Osmium Converts Terminal Olefins to Carbynes: α-Hydrogen Migration Redox Isomers with Reversed Stability for Ruthenium and for Osmium

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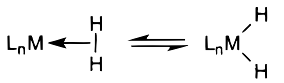
Received December 30, 1997

Summary: $Os(H)_2Cl_2L_2$ ($L = P^iPr_3$) reacts with propylene or styrene to give equimolar amounts of $OsHCl_2(CCH_2R)L_2$ and the hydrogenated olefin; these molecules are isomeric with the ruthenium carbenes $RuCl_2[C(H)CH_2R]L_2$, yet these distinct redox alternatives are thermodynamically preferred. Ab initio (B3LYP) calculations show that the unsaturated five-coordinate $MCl_2(CHMe)(PH_3)_2$ is more stable than the saturated hexacoordinate $MCl_2H(CMe)(PH_3)_2$ for M = Ru, while the two species are almost isoenergetic in the case of Os; computationally, it is found that the osmium hydrido carbyne involves a large activation energy (27.2 kcal/mol) to transform unimolecularly to its carbene isomer.

The great redox flexibility of the transition elements permits the possible existence of redox tautomers, or isomers, and the question of the comparative stabilities of these. Conceivable alternative structures (i.e., involving significant movement of atoms) in a number of cases include $M(\eta^2\text{-}EE')$ vs $M(E)(E')$, where E, E′ = O, S, NR, PR, CR_2. Some particularly striking examples of redox isomers are represented by dihydride/dihydrogen tautomers existing in thermal equilibrium (eq 1).[1]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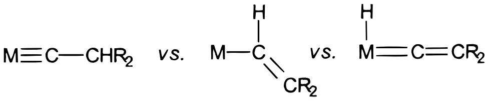
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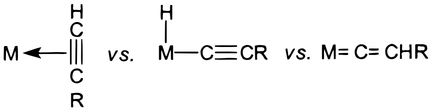
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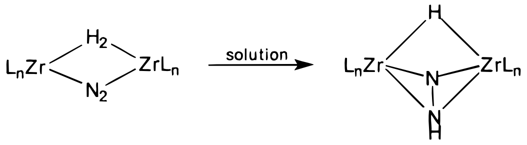
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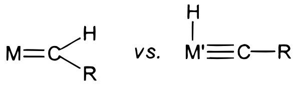
Equally remarkable are the examples where change of solvent alters the stable form from $L_nCu_2(\mu\text{-}O_2)$ to $L_nCu_2(\mu\text{-}O)_2$.[2] Isomers which differ by *hydrogen migration* represent fundamental transformations of organometallic chemistry (eq 2 and 3), and a hydrogen migration to N_2 (eq 4) has been reported with conversion from solution to the solid phase.[3] Conversion from a hydride/vinylidene complex to a carbyne has been reported on changing from $MeNO_2$ solvent to the solid phase.[4] We report here a unique situation: a case where changing from a 4d (M) to a 5d (M′) metal completely changes the ground-state structure, with concomitant change in valence electron count (eq 5). One related oxidation state reversal[5] is that of $(HBpz_3)Rh(C_2H_4)(CO)$ vs $(HBpz_3)IrH(CH{=}CH_2)(CO)$, but here both alternatives have the *same* electron count. Similarly, $RuHI(H_2)L_2$ is a dihydrogen complex, while $Os(H)_3IL_2$ contains Os(IV).[6]


(5)

Reaction (eq 6) of $Os(H)_2Cl_2L_2$ ($L = P^iPr_3$) with terminal olefins (mole ratio 1:(2−3)) occurs at convenient rates above 85 °C (in toluene) to produce equimolar amounts of alkane (i.e., the hydrogen abstraction product) and (e.g., from styrene) $OsHCl_2(CCH_2Ph)L_2$.[7,8] The latter product has the elemental composition

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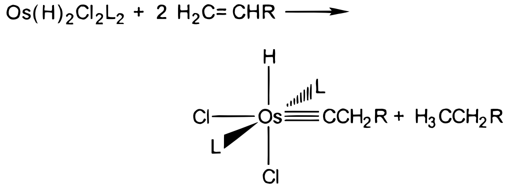

(6)

$OsCl_2L_2$·olefin, but the olefin has been transformed into a carbyne ligand by abstraction of both CH_2 hydrogens; one migrates to the metal, and the second migrates to C_β. An analogous product is derived, in quantitative yield, from propene.[9] All have spectroscopic properties consistent with trans phosphines and mutually cis chlorides. Examples of this structural type have been reported earlier,[10] but synthesized from terminal alkynes, not olefins.

