Generation of Coordinative Unsaturation at Osmium via Ring-Opening Equilibration of a 2-Pyridonato Chelate Complex

Thomas C. Flood,* John K. Lim, and Mark A. Deming

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0744

Received February 1, 2000

Ring opening of a strained chelate complex of osmium has been investigated as a means to transient coordinative unsaturation under mild conditions in normally kinetically inert, third-row, platinum-group metals. *cis*-$L_4Os(H)(NC_5H_4X)$ (L = PMe_3; X = O (**1**), NH (**2**), S (**3**)) were prepared by treatment of *fac*-$L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ with 2-$(HX)C_5H_4N$. An X-ray structure determination establishes **1** to be the κN tautomer with the keto group pointed away from the hydride and toward the PMe_3 ligand trans to hydride. NMR spectra support the κN structure in solution. Which nitrogen is coordinated in **2** is not established, but NMR supports the κS tautomer of **3** in solution. At 80 °C in C_6D_6, **1** incorporates **L′** ($P(CD_3)_3$) in a first-order reaction ($t_{1/2} \approx 14$ min) stereospecifically at site *b* (trans to hydride) with $\Delta H^{\ddagger} = 26.9 \pm 1.4$ kcal/mol and $\Delta S^{\ddagger} = 3.8 \pm 4.4$ eu for the substitution. Complex **2** at 80 °C also exchanges with **L′** only in site *b*, but more slowly than **1** ($t_{1/2} \approx 3.5$ h). Sublimation of **1** at 55 °C under vacuum yields *mer*-$L_3Os(H)(NC_5H_4O\text{-}\kappa^2N,O)$ (*mer*-**4**), believed to have *mer*-**4**-(HON) geometry (H trans to nitrogen). In toluene at reflux **1** loses L, forming *fac*-**4**. Heating *mer*-**4** in benzene 3 h at 110 °C forms *fac*-**4**. At 22 °C, **L′** adds to *fac*-**4** with $t_{1/2} \approx 3$ h, generating pure $(\mathbf{L}_a')(L_a)(L_b)(L_c)Os(H)(NC_5H_4O\text{-}\kappa N)$, which then undergoes the much slower exchange with **L′** typical of **1** specifically forming $(\mathbf{L}_a')(L_a)(\mathbf{L}_b')(L_c)Os(H)(NC_5H_4O\text{-}\kappa N)$. Reaction of *mer*-**4** with excess **L′** in ca. 2 h generates *trans*-$L_3\mathbf{L}'Os(H)(NC_5H_4O)$ then *trans*-$\mathbf{L}'_4Os(H)(NC_5H_4O)$ over 10 h, and finally *cis*-$\mathbf{L}'_4Os(H)(NC_5H_4O\text{-}\kappa N)$ over 10 days. A scheme is presented that correlates all of the above transformations. Several reactions of *fac*-**4** were examined. *fac*-**4** and CO_2 (10 atm, benzene-d_6, 80 °C, 1 h) afforded *fac*-$L_3Os(\kappa^1\text{-}O_2CH)(\kappa^2\text{-}NC_5H_4O)$, **5**. Heating pure **5** in C_6D_6 (110 °C, 2 h) regenerated **4**. Reaction of *fac*-**4** with D_2 gas (0.84 atm, C_6D_6, 80 °C) caused formation of Os-D with no other changes. *fac*-**4** in neat 1-hexene (80 °C, 17 h) gave *fac*-$L_3Os(n\text{-hexyl})(\kappa^2\text{-}NC_5H_4O)$ (**6**) quantitatively, while *fac*-**4** under 1 atm of ethylene (C_6D_6, 80 °C, 36 h) gave *fac*-$L_3Os(ethyl)(\kappa^2\text{-}NC_5H_4O)$ (**7**) quantitatively. Heating **6** in C_6D_6 at 80 °C for 48 h gave *fac*-**4** back again with a mixture of hexene isomers with a 2:1 terminal:internal alkene ratio. Heating **7** (C_6D_6, 80 °C) also regenerated **4** and ethylene. Heating at 80 °C for 7 days of a sample containing 1-hexene in C_6D_6 solvent and 5 mol % of *fac*-**4** under 1 atm of hydrogen gas quantitatively gave hexane, while **4** remained unchanged. This is a substantial increase in reactivity over $L_4Os(H)_2$ through the use of the strained chelate.

Introduction

The anion of 2-pyridone has been known for many years as an effective ligand for bridging two metals, and there is an abundance of this chemistry in the literature.[1] In contrast, the κ^2-pyridonato ligand as a chelate on one metal is rare,[2] and reports are all structural with no information on reactivity. We have been examining possible methods for the transient generation of coordinate unsaturation in organo-osmium phosphine complexes as representatives of normally kinetically inert, third-row, platinum-group metals.[3] Previously it was found that $P(CD_3)_3$ (**L′**) is an excellent label with which to measure rates and stereochemistry of PMe_3 dissociation from these complexes.[4] It was shown that the isotope effect on ^{31}P NMR chemical shifts exhibited by $P(CH_3)_3$ vs $P(CD_3)_3$ provides a convenient way to monitor phosphine dissociation rates at specific geometric sites. In this way, we have seen that $L_4Os(H)_2$ and $L_4Os(H)(C_6H_5)$ require temperatures in the range of

(1) (a) Rawson, J. M.; Winpenny, R. E. P. *Coord. Chem. Rev.* **1995**, *139*, 313. (b) Parsons, S.; Winpenny, R. E. P. *Acc. Chem. Res.* **1997**, *30*, 89.

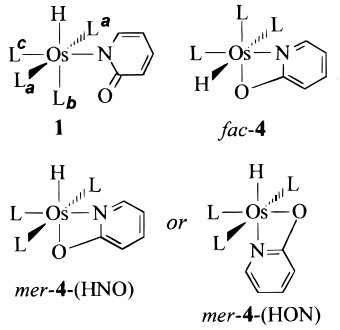
(2) (a) Clegg, W.; Berry, M.; Garner, C. D. *Acta Crystallogr., Sect. B* **1980**, *36*, 3110. (b) Rodman, G. S.; Mann, K. R. *Inorg. Chem.* **1985**, *24*, 3507. (c) Morrison, E. C.; Palmer, C. A.; Tocher, D. A. *J. Organomet. Chem.* **1988**, *349*, 405. (d) Lahuerta, P.; LaTorre, J.; Sanau, M.; Cotton, F. A.; Schwotzer, W. *Polyhedron* **1988**, *7*, 1311.

(3) Flood, T. C.; Lim, J. K.; Deming, M. A.; Keung, W. *Organometallics* **2000**, *19*, 1166.

(4) (a) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 7964. (b) Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *Organometallics* **1989**, *8*, 1377. (c) Shinomoto, R. S.; Desrosiers, P. J.; Harper, T. G. P.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704. (d) Harper, T. G. P.; Desrosiers, P. J.; Flood, T. C. *Organometallics* **1990**, *9*, 2523.

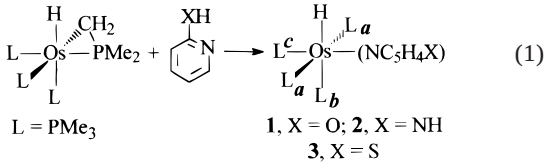
10.1021/om000077w CCC: $19.00
Publication on Web 05/10/2000

150−160 °C to compel exchange with first-order rate constants of about 10^{-4} s^{-1},[4c] $L_4Os(H)Me$, at 105 °C;[4a] $L_4Os(H)$(neopentyl), 80 °C;[4a] $L_4Os(H)(OC_6H_5)$, 105 °C;[3] $L_4Os(H)(SC_6H_5)$, 80 °C;[3] and $L_4Os(H)(NHC_6H_5)$, at 80 °C.[3] Lone pairs in the anilido and thiophenoxy ligands in particular labilize PMe_3 dissociation. Another obvious method to generate unsaturation would be to incorporate ring strain in a chelate. For this purpose, α-heteroatom-substituted pyridines were selected and their complexes $L_4Os(H)(NC_5H_4X)$ (X = O (**1**), NH (**2**), S (**3**)) were prepared. Pyridonato chelates *fac*-**4** and *mer*-**4** were generated, and their chemistry was examined.



