Phosphine Ligand Exchange in Tetrakis(trimethylphosphine)(hydrido)osmium Anilides, Phenoxides, and Thiophenoxides. Examples of Anion Dissociation and of Labilization by Ligand π-Base Effects

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The series of phenoxide complexes *cis*-$L_4Os(H)OC_6H_4Z$ ($L = PMe_3$; Z = H, OMe, CF_3, NH_2, CN), anilides *cis*-$L_4Os(H)NHC_6H_4Z$ (Z = H, OMe, CF_3), and thiophenoxides *cis*-$L_4Os(H)$-SC_6H_4Z (Z = H, OMe) have been prepared by treatment of *fac*-$L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ with the corresponding neutral arene. ^{1}H NMR spectra of coordinated phenoxides and thiophenoxides show rapid phenyl group rotation, while that of the anilides is slow. Rates and stereochemistry of substitution of $P(CH_3)_3$ (L) by $P(CD_3)_3$ (L′) were determined by ^{31}P NMR in benzene at 80 °C. Anilides substitute first only in the mutually trans sites (*a* sites) with cleanly first-order kinetics and subsequently into the site trans to the anilide (site *c*). The latter shows non-first-order behavior that is accurately modeled by iterative kinetics calculations using a mechanism of L dissociation only from the *a* sites presumably to give a quasi-trigonal-bipyramidal intermediate stabilized by π-electron donation from the anilide lone pair. A three-point Hammett plot against σ_p yielding $\rho = -1.8$ is consistent with transition state stabilization by π-donation. Association of L′ occurs only into site *a*, but subsequent substitution allows the resident L′ to move into site *c*. Thiophenoxides exhibit substitution rates and stereochemical patterns very similar to those of the anilides and are believed to proceed by the same mechanism. Phenoxide complexes incorporate L′ into all sites, with each site incorporating phosphine independently of the others since exchange rates at all sites are first order. A Hammett plot of exchange rates against sigma minus (σ^-) is somewhat scattered ($R^2 = 0.96$) but exhibits a positive slope $\rho^- = +0.36$. Phenoxide dissociation is postulated, but the fact that substantial concentrations of intermediates partially substituted in all positions is seen during the reaction is inconsistent with rate-determining phenoxide dissociation. An ionization preequilibrium followed by slower phosphine exchange steps in the ion pair is postulated. Treatment of $L_4Os(H)(OC_6H_4CN)$ with excess L in propylene carbonate, DMSO-d_6, DMF, or CD_3NO_2 at 80 °C all resulted in conversions to $[L_5OsH][OAr]$. These results suggest that low steady-state concentrations of $[L_5OsH][OAr]$ ion pairs in benzene are possible, consistent with an ion pair mechanism for ligand exchange.

Introduction

Catalysis of reactions of organic substrates by soluble metal complexes usually depends on the existence or transient generation of coordinative unsaturation. Because of the kinetic inertness of third-row platinum group metals, they were long considered to be unlikely candidates for homogeneous catalysis. Crabtree's discovery that iridium can serve as the basis for some of the most active soluble hydrogenation catalysts known[1] called attention to the potential of third-row metals for efficient catalysis. Nevertheless, the general inertness of heavy metal complexes remains a pervasive issue for which any general new approaches could be helpful.

Cis labilization effects of π-lone-pair-donor ligands have been well-known for many years in the context of classical coordination chemsitry.[2] In the 1970s Brown and co-workers developed an understanding of cis labilization in low-valent carbonyl complexes of the Mn[3] and Cr[4] groups. In the last 15 years a number of papers have appeared that deal with cis labilization of ligands and stabilization of unsaturation by π-donor ligands with late organotransition metal systems, and it is probably appropriate to say that organometallic chemists are now generally aware of these effects.[5,6] Nevertheless, the potential usefulness of π-donor ligands for

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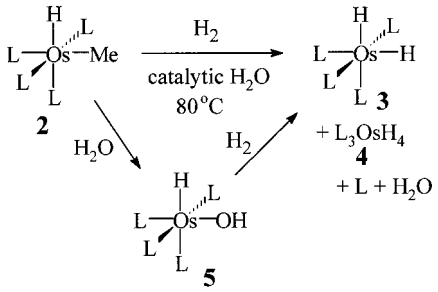
Scheme 1[a]



[a] L = PMe_3.

the generation of coordinative unsaturation in organometallics is probably still generally underappreciated. There are few published quantitative investigations into the capability of different π-basic ligands to induce dissociation, particularly for non-carbonyl-containing complexes. Indeed, we are aware of only one other investigation that quantitatively compares the relative π-donicities of O, S, and N in the same system.[5c]

Our interest in π-donor effects began a number of years ago as we examined an acid-catalyzed hydrogenolysis of the Os−C bond in *fac*-$L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ (**1**, L = PMe_3) and in $L_4Os(H)Me$ (**2**) that forms L_4OsH_2 (**3**) and involves $[L_4OsH_3]^+$ as an acid.[7] Intermediacy of coordinatively unsaturated $[L_4OsH]^+$, presumably in equilibrium with a solvated or weak-anion-coordinated $L_4Os(H)X$, was also inferred, where $[L_4OsH]^+$ is generated by the protonation-induced reductive elimination of the C−H bond from osmium. We also found [8] that water catalyzes a similar reaction, although it proceeds by a different mechanism and yields L_3OsH_4 (**4**) and L in addition to L_4OsH_2 (**3**), as illustrated for $L_4Os(H)Me$ (**2**) in Scheme 1. Residual water on oven-dried (110 °C) NMR tubes is sufficient to give very slow rates of hydrogenolysis. Intermediacy of $L_4Os(H)(OH)$ (**5**) was inferred from the data. Since **5** is saturated, efficacy of the catalytic cycle in Scheme 1 requires generation of an unsaturated derivative. We have previously found that $P(CD_3)_3$ (henceforth L′) is an excellent label with which to measure rates and stereochemistry of PMe_3 dissociation from metal complexes.[9] It was shown that $L_4Os(H)Me$ (**2**) undergoes PMe_3 dissociation at useful rates above 100 °C ($t_{1/2} \approx 4$ days at 105 °C),[9] and $L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ (**1**) exchanges above 140 °C.[10] On the other hand, $L_4Os(H)(OH)$ (**5**) undergoes hydrogenolysis as shown in Scheme 1 at 80 °C,[8] and heating of **5** with L′ at 80 °C revealed a kinetically competent rate of exchange of L/L′ in **5** at that temperature ($t_{1/2} \approx$ 2 h). Given that methyl and hydroxyl groups in **2** and **5**, respectively, are similar in size, clearly the hydroxyl group is causing a strong labilization of the phosphine ligands on osmium.