In octahedral, saturated $OsHCl_2(CR)L_2$, the hydride is cis to the carbyne ligand, a feature which raises the question of why the olefin metathesis catalyst[11] $RuCl_2(CHR)L_2$ is five-coordinate and unsaturated. That is, the Os and Ru complexes are isomeric, *not* isostructural, each at 25 °C and in the same solvent (e.g., arenes).[12] We have considered the possibility that one of these isolated species is merely a kinetic product and that both the 4d and 5d metals in reality have the same thermodynamic structural preference. In fact, $OsHCl_2(CCH_2Ph)L_2$ is unchanged on reflux in benzene for 30 h. The analogous carbene $RuCl_2(CHPh)(PCy_3)_2$[13] is not isomerized to a carbyne complex after 20 h at 70 °C in toluene. In addition, ^1H and ^{31}P NMR spectra of the ruthenium complex recorded at 70 °C show no evidence for population of a hydrido carbyne isomer.

Although these attempted thermolyses suggest that the isomeric compounds are thermodynamic products, we turned to a computational approach for an independent measure of thermodynamic stability. The model species $MHCl_2(C{-}CH_3)(PH_3)_2$ and $MCl_2(CHCH_3)(PH_3)_2$ for M = Ru, Os have been optimized by ab initio calculations at the DFT (B3LYP) level.[14] For both metals, the five-coordinate complex is a square pyramid with apical carbene coplanar with the MP_2 plane (Figure 1a). This maximizes interaction between the empty p orbital of the carbene and the metal d orbital destabilized by the Cl lone pairs. The six-coordinate complex has a slightly distorted octahedral geometry (Figure 1b). While the carbene isomer is 27.8 kcal mol^{-1} more stable than the hydrido carbyne for M = Ru, the difference is reduced to 6.4 kcal mol^{-1} for M = Os (the carbene is still calculated to be more stable for M = Os). The striking result is that, while the preference for carbene isomer is significant for Ru, the difference in energy is over 20 kcal mol^{-1} smaller in the case of Os. The electronically preferred orientation of the carbene ligand in $MCl_2(CHCH_3)(PH_3)_2$ has maximal steric hindrance between the bulky phosphines and the carbene substituents. This is why, in the three observed structures,[13,15] the carbene is rotated away from this ideal position; the calculated rotational barrier in the PH_3 model is only 4.6 kcal/mol. In contrast, the hydrido carbyne complex has less steric hindrance between the R group of the linear MCR and the phosphines. Thus, the PH_3-based calculations underestimate the stability of the hydrido carbyne with respect to the carbene isomer. This should play a role only in the case of Os, where the isomer energies are similar. This accounts for the greater stability observed for the Os hydrido carbyne complex, yet it leaves the carbene isomer close in energy.

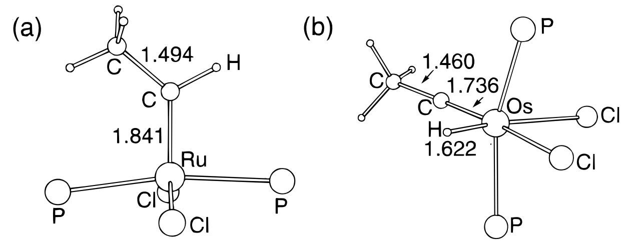

Figure 1. Optimized (B3LYP) structures of (a) $RuCl_2[C(H)CH_3](PH_3)_2$ and (b) $OsHCl_2(CCH_3)(PH_3)_2$.

$OsHCl_2(CEt)L_2$ reacts with CO within 14 h at 0.036 M and 25 °C in CD_2Cl_2 to form $OsCl_2(CHEt)(CO)L_2$.[16] A stereochemistry with trans phosphines and cis chlorides is established by the observation of two (diastereotopic) ^{i}Pr methyl groups, each as a (doublet of) virtual triplets.[17] A reaction of this rate *cannot* occur by a mechanism in which an equilibrium amount of preformed unsaturated carbene $OsCl_2(CHEt)L_2$ is attacked by CO, since DFT calculation of the energy of the optimized structure of the transition state for unimo-

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(8) **Synthesis of [OsHCl$_2$(CCH$_2$Ph)(P-*i*-Pr$_3$)$_2$].** To a suspension of $[OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2]$ (0.0500 g, 0.0857 mmol) in toluene (10 mL), was added $CH_2{=}CHPh$ (0.257 mmol, 29.4 μL). Refluxing the suspension (110−115 °C) for 24 h yielded a dark brown solution. The solution was cooled to room temperature and concentrated to approximately 1−2 mL under reduced pressure. The remaining solution was cooled to 0 °C, and excess pentane (25 mL) was added, yielding a brown precipitate after 1 h. The precipitate was collected, washed with pentane (10 mL), and dried under reduced pressure. Yield: 0.0216 g (41%). The spectroscopic data (NMR) for the product were the same as those cited previously. ^1H NMR (300 MHz, C_6D_6): δ −6.59 (t, J(PH) = 16.2 Hz, 1 H, Os-H), 1.32 (dvt, N = 14.1, J(HH) = 7.5 Hz, 18 H, PCHCH_3), 1.42 (dvt, N = 13.2, J(HH) = 7.2 Hz, 18 H, PCHCH_3), 2.07 (s, 2H, OsCCH_2-Ph), 2.57 (m, 6 H, PCHCH$_3$), 6.98−7.32 (m, 5 H, Ph). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 19.80 (s, P-*i*-Pr$_3$).