Results and Discussion

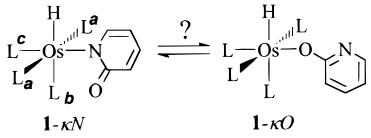
Synthesis of $L_4Os(H)(NC_5H_4X)$. The target molecules were prepared by treatment of the known[5] cyclometalated complex $L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ with the appropriate aromatic precursor (eq 1). Acid cleavage



(1)

reactions of this complex are well-known.[4a,5,6] The relative reactivities of the arenes parallel their acidities in that 2-mercaptopyridine reacts within 5 min at ambient temperature, pyridone requires about 20 min at 80 °C, and 2-aminopyridine requires heating at 80 °C for 40 h for complete reaction.

Structure and Bonding of the 2-Pyridonato Osmium Complex 1. 2-Pyridone itself exists in two tautomeric forms: the lactam (2-(1H-pyridone) and the lactim (2-hydroxypyridine). Which tautomeric isomer dominates the equilibrium depends on conditions, but in general, the equilibrium constant is close to 1.[7] A priori, one might expect the κ*N* tautomer of **1** to have an intrinsically stronger bond, but to be more crowded than the κ*O* isomer, so the bonding mode of the 2-pyridonato ligand cannot be convincingly predicted. NMR spectroscopy gives a reasonably good indication as to the solution structure of **1**. The chemical shifts of the $^{31}P\{^1H\}$ resonances of the mutually trans phosphines (site *a*) of phenoxido compounds *cis*-$L_4Os(H)(OC_6H_4X)$ (X = H, OMe, CF_3, NH_2, CN), all in C_6D_6 solvent, range between δ −35.9 and −36.9 ppm,[3] while those of anilido compounds *cis*-$L_4Os(H)(HNC_6H_4X)$ (X = H, CF_3, OMe) are located further upfield in the range of δ −41.5 to −42.2 ppm.[3] The site *a* phosphine resonance of **1** is in the latter range at δ −42.18 ppm. The coupling constants $^2J_{P_bP_c}$ of the mutually cis phosphines L_b and L_c have slightly different values for phenoxido (5.3−6.6 Hz) versus anilido complexes (8.5−9.4 Hz). Pyridonato complex **1** has $^2J_{P_bP_c}$ = 8.0 Hz for L_c at δ −50.52 (cis to H) and L_b at −57.65 ppm (trans to H). In addition, the ^1H hydride chemical shifts of the phenoxido complexes are all between δ −7.8 and −8.2 ppm, while those of the anilido complexes are between δ −8.3 and −8.7 ppm. That of **1** is δ −9.80 ppm. Taken together, these data suggest that **1** has the κ*N* structure in solution. An X-ray crystal structure confirms the fact that complex **1** is κ*N* in the solid as well (see below).



(2)

In view of the fact that we have used spectral data of *cis*-$L_4Os(H)(HNC_6H_4X)$ as a model for the spectra of *cis*-$L_4Os(H)(NC_5H_4O\text{-}\kappa N)$ (**1**), we would not expect to differentiate the bonding modes for *cis*-$L_4Os(H)(NHC_5H_4N)$ (**2**) in this way. Its relevant NMR data (C_6D_6 solvent) are as follows: ^{31}P mutually trans L_a δ −42.39 ppm; $^2J_{P_bP_c}$ of the mutually cis phosphines 9 Hz; ^1H hydride chemical shift δ −8.80 ppm. The data for *cis*-$L_4Os(H)(SC_5H_4N)$ (**3**), however, are quite clear (C_6D_6 solvent): ^{31}P mutually trans L_a δ −49.35 ppm; $^2J_{P_bP_c}$ of the mutually cis phosphines 13 Hz; ^1H hydride chemical shift δ −9.39 ppm. When compared to the data for *cis*-$L_4Os(H)(SC_6H_4X)$ (X = H, OMe) (C_6D_6 solvent): ^{31}P mutually trans L_a δ −49.61 and −50.37 ppm; $^2J_{P_bP_c}$ of the mutually cis phosphines 13 and 12 Hz; ^1H hydride chemical shift δ −9.50 and −9.50 ppm, respectively;[3] the data point to the κ*S* isomer, as would be expected from the greater bonding affinity of sulfur for the heavy metals.

Crystal Structure of *cis*-$L_4Os(H)(NC_5H_4O\text{-}\kappa N)$ (1). Crystals of $L_4Os(H)(NC_5H_4O)$ were formed by slow evaporation of pentane from a solution of **1** at −15 °C. There was a space group ambiguity in the collected data of either *Cc* or *C*2/*c*. Partial solution was carried out in the space group *Cc* and then in *C*2/*c*, wherein the remaining atoms were located and refined. Still, some of the Os−P−C bond angles and distances of the mutually trans phosphines and some of the ring distances were unreasonable, and several large residual electron density peaks were still present. Constraining the ring bond distances and angles as well as the bond distances of the mutually trans phosphines and subsequent refinement led to a final *R* factor of 4.6%. It may be that the residual atom peaks are the result of a packing disorder in which the ring and the mutually trans phosphines are interchanged at some lattice sites. The hydride ligand was not located, so its position was

(5) Werner, H.; Gotzig, J. *Organometallics* **1983**, *2*, 547.
(6) Desrosiers, P. J.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *Organometallics* **1989**, *8*, 2861.
(7) (a) Hatherley, L. D.; Brown, R. D.; Godfrey, P. D.; Pierlot, A. P.; Caminati, W.; Damiani, D.; Melandri, S.; Favero, L. B. *J. Phys. Chem.* **1993**, *97*, 46. (b) Nowak, M. J.; Lapinski, L.; Fulara, J.; Les, A.; Adamowicz, L. *J. Phys. Chem.* **1992**, *96*, 1562. (c) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 1645, and references therein.

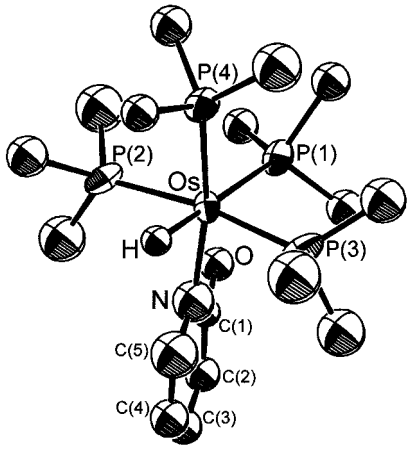
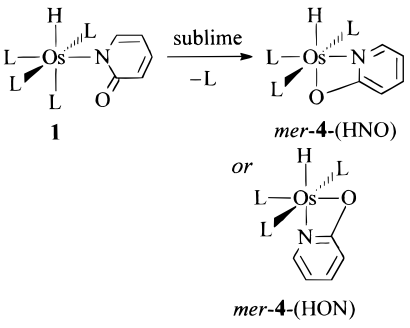


Figure 1. ORTEP drawing of *cis*-$L_4Os(H)(NC_5H_4O$-$\kappa N)$ (**1**). The hydrogen was not located.

calculated using data from a neutron diffraction study of $H_4Os(PMe_2Ph)_3$.[8]

Although the overall quality of the structure determination was rather poor, the final result was adequate to establish the basic structure and conformation of **1**, and it gave some surprising information. As mentioned above, the most notable feature is that the 2-pyridonato ligand is bound by the nitrogen atom to the osmium metal center (Figure 1), as inferred for the solution structure from spectroscopic data. Given that the ligand is κN bound, for steric reasons we would have expected the oxygen atom of the keto group to be turned in the direction of the Os−H bond. Instead, as illustrated in Figure 1, the oxygen atom faces toward the phosphine trans to the hydride, although the ring is slightly canted from the plane defined by P(1), P(4), H, and Os. It is possible that the conformation in the crystal is not dominant in solution, but it must certainly be accessible. As discussed below, this orientation positions the oxygen atom for coordination to the metal in the event of dissociation of the phosphine trans to the hydride (L_b).

