded *six*-coordinate species, with a $J_{PP'}$ value of 166 Hz. While this magnitude is large enough to be consistent with a transoid P—Ru—P structure, this value is considerably smaller than the 250 Hz usually seen in square pyramidal or octahedral species; this is strong evidence for its assignment as $MHCl(CH_2)(CO)L_2'$ (M = Ru), since the solid-state structure[1] of $OsHCl[CH(SiMe_3)](CO)(PPr^i_3)_2$ has ∠P—Os—P = 141°. As the temperature is raised (to −40 °C) on the above reaction solution, the AB $^{31}P\{^1H\}$ NMR pattern coalesces to one broad signal at 77 ppm (*i.e.*, phosphine rotation accelerates) and the peak due to $Ru(CH_3)Cl(CO)(PBu^t_2Me)_2$ grows. By −30 °C, the carbene species has rearranged completely to the methyl isomer. The variable-temperature ^1H NMR spectra confirm the above transformations and show (−75 °C) two inequivalent carbene hydrogens, at 16.1 and 15.3 ppm, and a hydride at −3.6 ppm. While all three of these peaks are broad at −75 °C, due to unresolved coupling to the inequivalent phosphorus nuclei, the chemical shifts are sufficiently close to those of $OsHCl(CH_2)(CO)(PPr^i_3)_2$ to confirm their assignments.

Can it really be that, in eqn. (1), one intercepts a kinetic product and, if so, why? If true, it should be possible to isomerize the osmium hydrido carbene complex to $Os(CH_3)(Cl)(CO)(PPr^i_3)_2$. Remarkably, the analogous chemistry with PPr^i_3 is very different from that of PBu^t_2Me, in

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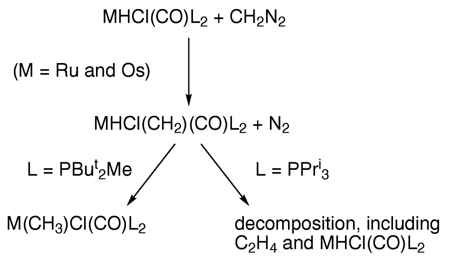
* E-mail: caulton@indiana.edu



Scheme 1 (M = Ru and Os)

spite of their having identical cone angles.[5] A C_6D_6 solution of the previous reported $OsHCl(CH_2)(CO)(PPr^i_3)_2$ is completely decomposed within 24 h at 25 °C, yielding $OsHCl(CO)(PPr^i_3)_2$ as the main (> 50%) product, with no formation of any $Os{-}CH_3$ species, as determined by NMR spectroscopy. This decomposition produces free ethylene whose signal at 5.49 ppm is broadened due to exchange in the equilibrium of eqn. (2)

$$OsHCl(CO)(PPr^i_3)_2 + C_2H_4 \rightleftharpoons OsHCl(C_2H_4)(CO)(PPr^i_3)_2 \quad (2)$$

which we have independently characterized by ^1H and ^{31}P NMR spectroscopy.[6] Also observed are three weak hydride doublet peaks, which suggest phosphine loss, perhaps to form methylene phosphorane ($H_2C{=}PPr^i_3$) coordinated to Os. For comparison, $RuHCl(CO)(PPr^i_3)_2$ reacts with CH_2N_2 with gas evolution and color change from orange to pale yellow already at −78 °C to give a $RuHCl(CH_2)(CO)(PPr^i_3)_2$ species wholly analogous to its Os analog: spectral features at −75 °C include a $^{31}P\{^1H\}$ NMR singlet, two CH_2 doublet of doublets at 16.6 and 15.9 ppm and a hydride (−3.3 ppm) triplet ($J_{PH} = 26$ Hz) of doublets of doublets. The approximate threefold symmetry of PPr^i_3 avoids the rotamers found for PBu^t_2Me. Again, analogous to the Os–PPr^i_3 case, above −20 °C $RuHCl(CH_2)(CO)(PPr^i_3)_2$ decomposes unappealingly to six unidentified phosphine-containing products. No $RuMeCl(CO)(PPr^i_3)_2$ [7] is formed.

