802 *Organometallics* **2006,** *25,* 802−804

Triple Benzylic Dehydrogenation by Osmium in an Amide Ligand Environment

Joo-Ho Lee, Maren Pink, and Kenneth G. Caulton*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received October 21, 2005

Summary: The three benzylic methyl hydrogens of p-isopropyltoluene (cymene) are cleaved by ligating $N(SiMe_2CH_2P^tBu_2)_2^-$ *to* $[(cymene)OsCl_2]_2$*, to give a carbyne complex; its chemical reactivity with* H_2*, with CO, and with HC≡CH are described.*

Precisely because of the predictive power of the periodic table, deviations from chemical periodicity are exceptionally important. For example, are 4d and 5d transition metals (here Ru and Os) merely carbon copies of each other?

The surprising character of the reaction of $ClMgN(SiMe_2CH_2P^tBu_2)_2$ (ClMg(PNP)) with $[(cymene)RuCl_2]_2$ is that cymene (p-$CH_3C_6H_4{}^iPr$) is expelled, even though what is left behind, (PNP)RuCl, is very electron deficient and has an unusually low coordination number: 4. Further consequences of this low-coordinate and π-basic (i.e. amide) ligand environment are as follows: (PNP)RuCl is planar, has $S = 1$ for a 4d element with six d electrons, and has no agostic interactions.[1,2] In our previous work[3] with monodentate phosphines and with hydride and chloride ligands, systematic comparison of the 4d and 5d analogues Ru and Os revealed that Os (vs Ru) preferred to be saturated (18 valence electrons), was in a higher oxidation state, had more metal−ligand bonds (at the expense of intraligand atom−atom′ bonds), and had a higher coordination number (cf. **A** and **B**).[4] The underlying cause of this difference could be

$$\underset{\mathbf{A}}{\mathrm{Ru^{IV}Cl_2({=}CHR)(PR_3)_2}} \text{ vs } \underset{\mathbf{B}}{\mathrm{Os^{VI}HCl_2({\equiv}CR)(PR_3)_2}}$$

rationalized by saying either that the 5d metal is generally more reducing than the 4d analogue *or* that the 5d metal forms stronger metal−ligand bonds. Against a background of these general principles, we report here an initial look at osmium reaction chemistry with the strongly electron donating, monoanionic PNP ligand. This shows surprising differences from the chemistry with ruthenium that, in hindsight, serve to strengthen the trends summarized above as one goes down the group from Ru to Os.

Reaction of $[(cymene)OsCl_2]_2$ with a source[5] of $[{}^tBu_2PCH_2SiMe_2]_2N^-$ in benzene proceeds to completion in 18 h at 22 °C according to Scheme 1. Differences here from the analogous reaction with ruthenium include loss of both chlorides from the metal, the consumption of *2* mol of amide per Os, and the retention of cymene on Os. One role of the amide reagent is thus to carry away one of the three H atoms which originates from the cymene methyl group. Since "extra" (vs Ru) chloride is also removed from Os, the combined effect of this equivalent of amide is dehydrohalogenation. In contrast to the case for Ru, an 18-electron, chloride-free osmium product results. The product for osmium is a dihydride (one hydride triplet at −1.02 ppm), and the cymene, while it is retained in the product complex, has been triply dehydrogenated exclusively at this ring methyl to produce a carbyne ligand (^{13}C chemical shift 259 ppm). The full ^1H and ^{31}P NMR spectra indicate the product to have C_{2v} symmetry. This was confirmed by X-ray diffraction (Figure 1), which shows the molecule to be six-coordinate and octahedral. Noteworthy features include the long Os−N distance (2.226(2) Å), consistent with the molecule having an 18-valence-electron configuration without any N→Os lone pair π-donation (hence, a single Os−N bond). The presence of a lone pair on the α-atom of the ligand has been termed "π-loaded,"[6] and $(PNP)Os(H)_2(\equiv CAr)$ ($Ar = C_6H_4{}^iPr$) shows an unusual degree of twist of the NSi_2 plane with respect to the P−Os−P plane (transoid dihedral angles P−Os−N−Si = 143.2 and 144.7°), which might serve to diminish the four-electron repulsion with a filled d_π orbital. If the synthetic reaction is carried out in neat toluene, there is no trace of $(PNP)Os(H)_2(\equiv CC_6H_5)$, indicating that the cymene is tightly held to osmium during its dehydrogenation (i.e. the dehydrogenation is intramolecular).