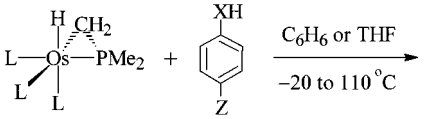
Motivated by the paucity of specific data concerning π-donor-induced dissociation, by our hydrogenolysis results, and by the potential generality and usefulness of π-basic ligands to facilitate generation of unsaturation, we undertook an examination of the labilization effect of π-donor ligands on phosphine ligands in *cis*-$L_4Os(H)X$ complexes. In addition to generating some useful quantitative comparisons of atom effects and substituent effects on π-basicity, we have uncovered an interesting alternative mechanism in this system that draws attention to the fact that in substitution reactions the relatively weak σ bonding of oxygen to heavy metals can result in ionization mechanisms dominating over π-donor-induced dissociation.[11]

Results and Discussion

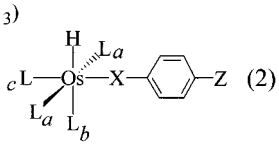
Synthesis. Most late transition metal hydroxide, alkoxide, and amide complexes have been prepared by simple ligand metathesis (eq 1) using sodium or lithium

$$L_nM\text{−}X + M'\text{−}Y \rightarrow L_nM\text{−}Y + M'\text{−}X \qquad (1)$$

alkoxide or amide salts, especially square-planar species for which associative substitution is usually fast. However, this technique was not effective with the inert Os(II) complexes of interest to us. It happened that the availability of *fac*-$L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ (**1**)[12] offered a general and effective direct route to *cis*-$L_4Os(H)X$ by protonolysis (eq 2). Such acid cleavages of metal−carbon



1 (L = PMe_3)



(2)

X \ Z	H	OMe	CF_3	NH_2	CN
O	**6a**	**6b**	**6c**	**6d**	**6e**
NH	**7a**	**7b**	**7c**		
S	**8a**	**8b**			

bonds have been known for many years and have been particularly useful for generation of complexes of weakly coordinating anions.[13] All of the heteroatom complexes listed in eq 2 were prepared by reacting highly basic **1** with slightly less than 1 equiv of the appropriate acid

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(8) Desrosiers, P. J. Ph.D. Thesis, University of Southern California, 1985. Deming, M. A. Ph.D. Thesis, University of Southern California, 1992.

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(10) Shinomoto, R. S.; Desrosiers, P. J.; Harper, T. G. P.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704−713.

(phenol, aniline, or thiophenol) in benzene or THF solvent followed by heating of the solution (for the anilides) in a sealed tube. The severity of conditions required is inversely proportional to the acidity of the substrate in that phenols and thiophenols react with **1** during the time of mixing, while anilines require heating for several days at 110 °C. Among the anilines, the rate parallels the effect of the para substituent on its acidity. For example, at 110 °C formation of *cis*-$L_4Os(H)(p\text{-}HNC_6H_4OMe)$ required 80 h and *cis*-$L_4Os(H)(p\text{-}HNC_6H_4CF_3)$ 40 h to complete. The products are thermolytically inert, with no changes in their ^1H and ^{31}P NMR spectra after several days at 110 °C.

Spectra. NMR spectroscopy is naturally the technique of choice for characterizing and following the chemistry of complexes **6**−**8**, with ^{31}P NMR the most informative regarding PMe_3 (L) lability. The $^{31}P\{^1H\}$ NMR spectra of *cis*-$L_4Os(H)(XC_6H_4Z)$ compounds exhibit an A_2MX, A_2XY, or A_2BX pattern, where the resonances for the mutually trans phosphines (site *a*, hereafter designated L_a) are invariably at lowest field. The chemical shifts are characteristic of the coordinating heteroatom X, but they vary little with the para substituent Z for a given X, differences being less than ±1 ppm for each phosphine site. Phenoxides **6** have the lowest field chemical shifts, with average δ at −36.5, −41.8, and −50.3 for mutually trans L (L_a), L trans to OsH (L_b), and L cis to OsH (L_c), respectively (see eq 2 for site labels). ^{31}P resonances for anilides **7** appear at higher field, with average δ at −41.8 (L_a), −50.6 (L_b), and −52 (L_c). Thiophenoxides **8** appear at higher field still, with the relative chemical shift of the two mutually cis L reversed in order from that of **6** and **7**: average δ at −50 (L_a), −51.2 (L_c), and −54.1 (L_b). In general, the two mutually cis L are distinguished by a selective off-resonance decoupling experiment that takes advantage of the fact that the phosphine located trans to the hydride (L_b) is strongly coupled with it ($^2J_{PH}$ 65−80 Hz), while L cis to the hydride (L_c) has a smaller $^2J_{PH}$ (20−25 Hz). Shifting of the ^1H R_f decoupling band to lower frequency decouples any carbon-bonded hydrogen from P, but leaves the OsH coupled, although with a slightly diminished $^2J_{PH}$ compared to that measured in the proton spectrum.

The Os−*H* ^1H NMR resonances, which appear as doublets of quartets, also progress to higher field across the series, with average δ for **6** at −7.9, **7** at −8.5, and **8** at −9.5 ppm. The NH_2 resonance of uncoordinated anilines, a broad singlet at ca. 2.7 ppm, becomes an anilide N*H* doublet ($^3J_{PH} \approx 6$ Hz) centered from 2.3 ppm (Z = H) to 1.9 ppm (Z = OCH_3) in the coordinated, deprotonated anilide of $L_4Os(H)NHC_6H_4Z$. In contrast to phenoxides **6** and thiophenoxides **8**, anilides **7** exhibit restricted rotation of the aromatic ring on the NMR time scale. Thus, all five aromatic resonances are apparent in the ^1H NMR spectrum of *cis*-$L_4Os(H)(HNC_6H_5)$ (**7a**), and in variable-temperature spectra, coalescence is observed at ca. 100 °C. Four distinct aromatic proton resonances are also evident in the spectra of **7b** and **7c** at ambient temperature. This restricted rotation is likely of steric origin since we assume that the presence of the N−H group substantially restricts the ability of the Os−N−Ar bond angle to deform toward linearity compared to Os−O−Ar and Os−S−Ar, so the anilide phenyl ring would be pushed more tightly against the phosphines.