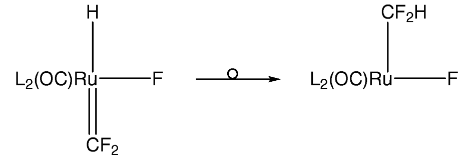
We suggest that this surprisingly different behavior of $MHCl(CH_2)(CO)L_2$ for $L = PBu^t_2Me$ and $L = PPr^i_3$ (summarized in Scheme 1) is due to the fact that migrating H and CH_2 ligands to mutual *cis* stereochemistry requires phosphine loss, and the marginally smaller[8] PPr^i_3 fails to dissociate effectively from M. As a result, intact $OsHCl(CH_2)(CO)(PPr^i_3)_2$ has a lifetime long enough for it to explore other reaction channels and the one involving 'CH_2 loss', regenerating $OsHCl(CO)(PPr^i_3)_2$, becomes operative. Indeed, $OsHCl[CH(SiMe_3)](CO)(PPr^i_3)_2$ is sufficiently long-lived to allow crystal structure determinations.[1] In the more crowded $MHCl(CH_2)(CO)(PBu^t_2Me)_2$, phosphine dissociation is evidently sufficient for rapid combination of initially *trans* H and CH_2 ligands. The hydrido carbene isomer in eqn. (1) for PPr^i_3 is thus metastable because the two ligands that might combine to make CH_3 are mutually *trans* and there is evidently no facile unimolecular process within the six-coordinate species that can bring these into mutually *cis* sites. Other, slow reaction channels thus operate and these are unselective.

Numerous attempts to prove inverse phosphine dependence on the rearrangement rate by lengthening the half-life of $OsHCl(CH_2)(CO)(PBu^t_2Me)_2$ by adding free PBu^t_2Me or PPr^i_3 to the cold solution after reacting $OsHCl(CO)(PBu^t_2Me)_2$ with CH_2N_2 gave only an array of *new* products. Thus, added phosphine acts not merely to shift equilibrium (3) to the left, but plays a more agressive role, perhaps by attack at the carbene carbon.

$$OsHCl(CH_2)(CO)(PBu^t_2Me)_2 \rightleftharpoons OsHCl(CH_2)(CO)(PBu^t_2Me) + PBu^t_2Me \quad (3)$$

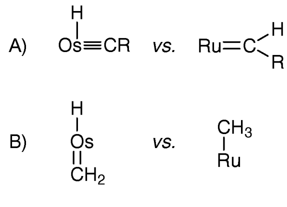
These results show an extreme dependence of chemical behavior on ligand identity for two such superficially similar (*i.e.*, isomeric) phosphines. The (apparently[9]) bulkier ligand PBu^t_2Me permits selective isomerization of mutually *trans* hydride and CH_2 ligands to the methyl alternative, while PPr^i_3 gives rise to highly unselective 'decomposition', with no high yield fate of the carbene ligand, to *regenerate* some $OsHCl(CO)(PPr^i_3)_2$ reagent. The latter case thus frustrates establishing the truth that the PBu^t_2Me example reveals: unsaturated $M(CH_3)Cl(CO)L_2'$ is more thermodynamically stable than $MHCl(CH_2)(CO)L_2'$.

The fact that the saturated, higher valent alternative, $OsHCl(CH_2)(CO)L_2$, with more metal ligand bonds, is not thermodynamically preferred stands in contrast to saturated $HOs(\equiv CR)Cl_2L_2$ being more stable than unsaturated $Os[{=}C(H)R]Cl_2L_2$, as was discovered recently.[10] In that work, it was shown[10] that $RuCl_2[C(H)R]L_2$ and $OsCl_2H(CR)L_2$ are the contrasting ground state structures. This was supported by quantum chemical computations and was also rationalized by general trends in 4d *vs.* 5d metal chemistry. However, these results are fully consistent with the thermodynamics of eqn (4).[11]

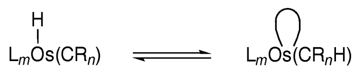


$$L_2(OC)Ru(H)(=CF_2)F \xrightarrow{o} L_2(OC)Ru(CF_2H)F \quad (4)$$

The balance of stability between metal formal oxidation states is thus very subtle among these Ru and Os complexes. These accumulated results at two different hydrocarbyl ligand oxidation levels (A[10] and B below),



being α-hydrogen migration reactions that relate any pair of redox isomers, represent a rearrangement that could be generally useful for creating unsaturation in the saturated osmium series [eqn. (5)].