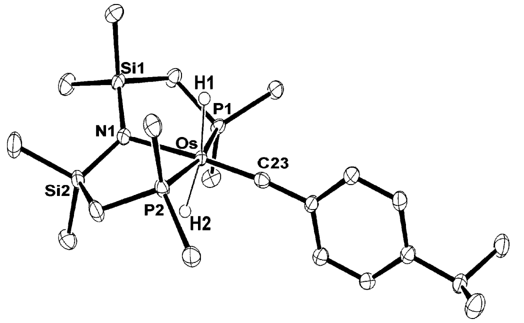


Figure 1. ORTEP drawing (50% probability) of $(PNP)Os(H)_2(CC_6H_4$-p-$^iPr)$ showing selected atom labeling. Only the hydride hydrogens are shown, and unlabeled atoms are carbon. Selected bond lengths (Å) and angles (deg): Os−C23, 1.746(3); Os−P1, 2.3899(7); Os−H1, 1.46(4); Os−H2, 1.52(4); C23−Os−N1, 175.86(10); P1−Os−N1, 83.72(6); P1−Os−P2, 167.10(2); C23−Os−P1, 95.64(8).

Despite the absence of empty orbitals on osmium in $(PNP)Os(H)_2(\equiv CAr)$, this molecule is completely consumed (Scheme 1) in less than 1 h at 22 °C in benzene under 1 atm (i.e. excess) of H_2. The resulting product, $(PNP)Os(H)_3$, shows (^1H and ^{31}P

---

* To whom correspondence should be addressed. E-mail: caulton@indiana.edu.

[1] Watson, L. A.; Ozerov, O. V.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2003**, *125*, 8426−8427.

[2] Walstrom, A. N.; Watson, L. A.; Pink, M.; Caulton, K. G. *Organometallics* **2004**, *23*, 4814−4816.

[3] Caulton, K. G. *J. Organomet. Chem.* **2001**, *617−618*, 56−64.

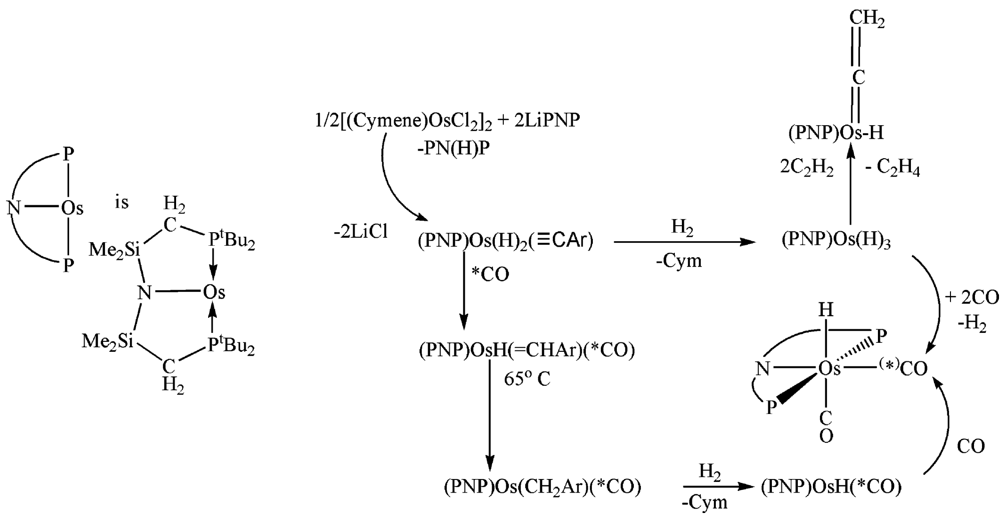
[4] See also: Gusev, D. G.; Lough, A. J. *Organometallics* **2002**, *21*, 2601−2603.