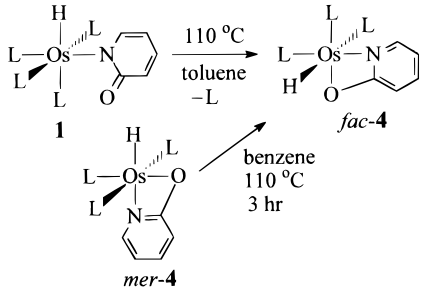
Synthesis of *mer*- and *fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ (4). Sublimation of white, powdery $L_4Os(H)(NC_5H_4$-O-$\kappa N)$ (**1**) under dynamic vacuum over a period of several days at 55 °C yielded *mer*-tris(trimethylphosphine)(hydrido)(2-pyridonato-$\kappa^2 N,O$)osmium(II) (*mer*-**4**) (eq 3). The bright yellow sublimate comprised a mixture



(3)

of the starting material and *mer*-**4**, so the sublimation was repeated several times until no **1** remained. The *mer*-**4**, obtained in an overall yield of about 50%, contained a few percent of the fac isomer. The ^{31}P NMR spectrum of *mer*-**4** exhibits a doublet centered at δ −27.80 ppm and a triplet at −43.26 ppm with relative integrals of 2:1 and $J_{PP} = 16$ Hz. The hydride resonance in the ^1H NMR spectrum is a doublet of triplets centered at δ −17.8 ppm. Whether the material is the HNO isomer or the HON isomer could not be determined crystallographically because attempts to harvest the delicate, spindle-like crystals from recrystallization caused them to break down into powder. For reasons discussed below, it is believed that the isolated mer complex probably has the HON geometry; so to simplify the presentation it is hereafter shown as **4**-(HON).

Heating a solution of $L_4Os(H)(NC_5H_4O$-$\kappa N)$ (**1**) in toluene at reflux for several days under a gentle stream of purified nitrogen gas to remove L led to a change of the solution from colorless to bright yellow. Removal of toluene left *fac*-**4** as a bright yellow powder (eq 4). As



(4)

in the case of *mer*-**4**, attempts to recover crystals of *fac*-**4** were unsuccessful due to their fragility. The ^{31}P NMR spectrum of *fac*-**4** exhibits an ABX pattern of three sets of doublet of doublets at δ −32.6, −33.0, and −37.2 ppm. Lowering the proton decoupling frequency decouples any C−H hydrogens from the phosphorus nuclei but leaves the Os−H hydrogen largely coupled. In this way it was established that the PMe_3 group whose resonance is at δ −32.6 ppm is trans to the hydride because its J_{PH} is substantially larger than the other two. The ^1H NMR hydride resonance was a doublet of triplets at δ −3.61 ppm, 14 ppm downfield from the location of the hydride in *mer*-**4**.

Over a period of several weeks at ambient temperature, a benzene solution of *mer*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ (*mer*-**4**) gradually converts to *fac*-**4**. Quantitative *mer*-**4** → *fac*-**4** isomerization occurs in less than 3 h at 110 °C in benzene in a sealed tube (eq 4). A good C, H, and N combustion analysis of *fac*-**4** completed its characterization. Since it was not possible to obtain a sample of *mer*-**4** free of *fac*-**4**, combustion analysis of *mer*-**4** was not carried out. The mer-to-fac conversion is quantitative by NMR, with no liberation of L or requirement for L, and the ^1H and ^{31}P spectra of both isomers are very clean and characteristic. In addition, all of the reactions presented below (e.g., L, CO_2, and ethylene uptake) give fully characterized products in quantitative yields (by NMR) whether using pure *fac*-**4** or various mixtures of *mer*-**4** and *fac*-**4**. Thus, the conclusion that the two are geometric isomers is well founded.

Ligand Exchange and Addition Reactions of 1 and 4 with $P(CD_3)_3$ (L′). At 80 °C in an inert solvent such as benzene, incorporation of **L′** ($P(CD_3)_3$) into *cis*-$L_4Os(H)(NC_5H_4O$-$\kappa N)$ (**1**) proceeds in a cleanly first-order manner with $k = (8.01 \pm 0.16) \times 10^{-4}$ s^{-1} ($t_{1/2} \approx$ 14 min). The exchange is highly stereospecific, occurring

(8) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557.

exclusively at site *b* (trans to hydride) to over 90% reaction. The ^{31}P NMR spectrum of exchanged **1** shows this specificity clearly by the isotopic shift of the doublet of triplets resonance for the L ($P(CH_3)_3$) at δ −57.65 ppm upfield by about 2 ppm for the corresponding **L′** ($P(CD_3)_3$). That this resonance corresponds to the phosphine trans to the hydride can be shown unambiguously from a selective, off-resonance decoupled, ^{31}P NMR spectrum, where this resonance is split by the hydride with a J_{PH} of 78 Hz, while the other two resonances exhibit much smaller coupling with the hydride (22 Hz). This stereospecificity is in stark contrast to phosphine ligand exchange patterns observed in anilido complexes *cis*-$L_4Os(H)(p\text{-}HNC_6H_4X)$ (X = H, OMe, CF_3),[3] where exchange occurs in the mutually trans *a* sites and trans to the heteroatom in site *c*. Phenoxides *cis*-$L_4Os(H)(OC_6H_4X)$ (X = H, OMe, CF_3, NH_2, CN) exchange phosphines in all sites independently.[3] Thus, there are distinctly different mechanistic pathways among the 2-pyridonato, phenoxido, and anilido osmium compounds with regard to both the rate and substitution pattern for phosphine ligand exchange. The rates of incorporation of labeled phosphine ligand were measured at various temperatures: 17.5 °C, 1.95×10^{-7} s^{-1}; 50 °C, 3.50×10^{-5} s^{-1}; 60 °C, 1.24×10^{-4} s^{-1}; 80 °C, 8.01×10^{-4} s^{-1}. An Arrhenius plot yielded $\Delta H^{\ddagger} = 26.9 \pm 1.4$ kcal/mol; $\Delta S^{\ddagger} = 3.8 \pm 4.4$ eu. The rather small value of $\Delta S^{\ddagger}$ would be consistent with a mechanism of L exchange that is dissociative but with an early transition state. In addition, if the oxygen of the pyridonato ligand were to coordinate more or less simultaneously with the loss of L, formation of the chelate coordination could entail a negative contribution to the transition state entropy that could reduce the size of the positive $\Delta S^{\ddagger}$. Note that such oxygen coordination would form the *mer*-**4**-HNO isomer, assuming simple ligand loss and oxygen coordination at the same site with no more complicated reversible rearrangement.

Exchange in *cis*-$L_4Os(H)(NHC_5H_4N)$ (**2**) with **L′** also stereospecifically forms *cis*-$(L_a)_2(\mathbf{L_b'})(L_c)Os(H)(NHC_5H_4N)$, but with $t_{1/2} \approx 3.5$ h compared with $t_{1/2} \approx 14$ min for **1**.

Reaction of *fac*-$L_3Os(H)(\kappa^2\text{-}NC_5H_4O)$ (*fac*-**4**) with **L′** at ambient temperature results in opening of the chelate with uptake of one **L′** to form labeled **1**. The **L′** is incorporated specifically at only one of the mutually trans *a* sites with $t_{1/2} \approx 3$ h. Subsequently, $(\mathbf{L_a'})(L_a)(L_b)(L_c)Os(H)(NC_5H_4O\text{-}\kappa N)$ undergoes much slower exchange of **L′** into site *b* as described before. A very specifically di-labeled $(\mathbf{L_a'})(L_a)(\mathbf{L_b'})(L_c)Os(H)(NC_5H_4O\text{-}\kappa N)$ is the result. No additional incorporation of any **L′** into the second mutually trans *a* site or into site *c* (cis to hydride) could be detected. The $(\mathbf{L_a'})(L_a)$ substitution pattern is unmistakable since the two strongly coupled phosphines ($J_{PP} \approx 270$ Hz) are now at chemical shifts that differ by ca. 2 ppm, and so a distinctive AB coupling pattern is observed. This pattern is distinct from any $(L_a)_2$ and $(\mathbf{L_a'})_2$ resonances, which are not present in this case.