Phosphine Ligand Exchange Studies. ^{31}P NMR Spectral Pattern Upon $P(CH_3)_3/P(CD_3)_3$ Exchange. The lability of phosphine toward dissociation and the resulting substitution pattern in **6**−**8** were examined by the use of deuterium-labeled phosphine $P(CD_3)_3$ (L′). Employing a large excess of L′ ensures that any dissociation event leads to incorporation of the label in place of the normal L, and so the rate of dissociation is clearly measurable. If dissociation of L is preferred from a specific site, then the principle of microscopic reversibility requires that the labeled ligand L′ reenter the same site, thus revealing the preference. These substitutional principles have been well discussed by Atwood and Brown.[14,15] The essential experiment in the *cis*-L_4OsXY system has been previously described in more detail,[9] and additional examples in osmium,[10] iridium,[16] and ruthenium[5c] chemistry have been given. A major advantage of using $P(CH_3)_3/P(CD_3)_3$ labeling is that there is a 3 ppm difference in the ^{31}P NMR chemical shifts of the free ligands L (δ −60.2) and L′ (δ −63.2) and usually ca. a 2 ppm difference when they are coordinated, with M−L′ also at higher field than M−L. This makes the determination of the labeling results relatively straightforward. The mutually trans L_aL_a are strongly coupled with $^2J_{PP} \approx 270$ Hz. Normally this coupling is not visible since the two P have the same chemical shift, but a single substitution of one of the trans phosphines gives L and L′ resonances that differ by ca. 2 ppm. The large $^2J_{PP}$ thus results in an AB pattern for the mutually trans L_aL_a' phosphines spanning ca. 5 ppm (at 146 MHz) and superimposed on the disappearing L_aL_a resonance and the growing $L_a'L_a'$ resonance. This region of the ^{31}P spectrum is shown in Figure 1 for $(L/L')_4Os(H)(OC_6H_4OMe)$ (**6b**). In addition, incorporation of L′ causes a small downfield isotopic shift (ca. 5 Hz at 146 MHz for ^{31}P) in the ^{31}P resonances of any other L that is cis to it. This allows one to tell whether any exchange in the mutually cis sites (L_b and/or L_c) occurs in addition to L_a exchange. Figure 2, for example, shows the L_aL_a doublet of doublets at δ −42.0 ppm and the more intense multiplet centered at δ −42.6 ppm of the A half of the L_aL_a' AB pattern of partially L/L′ exchanged $L_4Os(H)(NHC_6H_5)$ (**7a**). The multiplet at δ −42.6 ppm is seen to have a second doublet-of-doublet pattern of ca. 90% the intensity of the first at ca. 5 Hz lower field corresponding to part of the sample that is doubly exchanged, i.e., $(L_aL_a')(L_b)(L_c')Os(H)(NHC_6H_5)$. The absence of any doubling of the δ −42.0 ppm peak clearly indicates the absence of any $(L_a)_2(L_b)(L_c')Os(H)(NHC_6H_5)$ or $(L_a)_2(L_b')(L_c)Os(H)(NHC_6H_5)$.

(11) The synthesis and some aspects of the chemistry of the ruthenium analogues of our phenoxides and anilides, $(Me_3P)_4Ru(H)(XC_6H_4Z)$ (X = NH, O), have been reported. (a) Osakada, K.; Ohshiro, K.; Yamamoto, A. *Organometallics* **1991**, *10*, 404−410. (b) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875−1887.

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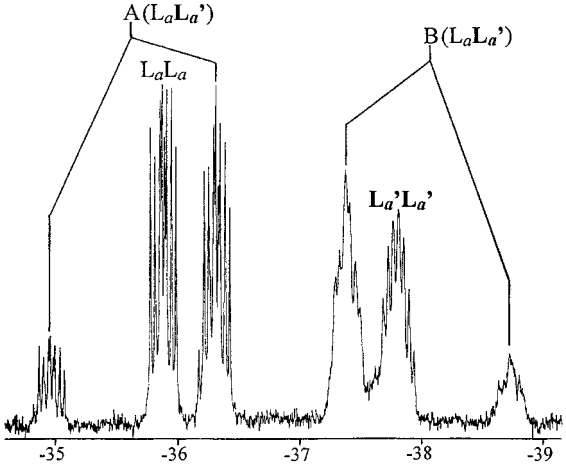


Figure 1. Partial $^{31}P\{^1H\}$ NMR spectrum of ca. half-$P(CH_3)_3$/$P(CD_3)_3$-exchanged (L/L′)$_4$Os(H)OC_6H_4OMe (**6b**). Shown is the region of the mutually trans ligand resonances L_aL_a, L_aL_a', and $L_a'L_a'$. See the text for interpretations.

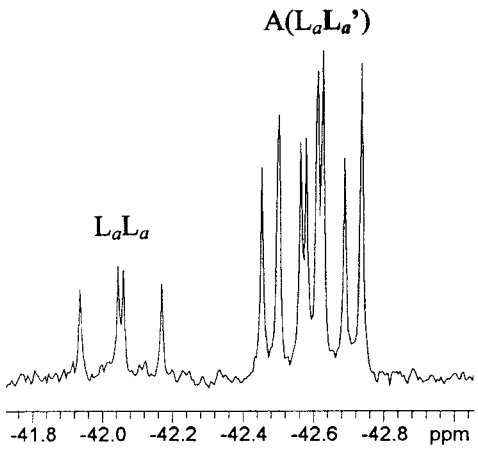


Figure 2. Partial $^{31}P\{^1H\}$ NMR spectrum of partially-(L/L′)-exchanged $L_4Os(H)NHC_6H_5$ (**7a**). Shown is the L_aL_a resonance and the most intense of the four L_aL_a' AB resonances. See the text for interpretations.