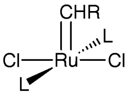


$$L_mOs(H)(CR_n) \rightleftharpoons L_mOs(CR_nH) \quad n = 1,2 \quad (5)$$

One conclusion from this work is that diazomethane does not 'deliver' CH_2 directly to the $Os{-}H$ bond. Instead, finding intact CH_2 *trans* to hydride in the kinetic product indicates that the open coordination site of square-pyramidal $OsHCl(CO)L_2$ is the point of attack by CH_2N_2.

The observed isomerization of hydrido carbene to methyl shows that an unsaturated form can be more stable than its saturated isomer, particular when a strong sigma donor ligand like methyl is *trans* to the empty site. While the location of CH_2 in $MHCl(CO)(CH_2)L_2$ in what was the empty site of $MHCl(CO)L_2$ reinforces the hypothesis that this is a kinetic product, it is clear from the PBu^t_2Me results that hydride and CH_2 *can* find each other rapidly at 25 °C.

The idea that the unfavorable insertion stereochemistry of a 'least motion' primary product can influence its ultimate fate is one that must be considered in catalyst optimization. Consider, for example, that the open coordination site in the olefin metathesis catalyst **C** is *trans* to the mechanistically essential carbene ligand. This explains why one metathesis mechanism[12] begins by dissociation of L from **C**.



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Supplementary material. Detailed syntheses and characterization data are available from the author.

Acknowledgements

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References and Notes

1 H. Werner, S. Stüer, M. Laubender, C. Lehmann and R. Herbst-Irmer, *Organometallics*, 1997, **16**, 2236.

2 Selected spectroscopic data for [$Os(CH_3)Cl(CO)(PBu^t_2Me)_2$]: ^1H NMR (300 MHz, C_6D_6, 25 °C): 1.90 (t, $^3J_{PH} = 4.8$ Hz, 3H, Os—CH_3); $^{13}C\{^1H\}$ NMR (75.3 MHz, C_6D_6, 25 °C): −37.88 (t, $^2J_{PC} = 4.1$ Hz, Os—CH_3), 182.38 (t, $^2J_{PC} = 9.6$ Hz, Os—CO; $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 25 °C): 16.78 (s, PBu^t_2Me); IR (C_6D_6, cm^{-1}): ν(CO) = 1883s).

3 ^1H NMR spectra (C_6D_6, 25 °C): 17.75 and 16.63 (br, CH_aH_b), −4.04 (t, $^2J_{PH} = 32$ Hz, Os—H); $^{31}P\{^1H\}$ NMR (C_6D_6 , 25 °C): 48.3 (s, Pbu^t_2Me).

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6 The reported chemical shift for the coordinated ethylene vinyl hydrogens is in error, being in fact that of free ethylene. The coordinated ethylene ^1H NMR signal is at 2.93 ppm and integrates correctly (4 : 6) against the Pr^i methine hydrogens. See M. A. Esteruelas and H. Werner, *J. Organomet. Chem.*, 1986, **303**, 221.

7 This compound has been synthesized independently from $RuCl_2(CO)(PPr^i_3)_2$ and MeLi. D. Huang and K. G. Caulton, to be submitted.

8 PPr^i_3 is less bulky than PBu^t_2Me. See C. Li, M. Oliván, S. P. Nolan and K. G. Caulton, *Organometallics*, 1997, **16**, 4223; C. Li, M. Ogasawara, S. P. Nolan and K. G. Caulton, *Organometallics*, 1996, **15**, 4900.

9 The hindered rotation around the M—P bond observed for $RuHCl(CH_2)(CO)(PBu^t_2Me)_2$ at low temperature supports the idea that this phosphine is bulkier than PPr^i_3.

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