Reaction of *mer*-$L_3Os(H)(\kappa^2\text{-}NC_5H_4O)$ (*mer*-**4**) with **L′** in 2 h at room temperature generates a new species with a hydride resonance visible in its ^{1}H NMR spectrum at δ −20.65 (pentet) that is assigned the structure *trans*-$L_3\mathbf{L'}Os(H)(NC_5H_4O)$. We cannot tell whether the pyridonato ligand is κN or κO. The ^{31}P NMR exhibits a rather complex set of resonances between −47 and −51 ppm initially, but the molecule continues to exchange its phosphine ligands with the result that over 10 h the ^{31}P resonance gradually converts to a broad singlet near δ −50 ppm for *trans*-$\mathbf{L'}_4Os(H)(NC_5H_4O)$ as the resonance for free L increases. The broad singlet gradually diminishes over about 10 days and transforms to the pattern of *cis*-$\mathbf{L'}_4Os(H)(NC_5H_4O\text{-}\kappa N)$, establishing the thermodynamic preference for the latter isomer.

To provide additional evidence for the proposed trans intermediate, ^{31}P NMR spectra of all of the *trans*-$(L)_n(\mathbf{L'})_{4-n}Os(H)(NC_5H_4O)$ exchange isotopomers were calculated using a standard computer simulation program. The experimental exchange spectra at different times were well modeled by superimposed combinations of the simulated $(L)_n(\mathbf{L'})_{4-n}Os(H)(NC_5H_4O)$ spectra in different proportions. See the Experimental Section for details.

Energy Surface for $L_4Os(H)(NC_5H_4O)$ and $L_3Os(H)(NC_5H_4O)$ + L Interconversions. Overall, the above observations are: (1) **1** exchanges with **L′** only in site *b* (trans to hydride) presumably via *mer*-**4**(HNO); (2) removal of L from **1** during sublimation gives *mer*-**4**; (3) removal of L from **1** heating in solution gives *fac*-**4**; (4) warming *mer*-**4** in the absence of L gives *fac*-**4**; (5) addition of L to *mer*-**4**(HON) gives *trans*-**1**; (6) *trans*-**1** converts to *cis*-**1**, quantitatively; (7) *trans*-**1** exchanges L much faster than it converts to *cis*-**1**; (8) *fac*-**4** and **L′** give only *cis*-$(\mathbf{L_a'})(L_a)(L_b)(L_c)Os(H)(NC_5H_4O\text{-}\kappa N)$. Our inferences are summarized in Figure 2, where the free energies are from rate constants or estimated reaction half-lives at room temperature (∼22 °C). The figure is qualitative in view of the crudity of some of the estimates. Observations 2, 3, and 4 above establish that *mer*-**4** is the kinetic product of L removal, while *fac*-**4** is the thermodynamic product. It is most reasonable to assume that oxygen coordination occurs during exchange of **L′** into site *b* of **1** (observation 1). In the absence of some complicated reversible reorganization and given the solid-state structure of **1**, oxygen coordination would require that the intermediate be *mer*-**4**(HNO). At the same time, observation 5 is that addition of **L′** to the *isolated* mer isomer generates *trans*-$(L)_n(\mathbf{L'})_{4-n}Os(H)(NC_5H_4O)$, not *cis*-$(L_a)_2(\mathbf{L_b'})(L_c)Os(H)(NC_5H_4O\text{-}\kappa N)$. We believe these observations require that the mer intermediate in substitution of **1** and the isolated mer isomer *be different from one another*. Thus, we assign the isolated mer isomer the **4**(HON) structure. When $L_4Os(H)(OC_5H_4N\text{-}\kappa N)$ (**1**) was heated in a sealed tube at 80 °C for 8 h in toluene-d_8, ^{31}P NMR showed ca. 2% of *fac*-$L_3Os(H)(OC_5H_4N\text{-}\kappa^2 N,O)$ (*fac*-**4**). The amount of L liberated is difficult to quantitate because of the vapor space in the NMR tube, but an approximate equilibrium constant is 2×10^{-5}, which puts *fac*-**4** + L approximately 8 kcal/mol above *cis*-**1**.

All of the transformations in Figure 2 are substitutions and/or isomerizations. It is not known where along the mechanistic continuum the mechanism of each substitution lies—dissociative (D), interchange (I_d or I_a), or associative (A). However, in these crowded d^6 complexes D or I_d paths are most likely and give a model that most easily accommodates the data. Dissociative reactions would involve discrete intermediates **A**, **B**, and **C**, and these would most readily account for the isomerization reactions as well.

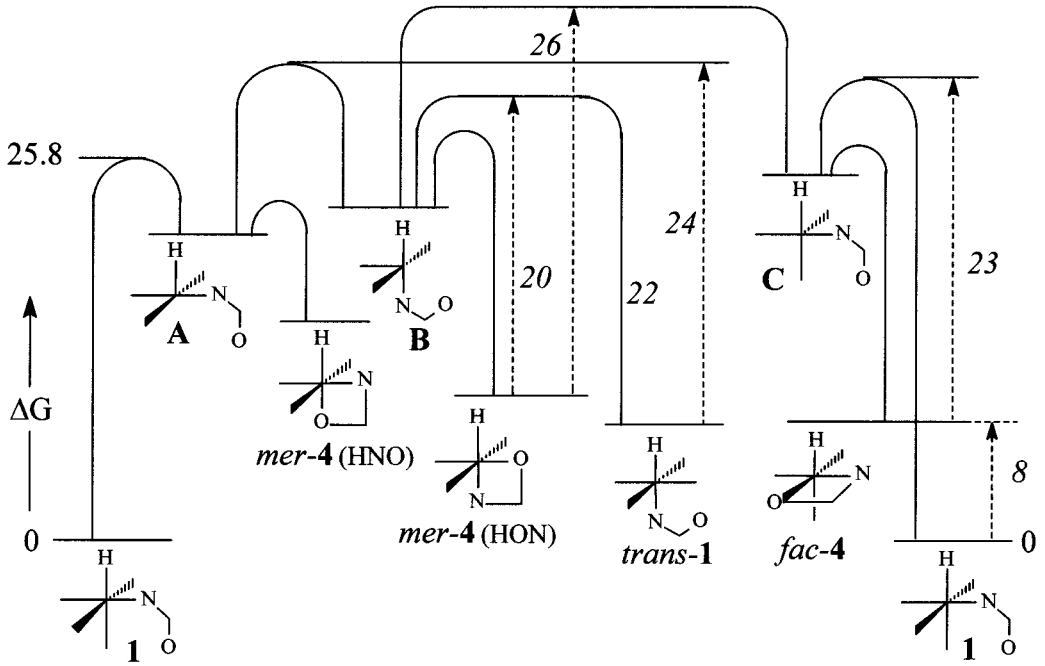
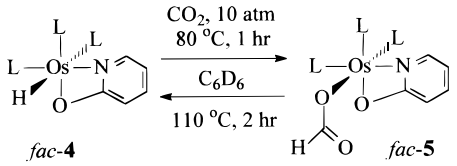


Figure 2. Qualitative free energy diagram for the proposed mechanisms of interconversions of $L_4Os(H)(NC_5H_4O)$ and $L_3Os(H)(NC_5H_4O)$ + L at 22 °C. Italicized numbers are for estimated rates or equilibria. See text for discussion.

In view of the dominance of bridging behavior of the pyridonate ligand with metals,[1] one must consider whether dinuclear or possibly larger clusters might be present in this system. Such intermediates cannot be ruled out, but their intervention is not required by the data, and they would only add difficult-to-accommodate complications to the scheme. We believe both isomers of **4** are monomeric since they sublime readily, and during isomerization and addition of L they shown no evidence of mixed intermediates. For example, there is no evidence of a dimeric *fac,mer*-**4** intermediate. In the addition reactions of CO_2, ethylene, and hexene (below) there is also no evidence of a monoaddition dimeric intermediate.

Reactions of *fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ (*fac*-4). The original motivation for preparation of *fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ (*fac*-**4**) was to determine whether it would be stable enough to handle easily, but reactive enough to show useful reactivity under conditions much milder than those generally available to inert, third-row metal complexes. It was predicted that such mild reactivity would have its origins in chelate ring strain and either the heterolytically weak Os−O bond or cis labilization from the oxygen π-symmetry lone pair. In the above sections have been described the preparation and substantial thermal stability of *fac*-**4**. In addition, the considerable facility with which *fac*-**4** adds PMe_3 to form $L_4Os(H)(NC_5H_4O$-$\kappa N)$ (**1**) suggests the ready availability of a site of unsaturation. The following sections describe several reactions of *fac*-**4** that illustrate its reactivity.