An important complication in these phosphine exchange reactions is that a five-coordinate intermediate may have a square-pyramidal or trigonal-bipyramidal structure or any structure between these, and/or it may be stereochemically labile by nondissociative reorganization (pseudorotation, more below). Thus, it is possible that mutually cis sites *b* and/or *c* could acquire label by partial reorganization or more extensive pseudorotation of the intermediate arising from L_aL_a dissociation, even if no L_b or L_c dissociation would occur. However, if dissociation of L_b and L_c did *not* occur, then the only way that L′ could appear in either of those sites would be to first have exchange into site *a* to form L_aL_a' and then to have the remaining L_a dissociate, whereupon the coordinated L_a' could migrate to site *b* or *c* in the intermediate. An important point here is that since free L′ is in large excess, only L′ will coordinate to the pentacoordinate intermediate to form product. As a result, *no L′ can appear in sites b or* c *unless it also appears in at least one of the a sites* as well, *unless* site *b* or *c* itself dissociates ligand at a competitive rate. Stated another way, no isotopically shifted unlabeled L_aL_a resonance will appear ca. 5 Hz downfield unless independent L_b and/or L_c dissociation is occurring. This turns out to be a useful phenomenon, as described below.

Table 1. Rates of Diasappearance of $P(CH_3)_3$ (L) $^{13}P\{^1H\}$ Resonances as They Are Replaced by $P(CD_3)_3$ (L′) in Specified Sites of *cis*-$L_4Os(H)(X)$ in C_6D_6 at 80 °C

cmpd	X	$10^7 \times k_a$[a]	$10^7 \times k_b$	$10^7 \times k_c$
6d	$OC_6H_4-NH_2$	14.8	4.69	1.53
6a	OC_6H_4-H	17.4	4.86	6.29
6b	OC_6H_4-OMe	20.2	4.70	5.05
6c	$OC_6H_4-CF_3$	37.8	9.74	12.2
6e	OC_6H_4-CN	51.1	14.0	17.2
7b	NHC_6H_4-OMe	5860	slow	(1300)[b]
7a	NHC_6H_4-H	2110	slow	(410)[b]
7c	$NHC_6H_4-CF_3$	225	slow	(50)[b]
8b	SC_6H_4-OMe	1997	slow	(210)[b]
8a	SC_6H_5	481	slow	(130)[b]

[a] Constant for rate of *first* substitution into mutually trans positions. [b] Behavior is not first order (see text). Rate constant is an approximation to first-order behavior given for comparison.

First-order rate constants for L/L′ exchange in individual sites are shown in Table 1. In the case of the anilides (**7**) and sulfides (**8**), the L_c resonance disappears in a kinetically more complicated way (see below), so the site L_c constants, given for comparison, are from an approximate (but incorrect) fit to a first-order plot.

Anilides: $L_4Os(H)(NHC_6H_4Z)$ (7). Phosphine exchange in the anilide compounds appears to proceed via phosphine dissociation that is facilitated by the π-basicity of the anilido group. Dissociation occurs at the mutually trans phosphine *a* sites *only*, and then label subsequently migrates into the *c* site (cis to the hydride). The basis of this conclusion can be seen in Figure 2, where the resonance at δ 42.0 ppm of the unexchanged L_aL_a site of **7a** is a clean doublet of doublets with no downfield doubling from isotopic labeling in the *c* site; that is, $(L_aL_a)(L_b)(L_c')Os(H)(NHC_6H_5)$ is *not* present and none is detectable even when the L_aL_a δ 42.0 resonance is nearly gone. This is in contrast to the previously discussed L_aL_a' multiplet of **7a** at δ 42.6 ppm, which is clearly doubled, indicating the presence of a mixture of $(L_aL_a')(L_b)(L_c)Os(H)(NHC_6H_5)$ and $(L_aL_a')(L_b)(L_c')Os(H)(NHC_6H_5)$.

Further evidence for the requirement for the presence of L_a' prior to L_c' incorporation comes from interpretation of the rates of exchange at specific sites. Figure 3 shows the time dependence of the integrals of the L_aL_a and L_c phosphine resonances, where symbols are the experimental data, and the lines are calculated using an iterative kinetics modeling program developed by Weigert.[17] It is assumed for the calculation that the intermediate is a distorted trigonal bipyramid with an equatorial amido ligand and that dissociation occurs only from the *a* sites. These suppositions are illustrated in Scheme 2. Starting **9a** dissociates L from site *a* with simultaneous reorganization of the two remaining equatorial L to form a distorted trigonal bipyramid, **10a**. This distortion assumes that the amido lone pair of electrons is oriented so as to lie in the equatorial plane as shown in structure **11**. CPK space-filling models suggest there should be a steric preference for the amide aryl group

(17) (a) "Gear", copyright 1995 by F. J. Weigert. (b) Stabler R. N.; Chesick, J. *Int. J. Kinet.* **1978**, *10*, 461−469. (c) Weigert, F. J. *Comput. Chem.* **1987**, *11*, 273.

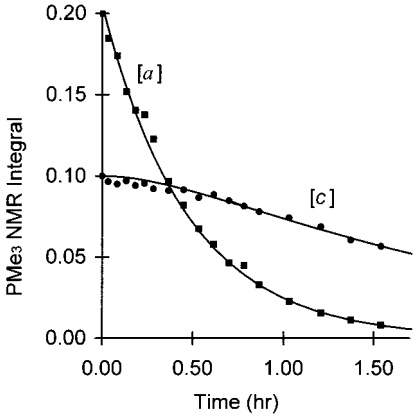
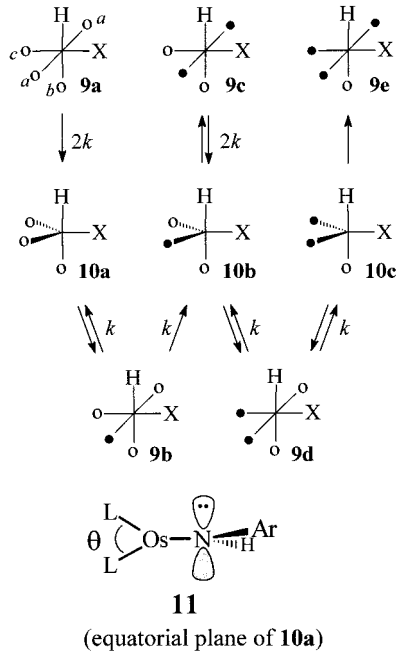


Figure 3. Plot of the relative ^{31}P NMR integrals of unlabeled L in sites L_aL_a and L_c vs time in the exchange of L for L′ into $L_4Os(H)(NHC_6H_4OMe)$ (**7b**). Symbols are data, and lines are calculated (see text).