(9) ^1H NMR (300 MHz, C_6D_6): δ −7.00 (t, J(PH) = 16.5 Hz, 1 H, Os−H), 1.29 (dvt, N = 14.1, J(HH) = 7.2 Hz, 18 H, PCHCH_3), 1.41 (dvt, N = 13.5, J(HH) = 7.2 Hz, 18 H, PCHCH_3), 2.59 (m, 6 H, PCHCH$_3$); the CH_2 and CH_3 resonances of the ethyl group were obscured by the P-*i*-Pr$_3$ proton signals. $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): 6.58 (s, OsCCH$_2$$CH_3$), 19.84 (s, PCH$CH_3$), 19.97 (s, PCH$CH_3$), 27.01 (vt, N = 26.1, PCHCH$_3$), 45.11 (s, OsCCH$_2$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): 20.68 (s, P-*i*-Pr$_3$).

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(12) A related redox reversal is based on α-H migration from an alkyl group: $[N_3N]$Mo(cyclopentyl) vs $[N_3N]$W(H)(cyclopentylidene). See also: Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Shih, K.; O'Donoghue, M. B.; Davis, W. M.; Reiff, W. M. *J. Am. Chem. Soc.* **1997**, *119*, 11876.

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(14) The calculations were performed with the Gaussian 94 package. The pseudopotential and basis sets for Os, Ru, and P are those of LANL2DZ. C and C-bonded hydrogens are described with a split valence basis set. Polarization functions have been added to P, C, and C-bonded H. Hydrogens of PH_3 are described with a minimal basis set. Optimization was carried out at the B3LYP level. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision D.I; Gaussian, Inc., Pittsburgh, PA, 1995.

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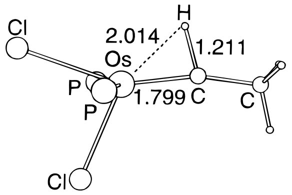

Figure 2. Optimized transition state for the unimolecular rearrangement of $OsHCl_2[CCH_3](PH_3)_2$ into $OsCl_2[C(H)CH_3](PH_3)_2$.

lecular rearrangement between hydride/carbyne and carbene (Figure 2) gives an energy of 27.2 kcal mol^{-1}, above the carbyne, which is too large to be consistent with the observed reaction rate to form the carbonylation product. Therefore, the mechanism of this reaction must involve nucleophilic assistance of the hydrido-to-carbyne-carbon migration; Os−CO bond making will lower the activation energy from its unimolecular value.

These results are more than a simple curiosity. Since the osmium isomer is saturated, it may not be a good olefin metathesis catalyst *unless* the α-H migration in the actual complex (not the PH_3 species shown in the Figures) is only mildly endergonic.

The greater stability of the carbyne isomer for osmium may be due to the 5d metal preferring a higher oxidation state (i.e., carbyne is more oxidizing than carbene) and having a stronger desire for an 18-valence electron count. This can explain the contrasting structures of $Cp^*{}_2Nb[\eta^2\text{-}H_2B(\text{catecholate})]$ and *endo*-$Cp_2Ta(H)_2[B(\text{catecholate})]$, which contain Nb^{III} and Ta^{V}.[18] It is also true that metal−ligand bond strength is generally stronger for 5d vs 4d metals,[19] and the hydrido carbyne has more metal−ligand bonds.

Acknowledgment. This work was supported by the U.S. National Science Foundation, the French CNRS, the University of Montpellier 2, and an NSF/CNRS (PICS) grant for international collaboration.

Supporting Information Available: Text giving synthetic and spectroscopic data for the reactions described (1 page). Ordering information is given on any current masthead page.

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(16) **Synthesis of $[OsCl_2(CO)(CHCH_2CH_3)(P\text{-}i\text{-}Pr_3)_2]$.** In an NMR tube with a Teflon valve, $[OsHCl_2(CCH_2CH_3)(P\text{-}i\text{-}Pr_3)_2]$ (0.0100 g, 0.0181 mmol) was dissolved in approximately 0.5 mL of CD_2Cl_2 under Ar to give an orange solution. The solution was frozen in liquid N_2, evacuated on a vacuum line, and refilled with 1 atm of CO. The solution was thawed and mixed (tumbling) for 14 h, after which time it had turned pale yellow. ^{31}P and ^{1}H NMR spectroscopy both indicated that all of $[OsHCl_2(CCH_2CH_3)(P\text{-}i\text{-}Pr_3)_2]$ had reacted and revealed the presence of a new species formulated as $[OsCl_2(CO)(CHCH_2CH_3)(P\text{-}i\text{-}Pr_3)_2]$. Diagnostic spectra: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 18.62 (tt, $J(HH) = 6.0$ Hz, $J(PH) = 1.2$ Hz, $OsC\mathit{H}CH_2CH_3$); ^{31}P NMR (121.4 MHz, CD_2Cl_2) δ 12.08 (s, $P\text{-}i\text{-}Pr_3$). No hydride signal was present in the ^{1}H NMR spectrum.

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