Reaction of *fac*-4 with CO_2. The activation of carbon dioxide has been of interest over the years, and, in this context, insertions of CO_2 into metal−hydride and metal−alkyl bonds have been widely investigated.[9] Insertions of CO_2 into metal−hydride bonds usually result in generation of formate complexes. On treatment of *fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ (*fac*-**4**) with 10 atm of CO_2 in benzene-d_6 at 80 °C in a sealed NMR tube, formation of the formato complex *fac*-$L_3Os(\kappa^1$-$O_2CH)(\kappa^2$-$NC_5H_4O)$, **5**, was observed within an hour. Formate resonances



(5)

are seen at δ 7.99 ppm in the ^1H NMR spectrum and δ 167.36 ppm in the ^{13}C spectrum with J_{CH} = 193 Hz. A new set of facial ABC ^{31}P resonances at δ −30.5, −35.8, −38.4 ppm replaces those of the starting material, and the starting *fac*-**4** hydride resonance at δ −3.61 ppm disappears as product forms. The spectral data assigned to the formato group compares closely to that of known formate complexes.[9,10] Relaxation delays in excess of 60 s were necessary to accurately integrate the formate C and H resonances, consistent with the long relaxation times observed in organic formates.

Reversibility of the CO_2 insertion was demonstrated by heating isolated **5** in C_6D_6 in a sealed tube. The exclusive product after 2 h at 110 °C was *fac*-$L_3Os(H)$-$(\kappa^2$-$NC_5H_4O)$ (**4**). Upon standing at ambient temperature for about a week, a significant quantity of the $^{31}P\{^1H\}$ resonances were again those of formato complex **5**. Thus, the equilibrium constant for CO_2 insertion is not far from 1.0.

Reaction with $^2H_2$. The reaction of *fac*-$L_3Os(H)$-$(\kappa^2$-$NC_5H_4O)$ with deuterium gas (0.84 atm) was monitored by observing the disappearance of the ^1H hydride resonance at δ −3.62 ppm. The facial AMX $^{31}P\{^1H\}$ resonance pattern progressively broadened as *fac*-L_3Os-$(D)(\kappa^2$-$NC_5H_4O)$ formed. A plot of $\ln([\mathbf{4}]/[\mathbf{4}]_o)$ vs time was

(9) Leitner, W. *Coord. Chem Rev.* **1996**, *153*, 257, and references therein.

(10) Merrifield, J. H.; Gladysz, J. A. *Organometallics* **1983**, *2*, 782.

clearly nonlinear, but no attempt was made to determine the reaction order in $^2H_2$.

Reaction of 4 with Hexene and Ethylene. One potentially useful reaction of **4** would be the insertion of alkenes into the Os−H bond; so an especially interesting question is whether an alkene can compete with chelate reclosure for coordination to the osmium center. Reaction of an approximately 80:20 mixture of *mer*- and *fac*-$L_3Os(H)(\kappa^2\text{-}NC_5H_4O)$ (**4**) in neat 1-hexene at 80 °C resulted in clean, quantitative conversion in about 17 h of both isomers to a single new facial compound assigned the structure *fac*-$L_3Os(n\text{-hexyl})(\kappa^2\text{-}NC_5H_4O)$ (**6**). Three doublet of doublets at δ −34.15, −37.59, and −38.03 ppm are seen in the ^{31}P NMR spectrum in C_6D_6, and no hydride is observed in the proton spectrum. Although the spectra of *fac*-$L_3Os(hexyl)(\kappa^2\text{-}NC_5H_4O)$ (**6**) are clean, the light-brown isolated product was very tacky and could not be rendered solid. Rather than struggle with this material, it was decided to prepare the ethyl derivative in the hope that it would have more tractable properties. Reaction of *fac*-$L_3Os(H)(\kappa^2\text{-}NC_5H_4O)$- in C_6D_6 in a sealed tube at 80 °C under 1 atm of ethylene resulted in quantitative conversion of (*fac*-**4**) to *fac*-$L_3Os(ethyl)(\kappa^2\text{-}NC_5H_4O)$ (**7**). Complete conversion required about 36 h, presumably because of the low ethylene concentration. NMR spectra were definitive with ^{31}P resonances at δ −33.83, −37.47, and −37.75 ppm, no hydride in the ^1H spectrum, and an ethyl multiplet around δ 1 ppm.

The alkene insertion reactions are reversible. Heating a solution of *fac*-$L_3Os(hexyl)(\kappa^2\text{-}NC_5H_4O)$ (**6**) in C_6D_6 in a sealed tube at 80 °C for 48 h resulted in quantitative conversion to *fac*-$L_3Os(H)(\kappa^2\text{-}NC_5H_4O)$ (*fac*-**4**). Analysis of the ^1H NMR spectrum of the volatiles from this reaction revealed that the liberated alkene was a mixture of hexene isomers. A complete analysis of the isomeric composition of the hexene mixture would not have been particularly informative, but the δ 5.75 ppm resonance of 1-hexene is clearly distinguishable from the internal cis/trans vinyl proton resonances of 2- and 3-hexene at δ 5.35−5.45 ppm, so that the terminal/internal isomer ratio could be determined to be approximately 2:1. β-Hydride elimination was similarly observed from *fac*-$L_3Os(ethyl)(\kappa^2\text{-}NC_5H_4O)$ (**7**) on heating in C_6D_6 at 80 °C with generation of *fac*-$L_3Os(H)(\kappa^2\text{-}NC_5H_4O)$ and ethylene. Hence, β-hydrogen elimination clearly occurs from the facial osmium alkyls, and *fac*-**4** is demonstrated to be an alkene isomerization catalyst. Since $L_4Os(H)_2$ has been demonstrated to exchange with $P(CD_3)_3$ with a half-life of about a week at 155 °C,[4c] it is likely that it would be similarly less reactive in alkene isomerization. Thus, **4** does offer a substantial increase in reactivity of the osmium complex for organic transformations.

Hydrogenation of 1-Hexene. Since the overall goal of this project is to generate increased reactivity for potential use in catalysis at an ordinarily inert osmium center, it was desirable to demonstrate at least one type of catalysis using *fac*-$L_3Os(H)(\kappa^2\text{-}NC_5H_4O)$ (**4**). All of the mechanistic components of a typical homogeneous hydrogenation catalyst appeared to be associated with **4**, so the catalytic hydrogenation of 1-hexene was undertaken. A sample in a sealed NMR tube was prepared containing 1-hexene in C_6D_6 solvent and 5 mol % of *fac*-$L_3Os(H)(\kappa^2\text{-}NC_5H_4O)$ (**4**) under 1 atm of hydrogen gas. After 7 days at 80 °C the 1-hexene was quantitatively converted to hexane, and **4** remained unchanged.

The world has not been waiting for another slow homogeneous hydrogenation catalyst, but considering that temperatures at least 70° higher would be necessary to see comparable rates of hydrogenation using $L_4Os(H)_2$, it does represent a substantial increase in reactivity through the use of the strained chelate. At the same time, **4** is stable and can be re-isolated.

Experimental Section

General Comments. $(Me_3P)_4OsXY$ compounds, especially when X/Y include hydrocarbyls and/or hydrides, are highly air sensitive and require careful attention to anaerobic techniques. Manipulations were carried out using an inert atmosphere glovebox, Schlenk apparatus, or vacuum line techniques with argon or dinitrogen atmosphere passed through an oxygen scrubber (BASF Ridox R3-11) and water absorbent (Mallinckrodt Aquasorb). Solvents were reagent grade and further purified as follows. Hydrocarbon solvents (alkane and aromatic) were stirred over concentrated sulfuric acid (repeated until the acid phase remained colorless), stirred over calcium hydride (24 h), distilled onto sodium-benzophenone, stirred at reflux until dark blue, or preferably, deep purple, and distilled from this immediately before use. THF and diethyl ether from fresh containers were dried over calcium hydride (24 h) and distilled from deep-purple sodium-benzophenone solutions immediately before use. Deuterated solvents were stored in the glovebox over highly activated (6 h at 450 °C in vacuo) type 4A molecular sieves in a gastight, screw-cap vial and used without further purification. NMR spectra were referenced to TMS for ^1H and ^{13}C, 85% H_3PO_4 for ^{31}P, and $CFCl_3$ for ^{19}F. All of the substituted phenols, anilines, and thiophenols were commercial. Solids were sublimed and liquids were distilled prior to use. For ease in handling during weighing, *fac*-$L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$[5] was cooled to −20 °C just prior to use. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