Scheme 2



11

(equatorial plane of **10a**)

to be oriented toward the hydride in starting materials **7**, with the result of aligning the nitrogen lone pair with the mutually trans phosphine ligand axis as depicted in structure **11**. Presumably such an alignment should direct π-symmetry overlap of the lone pair with the developing vacant osmium orbital aligned along the P−Os−P axis upon dissociation of one of the mutually trans phosphine ligands, thus stabilizing the transition state for its dissociation. This combination of sterically based orientation and single-faced π-bonding account for the stereospecificity of substitution in the anilido complexes. The picture of heteroatom π-donation stabilizing the dissociation transition state and the dissociated intermediate and the geometry change illustrated in structure **11** above are both amply corroborated by theoretical calculations at several levels.[3b,18] Now, when L′ coordinates with **10a**, the principle of microscopic reversibility requires that it enter cis to X to form

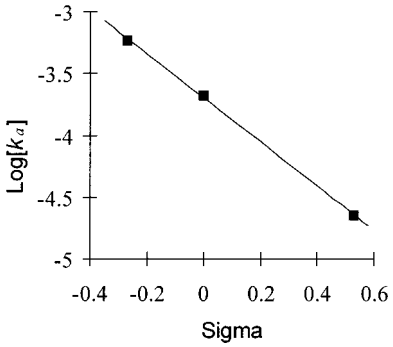


Figure 4. Log of the rate constant for replacement of the *first* L by L′ at site L_aL_a in $L_4Os(H)(NHC_6H_4Z)$ (**6**, Z = OMe, H, CF_3) plotted against the Hammett sigma (σ). The slope (ρ) is −1.8.

9b. Dissociation of the other L_a now forms **10b**, the labeled equivalent of **10a**, and entry of L′ from behind the page into the cis position as shown in Scheme 2 forms **9c** and from the front gives **9d**. Use of this model in the iterative kinetic calculations gave a good visual fit to the non-first-order concentration dependence of disappearance of the L_c ^{31}P resonance shown in Figure 3. None of the processes shown in Scheme 1 lead to label incorporation into position *b*, so other much slower fluxionality of the unsaturated intermediates or perhaps a much slower direct dissociation from site *b* accounts for the eventual complete exchange of all positions in the amido complexes.

Figure 4 shows a Hammett plot of the para-substituted amido series with a good (albeit 3-point) linear relationship ($\rho_p = -1.8$), where the electron-donating substituent increases the rate of phosphine ligand dissociation. The relative rates of total phosphine dissociation are greater for the amides than for the phenoxides, consistent with the greater basicity of nitrogen (Table 1). The basicity of nitrogen also mitigates against dissociation of anilide anion, which would lead to the type of ion pair mechanism by which the phenolate complexes appear to react (see below).

Thiophenoxides: $L_4Os(H)(SC_6H_4Z)$ (8). Phosphine ligand exchange at 80 °C in **8a** and **8b** occurs at the *a* and *c* sites, although the exchange at the former is faster, with the rates of exchange comparable to those of the anilides. Quantifying the exchange kinetics is more difficult than with the phenoxides or amides because the ^{31}P NMR site *a* resonances overlap slightly with the L_c resonance. Only the two derivatives **8a** and **8b** were prepared and rates measured, but the ratio of **8** site *a*:*b*:*c* exchange rates (3:slow:1) is essentially the same as for anilides **7** (4:slow:1), suggesting a similar mechanism for ligand labilization. Examination of the L_aL_a triplet resonance of the A_2MX pattern in the ^{31}P-{^{1}H} NMR spectra shows no isotopic doubling, so exchange into the *c* site does *not* occur independently. Thus, an *a* phosphine must be substituted before label is incorporated into the *c* site, and the most probable interpretation is the same as that just described for the anilides.

The π-bonding nature of metal thiolates is well-known.[19] One of the lone pairs is in an $3sp^2$ orbital, and the other is in an essentially 3p orbital. Since an sp^2 orbital is more electronegative than a p orbital, the sp^2 electron pair is less basic than the p pair. Furthermore,

(18) (a) Davy, R. D.; Hall, M. B. *Inorg. Chem.* **1989**, *28*, 3524−3529. (b) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pelissier, M. *Organometallics* **1992**, *11*, 729−737

the sp^2 pair is pointed away from the metal, while the p pair is aligned optimally for π-interaction with the metal. The phenyl group should prefer to orient itself toward the hydride site just as would be supposed for the anilides or phenoxides, and so the p electron pair would be aligned along the mutually trans phosphine P−M−P axis, accounting for the stereochemical preference for their dissociation. Thus the mechanism of labilization and stereospecificity are believed to be the same as those discussed above for the amide complexes.

In view of the fact that complexes **6** undergo L/L′ exchange by phenoxide ionization (see below), it is interesting to consider why the thiophenoxide complexes should exchange via a lone pair-induced phosphine dissociation instead. The heterolytic cleavage of the Os−OPh and Os−SPh bonds can be considered as the sum of the specific bond dissociation energy (SBDE) for homolysis, the ionization potential (IP) of the osmium radical in the given solvent, and the electron affinity (EA) of the OPh and SPh radicals in the given solvent. From the literature,[20] the gas-phase EA of phenoxy radical equals 52.0 kcal/mol and that of thiophenoxy radical is 57 kcal/mol. From other literature data[21] one can calculate the aqueous phase EA, *both* of which are close to 134 kcal/mol. In organic solvents one may estimate that the difference in EA is therefore between 0 and 5 kcal/mol. A *lower limit* for the difference in homolytic SBDE of $Cp^*Ru(PMe_3)_2-X$ (X = SH, OH) has been estimated to be 18.5 kcal/mol.[22] Assuming that the heats of solution of PhOH, PhSH, PhO•, PhS•, and H• are all small in benzene or THF and that their differences are therefore negligible, and assuming that the difference in bond energies of Os−S and Os−O is at least as large as for ruthenium (presumably it would be larger), one finds that the *lower limit* for the difference in ionization energy is about 13 kcal/mol. Thus, very probably the intrinsic Os−S bond strength slows down the intervention of an ion pair mechanism, and the greater π-basicity of sulfur toward osmium accelerates the L dissociation path compared to oxygen, accounting for the mechanistic preference of **8** versus **6**.