[5] The lithium salt employed has the formula $Li_3Cl(PNP)_2$ (i.e. is ether-free), and it also forms (PNP)RuCl from $[(cymene)RuCl_2]_2$: Fryzuk. M. D.; Giesbrecht. G. R.; Tettig, S. J. *Organometallics* **1997**, *16*, 725.

[6] Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239−482.

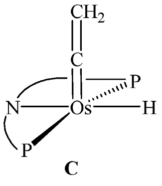
10.1021/om050916k CCC: $33.50

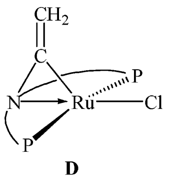
Scheme 1



NMR) C_{2v} symmetry, with the added feature of dynamic averaging of the three hydrides to a single triplet. Free cymene is also detected. Under 1 atm of H_2 in benzene the hydride NMR signal has an unchanged chemical shift but is broadened (36 Hz full width at half-height) at 22 °C, reflecting the operationally unsaturated character of (PNP)Os$(H)_3$ but the low K_{eq} for binding H_2 to this six-coordinate d^4 Os^{IV} center. Consistent with this, under 1 atm of D_2 at 22 °C, the hydride resonance is gone from the ^1H NMR spectrum within 30 min; ^2D NMR of the resulting sample shows the Os$(D)_3$ signal but negligible deuterium at any site of the coordinated PNP ligand, even after 24 h under 1 atm of D_2 at 22 °C.

(PNP)Os$(H)_3$ is completely consumed (Scheme 1) by excess (1 atm) HCCH in less than 30 min in benzene at 22 °C. Two H atoms have been lost to 1 equiv of alkyne, producing ethylene (^1H NMR assay) together with a primary product, (PNP)Os(C=CH_2)H, with mirror symmetry and a unit intensity hydride triplet. The $^{13}C\{^1H\}$ NMR of the product from $H_2{}^{13}C_2$ supports the vinylidene ligand, via chemical shifts of 285.6 (dt, C_α) and 90.7 ppm (C_β, d from $J_{C_a-C_b}$); the $^{31}P\{^1H\}$ NMR of this isotopomer is a doublet of doublets (coupling to C_α and C_β), and the hydride signal is a triplet of doublets (10.8 Hz coupling to C_α). The deuterium NMR of the product from DCCD shows peaks at 0.4 ppm (=C=CD_2) and −16 ppm (Os−D), indicating scrambling of hydride with acetylene protons at some point in the reaction. The preferred vinylidene structure for Os (**C**) is


C


D

thus in contrast with that for Ru[2] (**D**), a distinction which is also reported for the phenyl-based pincer ligand 2,6-$(CH_2PR_2)_2C_6H_3$ on these two metals.[7]

(PNP)Os$(H)_2$(≡CAr) reacts completely with 1 atm of CO within 10 min at 22 °C in benzene (Scheme 1). The product, (PNP)OsH(=CHAr)(CO), has mirror symmetry (e.g. 2 equiv of P) but no second symmetry element: two ^{t}Bu virtual triplets and two SiMe singlets by ^1H NMR. One hydride triplet of doublets has unit intensity, and the second former hydride proton now appears as a triplet (P) of doublets (from Os−H) at +19.5 ppm, a chemical shift generally indicative of H directly bound to a carbene carbon. Carbene (269.6 ppm) and CO (194.9 ppm) chemical shifts are also evident. The high rate of this *addition* to saturated osmium in (PNP)Os$(H)_2$(≡CAr) suggests that there is some preequilibrium to produce a kinetically significant concentration of unsaturated (PNP)OsH[=C(H)Ar], and this is what actually is attacked by CO. This rearrangement also increases the d electron count (i.e. reduces Os), enhancing the back-donating potential toward CO.

Over 4 h at 65 °C in benzene solution under argon (Scheme 1), the carbene complex transforms completely into a product with no hydride or carbene =CH ^1H NMR signal, but with an intensity 2 ^1H NMR signal at 4.76 ppm. In this species, (PNP)Os(CH_2Ar)(CO), the CO stretching frequency has decreased to 1865 cm^{-1} from the value in the carbene carbonyl (1991 and 1963 cm^{-1}).