$L_4Os(H)(NC_5H_4O\text{-}\kappa N)$ (1). A Schlenk flask was charged with 100 mg (0.20 mmol) of *fac*-$L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ and 17 mg (0.18 mmol) of 2-hydroxypyridine. Cold THF (−20 °C, ca. 3 mL) was added, and the clear, golden-yellow solution was allowed to warm slowly to room temperature. The solvent was evaporated under vacuum, and the residue was washed with hexanes (5 × 10 mL) at −78 °C. Drying under vacuum afforded 91 mg of bright-white powder (86% yield). ^1H NMR (C_6D_6): δ −9.80 (dt, 1H, J = 78, 22 Hz, Os*H*), 1.24 (d, 9H, J = 8 Hz, $P(CH_3)_3$), 1.27 (vt, 18H, N = 6 Hz, $2P(CH_3)_3$), 1.62 (d, 9H, J_{PH} = 6 Hz, $P(CH_3)_3$), 5.68 (t, 1H, J = 6 Hz), 6.66 (d, 1H, J = 9 Hz), 7.10 (dd, 1H, J = 6, 9 Hz), 8.67 (d, 1H, J = 6 Hz). $^{13}C\{^1H\}$ NMR: δ 23.42 (vt, N_{PC} = 31 Hz), 26.53 (d, J_{PC} = 25 Hz), 28.15 (d, J_{PC} = 31 Hz), 104.76 (d, J_{PC} = 2 Hz), 115.98, 136.62, 162.52 (d, J_{PC} = 6 Hz), 173.02. $^{31}P\{^1H\}$ NMR: δ −42.18 (dd, 2P, J = 19, 16 Hz, mutually trans *P*Me_3), −50.52 (dt, 1P, J = 16, 8 Hz, *P*Me_3 cis to OsH), −55.60 (dt, 1P, J = 19, 8 Hz, *P*Me_3 trans to OsH). Anal. Calcd for $C_{17}H_{41}ONP_4Os$: C, 34.63; H, 7.01. Found: C, 34.36; H, 6.75.

$L_4Os(H)(HNC_5H_4N)$ (2). A 9 mm NMR tube with a 14/20 joint was charged with 283 mg (0.57 mmol) of $L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ and 39 mg (0.41 mmol) of 2-aminoypyridine. THF (ca. 3 mL) was added, and the tube was fused shut under vacuum. The clear, orange-red solution was heated at 80 °C with reaction progress periodically monitored by $^{31}P\{^1H\}$ NMR. After 40 h at 80 °C, the sample was cooled to room temperature, resulting in formation of bright-yellow, fine needles. The mixture was taken to dryness under vacuum, and the residue was washed with hexanes at −78 °C (5 × 10 mL). The bright-yellow powder weighed 232 mg (95% yield). ^1H NMR (C_6D_6):

δ −8.80 (dq, 1H, J = 74, 22 Hz, Os*H*), 1.08 (d, 9H, J = 6 Hz, P(CH_3)$_3$), 1.22 (d, 9H, J = 7 Hz, P(CH_3)$_3$), 1.29 (vt, 18H, N = 5.4 Hz, 2P(CH_3)$_3$), 3.97 (br d, 1H, J = 5 Hz, N*H*), 6.14 (t, 1H, J = 6 Hz), 7.17 (d, 1H, J = 11 Hz), 7.34 (dd, 1H, J = 11, 6 Hz), 8.30 (d, 1H, J = 5 Hz). ^{31}P{^{1}H} NMR: δ −42.39 (dd, 2P, J = 18, 17 Hz), −50.55 (dt, 1P, J = 9, 18 Hz), −52.28 (dt, 1P, J = 9, 17 Hz). Anal. Calcd for $C_{17}H_{42}N_2P_4Os$: C, 34.69; H, 7.19. Found: C, 34.71; H, 6.90.

$L_4Os(H)(SC_5H_4N$-κS) (3). The same procedure as above for **2** was employed, using 100 mg (0.20 mmol) of $L_3Os(H)(\eta^2$-CH_2-$PMe_2)$ and 20 mg (0.18 mmol) of mercaptopyridine and heating at 80 °C. ^{31}P{^{1}H} NMR spectra showed the reaction complete in about 6 h. The THF was removed under vacuum, and the solid residue was washed with hexanes at −78 °C (5 × 10 mL). The pale green, powdery residue weighed 85 mg (78% yield). ^{1}H NMR (C_6D_6): δ −9.39 (dq, 1H, J = 65, 23 Hz, Os*H*), 1.26 (d, 9H, J = 6 Hz, P(CH_3)$_3$), 1.29 (d, 9H, J = 8 Hz, P(CH_3)$_3$), 1.45 (vt, 18H, N = 6 Hz, 2P(CH_3)$_3$), 6.43 (dd, 1H, J = 5, 7 Hz), 7.07 (t, 1H, J = 7 Hz), 8.29 (d, 1H, J = 7 Hz), 8.46 (d, 1H, J = 5 Hz). ^{13}C{^{1}H} NMR: δ 23.01 (d, J_{PC} = 23 Hz), 23.74 (vt, N_{PC} = 33 Hz), 28.47 (d, J_{PC} = 30 Hz), 114.32, 125.21, 133.26, 149.09. ^{31}P{^{1}H} NMR (C_6D_6): δ −49.33 (dd, 2P, J = 19, 18 Hz), −50.43 (dt, 1P, J = 13, 19 Hz, trans to OsH), −53.78 (dt, 1P, J = 13, 18 Hz, cis to OsH). Anal. Calcd for $C_{17}H_{41}P_4SNOs$: C, 33.71; H, 6.82. Found: C, 33.86; H, 6.65.

***mer*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ (*mer*-4).** Sublimation of 100 mg (0.17 mmol) of $L_4Os(H)(NC_5H_4O$-$\kappa N)$ at 55 °C for a week under dynamic vacuum to remove PMe_3 (air condenser) led to collection of 44 mg (48%) of a bright-yellow solid. Use of higher temperatures for prolonged periods led to decomposition of starting material and reduced yields of product. ^{31}P{^{1}H} NMR showed the sublimate to be *mer*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ containing ca. 2% of *fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$. ^{1}H NMR (C_6D_6): δ −16.83 (dt, 1H, J = 18, 21 Hz, Os*H*), 1.30 (vt, 18H, N = 6 Hz, 2P(CH_3)$_3$), 1.39 (d, 9H, J = 8 Hz, P(CH_3)$_3$), 6.08 (d, 1H, J = 8 Hz), 6.17 (dd, 1H, J = 5, 8 Hz), 7.03 (t, 1H, J = 8 Hz), 7.79 (d, 1H, J = 5 Hz). ^{31}P{^{1}H} NMR: δ −27.80 (d, 2P, J = 16 Hz), −43.26 (t, 1P). No elemental analysis was performed on this compound, as small amounts of the fac isomer were present and attempts to crystallize the mer isomer increased isomerization to the fac material. (See the Results section.)

***fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ (*fac*-4).** A solution of 100 mg (0.17 mmol) of $L_4Os(H)(NC_5H_4O$-$\kappa N)$ in ca. 20 mL of toluene was heated at reflux. Nitrogen gas was admitted at the bottom of the reflux condenser via a long needle through the septum at the top and was vented through a short needle at the top to remove PMe_3 vapor. More toluene was added as needed. After 3 days at reflux, toluene was removed under vacuum and the residue was sublimed under dynamic vacuum for several hours to give bright-yellow, crystalline *fac*-$L_3Os(H)$-$(\kappa^2$-$NC_5H_4O)$ in ca. 80% yield. ^{1}H NMR (C_6D_6): δ −3.61 (dt, 1H, J = 93, 22 Hz, Os*H*), 1.03 (d, 9H, J = 7 Hz, P(CH_3)$_3$)), 1.36 (d, 9H, J = 9 Hz, P(CH_3)$_3$), 1.46 (d, 9H, J = 9 Hz, P(CH_3)$_3$), 6.05 (d, 1H, J = 8 Hz), 6.13 (t, 1H, J = 6 Hz), 6.95 (dd, 1H, J = 8, 6 Hz), 7.84 (d, 1H, J = 6 Hz). ^{31}P{^{1}H} NMR: δ −33.30 (dd, 1P, J = 6, 8 Hz), −33.78 (dd, 1P, J = 14, 8 Hz), −37.92 (dd, 1P, J = 6, 14 Hz). Anal. Calcd for $C_{14}H_{32}ONP_3Os$: C, 32.74; H, 6.28; N, 2.73. Found: C, 32.96; H, 6.47; N, 2.53.