Phenoxides: $L_4Os(H)(OC_6H_4Z)$ (6). On heating each para-substituted phenoxide compound at 80 °C with free L′ in benzene-d_6, labeled phosphine is incorporated into all three sites, with each site apparently incorporating phosphine independently of the others. The conclusion that some sites are not exchanged first as a prerequisite for others to substitute comes from two lines of evidence. First, the ^{31}P NMR spectra show the isotopic doubling phenomenon discussed above. That is, a substantial portion of the ^{31}P resonance of the *unlabeled* mutually trans L_aL_a in $L_4Os(H)(OAr)$ is shifted ca. 5 Hz downfield. As shown in Figure 1 for **6b**, the doublet-of-doublets for unexchanged L_aL_a at δ −35.9 ppm is doubled again to a total of eight peaks by the deuterium isotope effect of L_b' or L_c' incorporation. As L_b' or L_c' incorporation progresses, the isotopically shifted L_aL_a multiplet becomes more dominant. Thus, independent exchange of L′ into either sites L_b or L_c or both is occurring without necessary prior L_a dissociation. Late in the exchange reaction a *third* set of peaks begins to form within the L_aL_a' resonance, probably corresponding to the additive cis isotope effect in $(L_aL_a')(L_b')(L_c')Os(H)(OC_6H_4OMe)$, but no tripling of the L_aL_a resonance occurs, indicating that no detectable $(L_aL_a)(L_b')(L_c')Os(H)(OC_6H_4OMe)$ forms. This observation is reasonable on the basis of probability. A second indication that substitutions at sites *b* and *c* do not require prior site *a* exchange comes form the fact that L/L′ exchange rates at all sites are first order, as illustrated for $L_4Os(H)(OC_6H_4OMe)$, **6b**, in Figure 5. As shown for the anilido complexes above, substitutions that require prior labeling in other parts of the molecule tend not to exhibit first-order behavior.

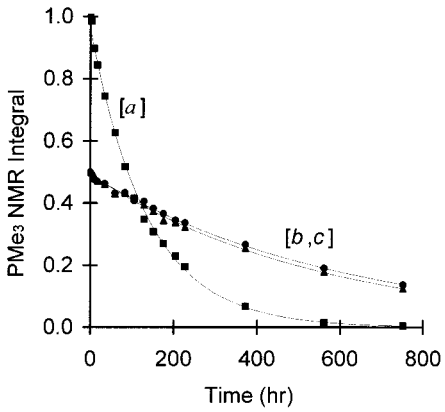


Figure 5. Plot of the relative ^{31}P NMR integrals of unlabeled L in sites L_aL_a, L_b, and L_c vs time in the exchange of L for L′ into $L_4Os(H)(OC_6H_4OMe)$ (**6b**). Symbols are data, and lines are calculated for a first-order decay.

A plot of the log of the sum of rate constants for disappearance of L resonances corresponding to sites L_aL_a, L_b, and L_c in $L_4Os(H)(OC_6H_4Z)$ (**6**, Z = NH_2, OMe, H, CF_3, CN) versus the Hammett sigma (σ_p) is somewhat scattered ($R^2 = 0.93$) with $\rho_p = +0.42$. There is a slight improvement on plotting the exchange rate data against sigma minus (σ^-): $\rho^- = +0.36$ ($R^2 = 0.96$) (Figure 6). In any event, it is clear that the magnitude of the slope is small. The observations that the correlation is marginally better with σ^- and the slope is positive suggest that phenoxide character exists in the transition state of the rate-determining step of phosphine exchange. The most consistent interpretation is that phenoxide dissociation is occurring, although the stereochemical data are inconsistent with rate-determining phenoxide dissociation (more below). The small size of ρ^- is puzzling since an ionization preequilibrium followed by slower phosphine exchange steps should show the full equilibrium effect of the phenoxide stabilities on the slope of the Hammett plot. If the ionization mechanism does operate, then it must be that the size of the substituent effects is somehow attenuated in ion

(19) (a) Ashby, M. T.; Enemark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 730−733. (b) Ashby, M. T.; Enemark, J. H.; Lichtenberger, D. L. *Inorg. Chem.* **1988**, *27*, 191−197. (c) Ashby, M. T. *Comments Inorg. Chem.* **1990**, *10*, 297−313.

(20) *Handbook of Chemistry and Physics*, 80th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1999; pp 10−153.

(21) Some literature data (kcal/mol): (E = O, S); pK_a of $PhEH^a$ = 10.0, 6.5; aqueous $\Delta H_{ionization}$ of PhEH = 5.6,[b] 2 (estimated); SBDE of $PhE-H^c$ = 86.5, 83.3; gas-phase IP of H• = 313.6;[d] $\Delta H_{hydration}$ of $H^{(+)}_{(g)}$ = −261.[e] From the last two numbers, the aqueous phase IP of H• = 53, and from these data the numbers in the text can be calculated. (a) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−462. (b) Isaacs, N. S. *Physical Organic Chemistry*, 2nd ed.; Longman Scientific and Technical: Essex, UK, 1995; p 239. (c) *Handbook of Chemistry and Physics*, 80th ed.; *op cit.*; pp 9−65. (d) *Ibid.*, pp 10−162. (e) Atkins, P. W. *Physical Chemistry*, 5th ed.; W. H. Freeman: New York, 1994; p 88.

(22) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444−1456.

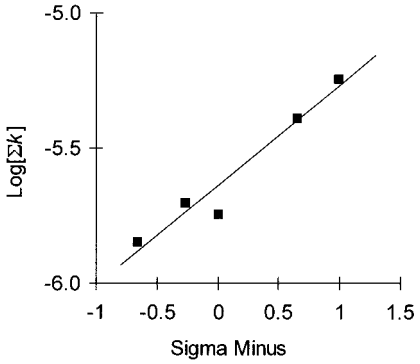


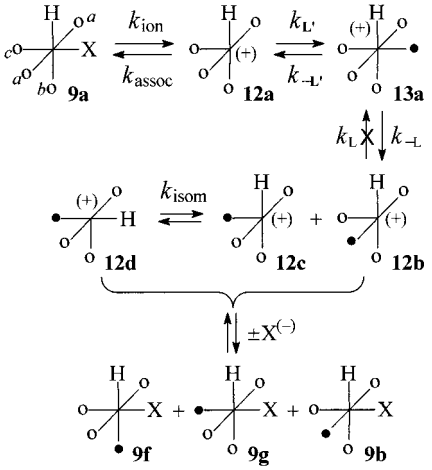
Figure 6. Log of the sum of rate constants at sites L_aL_a, L_b, and L_c for replacement of L by L′ in $L_4Os(H)(OC_6H_4Z)$ (**6**, Z = NH_2, OMe, H, CF_3, CN) plotted against the Hammett sigma minus (σ^-): $\rho^- = +0.36$.