With similar facility, operationally unsaturated (PNP)Os$(H)_3$ is consumed by 1 atm (i.e. excess) of CO in benzene at 22 °C within 30 min to liberate H_2 (^1H NMR detection) and form (PNP)OsH$(CO)_2$, identified by a hydride triplet, by diastereotopic ^{t}Bu, CH_2, and SiMe proton NMR signals, and by CO vibrational frequencies at 1963 and 1898 cm^{-1} (Scheme 1). The $^{31}P\{^1H\}$ NMR singlet becomes a doublet on selective hydride coupling. Elimination of H_2 is a typical consequence of binding a π-acidic ligand (CO) to a polyhydride due to depletion of metal electron density needed to keep H at the monoatomic H^- (vs H_2) oxidation state. It is thus interesting that this does *not* occur for CO reacting with PNPOs$(H)_2$(≡CAr).

Reaction of (PNP)Os$(^{13}CO)(CH_2Ar)$ with 1 atm of H_2 (excess) in benzene produces (PNP)OsH(^{13}CO) and free cymene within 30 min at 22 °C (Scheme 1). The selectively hydride coupled ^{31}P NMR spectrum (dd, coupled to ^{13}CO and Os*H*) shows the product to be a monohydride. In addition, the very negative chemical shift (−29.4 ppm) of the monohydride indicates that there is a vacancy trans to the hydride. The full ^1H and ^{31}P NMR spectra show that the resulting product has C_s symmetry. Under 1 atm of H_2, the signal at 4.1 ppm (dissolved H_2) is broadened, as is the hydride signal, but without change in chemical shifts. Addition of excess isotopically normal CO (1 atm, 22 °C) to this monocarbonyl forms (PNP)OsH(^{13}CO)(CO) (Scheme 1). The change in the hydride chemical shift to −4.8 ppm indicates that one CO is now trans to the hydride. The ^1H and ^{31}P NMR chemical shifts show that the resulting product is the same as that from the reaction of (PNP)Os$(H)_3$

---

[7] Wen, T. B.; Cheung, Y. K.; Yao, J.; Wong, W.-T.; Zhou, Z. Y.; Jia, G. *Organometallics* **2000**, *19*, 3803−3809.

with CO. ^{13}C NMR (187.4 ppm as a natural-abundance doublet of triplets and 183.5 ppm as a strong, ^{13}C-enriched triplet), ^{1}H NMR (Os−H, doublet of triplets), and ^{31}P{^{1}H} NMR (one doublet) show that there is no scrambling of CO. Comparison of the ^{13}CO coupling constants (J_{CH}) of (PNP)OsH(^{13}CO) (10.8 Hz)and (PNP)OsH(^{13}CO)(CO) (6 Hz) indicates that ^{13}CO occupies the site cis to hydride in the latter compound (Scheme 1); thus, the reaction is stereoselective.

The reactions of (PNP)Os(H)$_2$(≡CAr) and of (PNP)Os(H)$_3$ reported here all occur unusually quickly for the normally kinetically sluggish six-coordinate osmium. We suggest that this originates from a combination of operational unsaturation[8,9] (from the amide N lone pair) and a facile hydride migration from Os to the carbyne C. In addition, all of these results support the generalizations at the beginning of this paper regarding contrasts between Ru and Os. The cleavage of H−C(sp^3) bonds effected here by Os suggests there might be potential for use of operationally unsaturated Os complexes for nonphotochemical alkane dehydrogenation at or near 20 °C.[10−12]

Acknowledgment. This work was supported by the NSF.

Supporting Information Available: Crystallographic details, as a CIF file, for the carbyne complex and text and figures giving full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050916K

---

(8) Merle, N.; Koicok-Kohn, G.; Mahon, M. F.; Frost, C. G.; Ruggerio, G. D.; Weller, A. S.; Willis, M. C. *Dalton Trans.* **2004**, 3883−3892.

(9) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190−3191.

(10) Esteruelas, M. A.; Lopez, A. M. *Organometallics* **2005**, *24*, 3584−3613.

(11) Baya, M.; Buil, M. L.; Esteruelas, M. A.; Onate, E. *Organometallics* **2004**, *23*, 1416−1423.

(12) Barrio, P.; Castarlenas, R.; Esteruelas, M. A.; Onate, E. *Organometallics* **2001**, *20*, 2635−2638.