***mer*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ to *fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ Isomerization**. A solution of 8 mg of *fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ in 0.5 mL of benzene-d_6 in a 5 mm NMR tube was submitted to the usual three freeze−pump−thaw cycles and the tube was sealed. The sample was heated at 110 °C and monitored by ^{31}P NMR. The isomerization of *mer*-**4** to *fac*-**4** was complete in 3 h.

***fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ + $P(CD_3)_3$.** A solution of 9 mg of *fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ in 0.5 mL of benzene-d_6 was prepared in a 5 mm NMR tube, and after three freeze−pump−thaw cycles, ca. 15 equiv per Os of **L′** was condensed in and the tube was sealed. The thawed sample was immediately placed into the NMR spectrometer (probehead temperature ≈ 29 °C). Labeled phosphine was incorporated exclusively into only one of the two mutually trans (*a*) sites with a half-life of incorporation of ca. 3 h. The sample was stored at 19 °C and a ^{31}P NMR spectrum periodically acquired. An additional L′ was incorporated into the *b* position trans to the hydride with $k = 1.98 \times 10^{-7}$ s^{-1} ($t_{1/2}$ = 40.6 days).

***mer*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ + $P(CD_3)_3$.** A solution of 5 mg of *mer*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ in 0.4 mL of benzene-d_6 was prepared in a 5 mm NMR tube. After three freeze−pump−thaw cycles, ca. 20 equiv of **L′** per Os was condensed in and the tube was sealed. A ^{31}P NMR spectrum of the sample taken after 2 h at room temperature showed that the 2:1 doublet/triplet *mer*-**4** L_3 resonance pattern had disappeared and a complex set of resonances was seen between δ −47 and −51 ppm. Calculated spectral simulations showed that the early pattern is consistent with *trans*-L_3**L′**$Os(H)(NC_5H_4O)$. The ^{1}H NMR spectrum showed no *mer*-**4** hydride resonance, but a new hydride pentet had appeared at δ −20.65 ppm. Whether the pyridonato ligand is κN or κO could not be determined form our data. The phosphine exchange continued and the ^{31}P multiplets gradually convert to a broad singlet near δ −50 ppm for *trans*-**L′**$_4Os(H)(NC_5H_4O)$ as the resonance for free L increased. ^{31}P NMR spectra of all of the *trans*-$(L)_n$(**L′**)$_{4-n}$Os-$(H)(NC_5H_4O)$ exchange isotopomers were calculated using a standard simulation computer program. Parameters $\Delta\delta$ = 400 Hz (2 ppm, **L′** at higher field), J_{trans} = 270 Hz, and J_{cis} = 20 Hz gave good qualitative fits to the observed spectra, initially to *trans*-L_3**L′**$Os(H)(NC_5H_4O)$, and then superimposed combinations of the simulated $(L)_n$(**L′**)$_{4-n}Os(H)(NC_5H_4O)$ spectra in different proportions reproduced the continuing experimental exchange up to the observation of the δ −49 ppm singlet after 10 h, consistent with fully exchanged *trans*-**L′**$_4Os(H)(NC_5H_4O)$. After 10 days at room temperature, the sample had isomerized to *cis*-**L′**$_4Os(H)(NC_5H_4O$-$\kappa N)$.

***fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ + CO_2.** A 9 mm NMR tube was charged with 75.0 mg (0.14 mmol) of *fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ and 2 mL of C_6D_6, forming a clear, bright golden yellow solution. After three freeze−pump−thaw cycles about 10 atm of dry CO_2 was admitted. The tube was sealed and placed in the NMR spectrometer probe at 80 °C. Conversion to *fac*-L_3-$Os(HCO_2)(\kappa^2$-$NC_5H_4O)$, **5**, was complete in an hour. The tube was broken, and removal of solvent under vacuum gave a high yield of product. ^{1}H NMR (C_6D_6): δ 0.98 (d, 9H, J = 9 Hz, P(CH_3)$_3$)), 1.22 (d, 9H, J = 9 Hz, P(CH_3)$_3$)), 1.42 (d, 9H, J = 9 Hz, P(CH_3)$_3$)), 6.08 (d, 1H, J = 8 Hz), 6.14 (t, 1H, J = 8 Hz), 6.92 (t, 1H, J = 8 Hz), 7.99 (d, 1H, $^4J_{PH}$ = 5 Hz, OsO_2CH), 8.84 (d, 1H, J = 8 Hz). ^{13}C{^{1}H} NMR: δ 17.70 (dd, J_{PC} = 33, 6 Hz), 18.67 (d, J_{PC} = 34 Hz), 21.58 (dd, J_{PC} = 34, 5 Hz), 108.60 (d, J_{PC} = 10 Hz), 112.34 (d, J_{PC} = 10 Hz), 137.31, 146.8, 167.36 (OsO_2CH), 179.82. The resonance at δ 167.36 showed $^1J_{CH}$ = 193 Hz with off-resonance decoupling. ^{31}P{^{1}H} NMR: δ −30.5 (t, J = 13 Hz), −35.8 (t, J = 14 Hz), −38.4 (t, J = 13 Hz). Anal. Calcd for $C_{15}H_{36}NO_3P_3Os$: C, 32.31; H, 5.79; N, 2.51. Found: C, 32.35; H, 5.98; N, 2.41.

Reversibility of CO_2 Insertion. A solution of ca. 10 mg (0.017 mmol) of formato complex **5** in 0.4 mL of benzene-d_6 was prepared in a 5 mm NMR tube, and the tube was sealed after three freeze−pump−thaw cycles. The sample was heated at 110 °C for 2 h, after which ^{31}P{^{1}H} NMR revealed that *fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ was the exclusive product. After the sealed sample had stood at room temperature for about a week, a significant quantity of the ^{31}P{^{1}H} resonances were again those of the formato complex.

***fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ + 1-Hexene.** A solution of 16 mg (0.030 mmol) of *fac*-$L_3Os(H)(\kappa^2$-$NC_5H_4O)$ in ca. 5 mL of 1-hexene was sealed in a medium-walled, 9 mm NMR tube after three freeze−pump−thaw cycles. The sample was heated for 17 h at 80 °C, after which NMR showed quantitative conversion to *fac*-$L_3Os(n$-$C_6H_{13})(\kappa^2$-$NC_5H_4O)$, **6**. ^{1}H NMR (C_6D_6): δ 0.8−1.2 (br m, OsC_6H_{13}), 1.03 (d, J = 6 Hz, PCH_3), 1.24 (d, 9H, J = 8 Hz, PCH_3), 1.30 (d, 9H, J = 8 Hz, PCH_3), 6.10 (d,

1H, J = 8 Hz), 6.16 (dd, 1H, J = 8, 5 Hz), 7.01 (t, 1H, J = 8 Hz), 7.69 (d, 1H, J = 5 Hz). $^{13}C\{^1H\}$ NMR: δ 14.62 (C_6), 15.13 (dt, J = 59, 6 Hz, OsCH_2), 18.90 (d, J = 22 Hz, P(CH_3)$_3$), 19.06 (d, J = 32 Hz, P(CH_3)$_3$), 22.15 (d, J = 32 Hz, P(CH_3)$_3$), 23.51, 31.44, 32.81, 37.18. $^{31}P\{^1H\}$ NMR: δ −34.62 (dd, J = 15, 6 Hz), −38.09 (dd, J = 6, 4 Hz), −38.43 (dd, J = 15, 4 Hz). Attempts to crystallize the oily material were unsuccessful, so no elemental analysis was obtained.