pairs in benzene relative to free phenoxide ions in water. Substitution reactions of organometallic complexes that involve dissociation of OH, OR, or OAr have been postulated by others.[23]

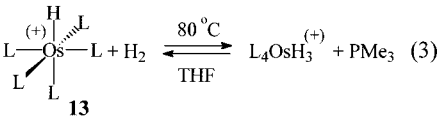
The rates of label incorporation into individual sites *b* and *c* are directly measurable, but the precise rate constant for incorporation into the two *a* sites is not as straightforward. The L_aL_a doublet of doublets contains the intensity of two phosphorus nuclei, but a single L′ substitution in site *a* moves the intensity of both away from the L_aL_a chemical shift and into the L_a and L_a' resonances of the second-order AB resonance set. Thus, the disappearance of the L_aL_a resonance is exactly the rate of the *first* substitution into the *a* site. However, since there are two identical sites from which L can dissociate, the rate constant for disappearance of the L_aL_a resonance would be twice that of a corresponding single site substitution in a mechanism that proceeds by substitution one site at a time. If all sites had the same rate constant for phosphine dissociation and the intermediate was a rigid square pyramid, for example, then the ratio of rates for disappearance of phosphorus resonances L_aL_a (excluding L_aL_a')/L_b/L_c would be 2:1:1. In contrast, if an ion pair mechanism was operating with rate-determining ionization (k_i) followed by fast L/L′ exchange, every ionization would exchange all four sites and $k_{L_aL_a} = k_{L_b} = k_{L_c} = k_i$ and L_aL_a/L_b/L_c would be 1:1:1. In addition, no buildup of any partially substituted intermediates would be seen if ionization was fully rate determining. In fact, this is contrary to observation since substantial concentrations of intermediates partially substituted in all positions are seen during the reaction. The observed relative rates of substitution of label into each of the three sites $k_{L_aL_a}/k_{L_b}/k_{L_c}$, averaged over the five complexes **6a**−**6e**, are approximately 1/0.27/0.27, but the individual relative *b* and *c* rates vary between 0.10 and 0.36 with no obvious trends as a function of para substituent.

The kinetics program was used to calculate time versus concentration data for a mechanistic model, part of which is shown in Scheme 3. The assumptions were as follows: (1) the first step is ionization of phenoxide, **9** → **12**; (2) the rate constant for reassociation of the

Scheme 3



ion pair, **12** → **9**, is much faster than for L′ uptake, **12** → **13**, guaranteeing a fast preequilibrium; (3) intermediate **12** is a square pyramid; (4) coordination of L′ to form **13** and dissociation of L/L′ from **13** occur only in the radial plane; (5) the only fluxionality of intermediate **12** is the hydride shift equilibration **12c** ⇄ **12d**, which is extremely rapid; (6) L′ is in large excess so that only it coordinates. Assumption (5) is reasonable since ambient-temperature ^{31}P NMR spectra of $L_4OsH(OTf)$ reveal rapid averaging of the L_b and L_c resonances even in a solvent as coordinating as THF, while the L_aL_a resonance remains sharp.[7] It has also been shown that the equilibrium of eq 3 is established in less than 4 h at 80



°C, [7] so the phosphine dissociation step is kinetically competent for the present mechanism. Using these assumptions and five rate constants (see Experimental Section), calculated rate ratios were $k_{L_aL_a}/k_{L_b}/k_{L_c}$ = 1:0.36:0.36. Obviously, this is not a unique solution for this complex system, but it is one model and one solution that is sufficiently close to the experimentally observed data to corroborate the reasonableness of the ionic mechanism.

An ion pair mechanism would be expected to show a dependence on solvent polarity, so several other solvents were investigated. Treatment of $L_4Os(H)(OC_6H_4CN)$ (**6e**) with excess L in propylene carbonate (PPC, ϵ = 64.4), DMSO-d_6 (ϵ = 46.7), DMF (ϵ = 36.7), and CD_3NO_2 (ϵ = 35.9) over a period of hours at 80 °C all resulted in high-yield conversions to $[L_5OsH][OAr]$, with $^{31}P\{^1H\}$ NMR resonances at approximately δ −56 (d, 4P, J_{PP} = 17 Hz) and −61 (pent, 1P).[24] Solvent effects on the chemical shifts were small. Use of excess L′ led to a complicated spectrum for $[(L/L')_5OsH][OAr]$ because of the L/L′ chemical shift difference. Even *o*-$C_6H_4Cl_2$ (ϵ = 9.9) afforded a mixture of 22% of $L_4Os(H)(OAr)$ and 78% of $[L_5OsH][OAr]$ from **6e** and excess L after heating at 80 °C for 23 h. In THF (ϵ = 7.6) and in C_6D_6 (ϵ = 2.3) at 80 °C the salt was not formed to a great extent, but

(23) (a) Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179−2185. (b) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387−6389. (c) Simpson, R. D.; Bergman, R. G. *Organometallics* **1993**, *12*, 781−796.

(24) Ermer, S. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *Organometallics* **1989**, *8*, 1377−1378.

a very small doublet was observed in both solvents at δ −55.9 ppm, which corresponds to the resonance of the four radial phosphines in $[L_5OsH]^+$: the axial pentet was apparently too weak to be observed in the noise. Nevertheless, it is a reasonable supposition that the ion pair $[L_5OsH][OAr]$ was present in low steady-state concentrations in benzene and THF.

It is possible that a component of the overall substitution reaction might proceed via phosphine dissociation. Although one would expect the same stereospecific behavior by this mechanism that is seen in the anilides and thiophenoxides, it is at least possible that the phenoxy complexes might exhibit less stereospecificity in substitution by L′. For example, the π-basicity of the phenoxy group is substantially less than that of the anilides and probably the thiophenoxides, so there might be less rate acceleration and less control of the stereochemistry by the phenoxy groups. A phenoxide-assisted phosphine dissociation mechanism should show a negative Hammett ρ, and so a component of this mechanism in combination with positive ρ^- of the postulated ionization mechanism could help to account for the small size of ρ^- discussed above. Unfortunately, the possibility of a contribution by the phosphine dissociation mechanism cannot be evaluated from the extant data.