***fac*-L$_3$Os(H)(κ^2-NC$_5$H$_4$O) + Ethylene.** A thick-walled, 9 mm-o.d. NMR tube was charged with 86 mg (0.16 mmol) of *fac*-L$_3$Os(H)(κ^2-NC$_5$H$_4$O) and 1.5 mL of C_6D_6 to form a clear, golden-yellow solution. After three freeze−pump−thaw cycles, 1 atm of ethylene gas was admitted and the tube was sealed. The tube was heated at 80 °C, and reaction progress was monitored by ^{13}P NMR. At 36 h, the conversion to *fac*-L$_3$Os(ethyl)(κ^2-NC$_5$H$_4$O), **7**, was quantitative. The tube was broken, the solvent removed under vacuum, and the residue washed several times with cold hexane. The vacuum-dried solid amounted to 95% yield. ^1H NMR (C_6D_6): δ 0.8−1.10 (br m, 5H, OsCH_2CH_3), 1.03 (d, J = 6 Hz, PCH_3), 1.21 (d, 9H, J = 8 Hz, PCH_3), 1.28 (d, 9H, J = 8 Hz, PCH_3), 6.08 (d, J = 9 Hz, 1H), 6.15 (dd, J = 9, 5 Hz, 1H), 7.00 (t, J = 5 Hz, 1H), 7.64 (d, J = 5 Hz, 1H). $^{31}P\{^1H\}$ NMR: δ −33.83 (dd, J = 6, 16 Hz), −37.47 (dd, J = 4, 6 Hz), −37.75 (dd, J = 4, 16 Hz). Anal. Calcd for $C_{16}H_{36}O_1N_1P_3Os$: C, 35.48; H, 6.70; N, 2.59. Found: C, 35.10; H, 6.84; N, 2.56.

Elimination of Hexene from *fac*-L$_3$Os(C_6H_{13})(κ^2-NC$_5$H$_4$O). A solution of 4 mg of *fac*-L$_3$Os(C_6H_{13})(κ^2-NC$_5$H$_4$O) in 0.3 mL of benzene-d_6 was sealed under vacuum in a 4 mm NMR tube after three freeze−pump−thaw cycles. The tube was heated at 80 °C with progress monitored by ^{31}P NMR, with the eventual total heating time being 48 h. A mixture of L$_3$Os(C_6H_{13})(κ^2-NC$_5$H$_4$O) and isomeric hexenes was formed. See the Results section for details.

***fac*-L$_3$Os(H)(κ^2-NC$_5$H$_4$O) + $^2H_2$.** A solution of 2.2 mg of *fac*-L$_3$Os(H)(κ^2-NC$_5$H$_4$O) in 0.3 mL of benzene-d_6 was prepared in a 4 mm tube. After the usual freeze−pump−thaw cycles, hydrogen gas (0.84 atm) was transferred into the solution and the tube was sealed. The reaction was monitored by the disappearance of the ^1H NMR starting hydride resonance at δ −3.61 ppm relative to internal TMS. The ^{31}P spectrum showed gradual broadening of the starting material L$_3$ A−B−M pattern from deuterium−phosphorous coupling.

Hydrogenation of 1-Hexene. A clear, yellow solution of 6.5 mg (0.01 mmol) of *fac*-L$_3$Os(H)(κ^2-NC$_5$H$_4$O) and 20 μL (∼0.2 mmol) of 1-hexene in 0.4 mL of benzene-d_6 was prepared in a thick-walled, 5 mm NMR tube. After three freeze−pump−thaw cycles, 1 atm pressure of H_2 gas was admitted and the tube was sealed. The sample was heated at 80 °C and progress of the reaction monitored by ^{31}P NMR. After a total heating time of ca. 7 days, the 1-hexene resonances were no longer detectable in the ^1H spectrum and *n*-hexane resonances were observed in addition to the starting material, *fac*-L$_3$Os(H)(κ^2-NC$_5$H$_4$O).

X-ray Crystal Structure Determination of *cis*-L$_4$Os(H)(NC$_5$H$_4$O-κN) (1). Crystals of L$_4$Os(H)(NC$_5$H$_4$O) were prepared by slow evaporation of pentane from a solution of **1** at −15 °C. A suitable crystal was coated with "Paratone N" oil, inserted into a glass capillary, and mounted for data collection on a Siemens $P2_1$ diffractometer with Mo Kα X-rays. The structure was solved by conventional Patterson and difference Fourier techniques. There was a space group ambiguity of either *Cc* or *C*2/*c*, so refinement in the space group *Cc* was initially carried out. At this point the metal, the 2-pyridone ring, two of the phosphorus atoms, and several of the phosphine methyl carbon atoms were located, but two regions of residual electron density remained that made no chemical sense. The located atom coordinates were transferred to refinement in space group *C*2/*c*, wherein the remaining atoms were located. Still, some difficulties persisted: some of the ring atoms did not refine well, giving some poor C−C distances; two unassignable residual electron density peaks were still present; and the Os−P−C bond angles and distances of the mutually trans phosphines were unreasonable. Constraining the ring bond distances and angles as well as the bond distances of the mutually trans phosphines and subsequent refinement led to a final R factor of 4.6%. Residual atom peaks are thought to be the result of a minor packing disorder. The hydride position was calculated at an assigned Os−H distance of 1.66 Å using data from a neutron diffraction study of H$_4$Os(PMe$_2$Ph)$_3$.[8] A summary of the structure determination is given in Table 1, and selected bond lengths and angles are listed in Table 2. Complete data are given in the Supporting Information.

Table 1. Structure Determination Summary for *cis*-L$_4$Os(H)(NC$_5$H$_4$O-κN) (1)

empirical formula	$C_{17}H_{41}P_4ONOs$
color; habit	colorless, very air sensitive
space group	monoclinic *C*2/*c*
unit cell dimens	a = 11.041 (2) Å; b = 14.709 (2) Å; c = 15.188 (2) Å; β = 92.64 (5)°
volume of unit cell	2463.9 (5) Å^3
Z mol. per unit cell	4
fw	589.61
abs coeff	1.165 mm^{-1}
F(000)	672
radiation	Mo Kα (λ = 0.71069 Å)
sin(θ/λ) limit	0.538 Å^{-1}
index ranges	$0 \le h \le 13$; $0 \le k \le 16$; $-18 \le l \le 18$
no. of reflns used	867 ($I > 2.0\sigma(I)$)
solution and refinement	Patterson methods, full-matrix least-squares
quantity minimized	$\sum w(F_o - F_c)^2$
hydrogen atoms	riding model, fixed isotropic U
no. of params refined	290
final R indices (obsd data)	R = 4.47%, wR = 5.60%

Table 2. Selected Interatomic Distances (Å) and Angles (deg) of *cis*-L$_4$Os(H)(NC$_5$H$_4$O-κN) (1) with Estimated Standard Deviations

P(1)−Os	2.467(7)	N−C(1)	1.390(f)[a]
P(4)−Os	2.339(6)	N−C(5)	1.390(f)
N−Os	2.175(10)	C(1)−C(2)	1.390(f)
O−C(1)	1.297(18)	C(2)−C(3)	1.390(f)
P(2)−Os	2.326(f)	C(4)−C(5)	1.390(f)
P(3)−Os	2.326(f)	C(3)−C(4)	1.390(f)

P(1)−Os−P(2)	93.2(2)	C(1)−N−Os	126.0(8)
P(1)−Os−P(3)	97.4(2)	C(5)−N−Os	113.8(8)
P(1)−Os−P(4)	93.2(2)	O−C(1)−N	120.4(12)
P(2)−Os−P(3)	168.8(3)	O−C(1)−C(2)	119.6(12)
P(2)−Os−P(4)	94.1(2)	C(5)−N−C(1)	120.0(f)
P(3)−Os−P(4)	89.1(2)	C(2)−C(1)−N	120.0(f)
N−Os−P(1)	96.5(5)	C(3)−C(2)−C(1)	120.0(f)
N−Os−P(2)	90.1(6)	C(4)−C(3)−C(2)	120.0(f)
N−Os−P(3)	84.9(6)	C(5)−C(4)−C(3)	120.0(f)
N−Os−P(4)	169.2(6)	C(4)−C(5)−N	120.0(f)

[a] Parameters marked (f) were fixed in the refinement.

Acknowledgment. This work was supported by the National Science Foundation. We thank Prof. Robert Bau for assistance with the X-ray crystal structure determination.

Supporting Information Available: Complete X-ray data for **1** including a structure determination summary, interatomic distances, angles, and anisotropic displacement coefficients, and atomic coordinates and equivalent isotropic displacement coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000077W