Conclusions

Osmium complexes *cis*-$L_4Os(H)(XC_6H_4Z)$ are easily prepared from *fac*-$L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ (which is not so easily prepared) and the corresponding neutral arene. The coordinating heteroatom group X = O, S, or NH has a large effect on the phosphine substitution chemistry of the molecule. In the case of thiophenoxide and anilide ligands, heteroatom lone pair π-donation stabilizes the transition state for L dissociation only from the mutually trans sites. The data are inconsistent with either a square-pyramidal intermediate that is rigid during its short lifetime or with a five-coordinate intermediate that is fully fluxional. Most consistent is a quasi-trigonal-bipyramidal intermediate with one L rigidly trans to the hydride, where the molecule is stabilized by π-electron donation from the anilide or sulfide lone pair in the trigonal plane.

Exchange data for the phenoxide complexes are most consistent with a rapidly reversible ionization followed by slower exchange of L via presumed ion pairs $[L_5OsH]$-[OAr]. Dissociation of L from the cation $[L_5OsH]^+$ would be the overall rate-determining step in the exchange. The relatively high basicity of nitrogen prevents anilide ionization and results in strong π-donation, accounting for the mechanistic preference of **7**. Phenoxide's lower basicity and the relatively weak Os−O bond presumably result in an ionic pathway for **6**. In the case of thiophenoxide complexes, **8**, the preference for the L dissociation exchange path over the ionization path is apparently a result of the greater Os−S bond strength combined with its larger π-basicity compared to oxygen. The former retards ionization, and the latter accelerates phosphine dissociation.

Experimental Section

General Comments. Compounds of the type $(Me_3P)_4OsXY$, 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 which was passed through an oxygen scrubber (BASF Ridox R3-11) and water absorbent (Mallinckrodt Aquasorb). Solvents were reagent grade with further purification as follows. Hydrocarbon solvents (alkane and aromatic) were stirred over concentrated sulfuric acid (repeated with fresh acid 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 vendors' containers were dried over calcium hydride (24 h) and were treated the same as the hydrocarbon solvents. Deuterated solvents in vendors' sealed glass ampules were transferred and 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 reference scales used are all δ with respect to TMS for ^{1}H and ^{13}C, 85% H_3PO_4 for ^{31}P, and $CFCl_3$ for ^{19}F NMR. All of the aromatic substrates (para-substituted phenols, anilines, and thiols) were commercial. Solids were sublimed and liquids were distilled prior to use. Elemental analyses were carried out by Galbraith Laboratories, Inc. (Knoxville, TN).

$L_4Os(H)(OC_6H_5)$ (6a). Cold THF (−20 °C, ca. 3 mL) was added to a mixture of $L_3Os(H)(\eta^2\text{-}CH_2PMe_2)$[12] (100 mg, 0.2 mmol, for ease in handling cooled to −20 °C prior to weighing) and phenol (17 mg, 0.18 mmol) in a Schlenk flask. The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. The residue was washed at −78 °C with hexanes (5 × 10 mL) to remove residual **1**, and the residue was dried under vacuum. The bright white, powdery residue amounted to 85 mg, 80% yield. ^{1}H NMR (C_6D_6): δ −7.80 (dq, 1H, J_{PH} = 79, 23 Hz, Os*H*), 1.22 (d, 9H, J = 7 Hz, P(C*H*$_3$)$_3$), 1.25 (d, 9H, J = 8 Hz, P(C*H*$_3$)$_3$), 1.29 (vt, 18H, N = 7 Hz, *trans*-P(C*H*$_3$)$_3$), 6.68 (t, 1H, J = 8 Hz, Ar*H*$_p$), 7.21 (d, 2H, Ar*H*$_o$), 7.41 (t, 2H, J = 8 Hz, Ar*H*$_m$). ^{13}C{^{1}H} NMR (C_6D_6): δ 20.73 (d, J_{PC} = 21 Hz), 23.10 (dvt, J_{PC} = 3.5, N_{PC} = 32 Hz), 28.24 (d, J_{PC} = 31 Hz), 111.73 (s), 120.41 (d, $^4J_{PC}$ = 2.0), 129.17 (s), 171.05 (d, $^3J_{PC}$ = 6.3 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −36.16 (dd, 2P, J_{PP} = 19, 16 Hz), −41.74 (dt, 1P, J_{PP} = 5, 19 Hz, trans to OsH), −49.94 (dt, 1P, J_{PP} = 5, 16 Hz, cis to OsH). Anal. Calcd for $C_{18}H_{42}OP_4Os$: C, 36.73; H, 7.19. Found: C, 37.03; H, 7.16.

$L_4Os(H)(OC_6H_4OMe)$ (6b). The same procedure as with **6a** was used with 22 mg (0.18 mmol) of *p*-methoxyphenol and 100 mg (0.2 mmol) of **1**; yield 75 mg, 67%. ^{1}H NMR (C_6D_6): δ −7.82 (dq, 1H, J_{PH} = 79, 24 Hz, Os*H*), 1.24 (d, 9H, J = 8 Hz, P(C*H*$_3$)$_3$), 1.26 (d, 9H, J = 7 Hz, P(C*H*$_3$)$_3$), 1.31 (vt, 18H, N = 6 Hz, *trans*-P(C*H*$_3$)$_3$), 3.60 (s, OC*H*$_3$), 7.05 (d, 2H, J = 10 Hz), 7.13 (d, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 20.71 (d, J_{PC} = 22 Hz), 23.15 (dvt, J_{PC} = 3.5, N_{PC} = 31 Hz), 28.35 (d, J_{PC} = 31 Hz), 56.06 (O*C*H$_3$), 115.24 (s), 119.53 (d, $^4J_{PC}$ = 1.9), 148.37 (s), 165.54 (d, $^3J_{PC}$ = 4.9 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −36.40 (dd, 2P, J_{PP} = 19, 16 Hz), −42.20 (dt, 1P, J_{PP} = 6, 19 Hz, trans to OsH), −50.92 (dt, 1P, J_{PP} = 6, 16 Hz, cis to OsH). Anal. Calcd for $C_{19}H_{44}O_2P_4Os$: C, 36.89; H, 7.17. Found: C, 36.53; H, 7.10.

$L_4Os(H)(OC_6H_4CF_3)$ (6c). The same procedure as with **6a** was used with 29 mg (0.18 mmol) of *p*-trifluoromethylphenol and 100 mg (0.2 mmol) of **1**, yielding 89 mg, 72%. ^{1}H NMR (C_6D_6): δ −7.99 (dq, 1H, J_{PH} = 79, 24 Hz, Os*H*), 1.18 (m, 36H, P(C*H*$_3$)$_3$)), 7.06 (d, 2H, J = 8 Hz), 7.64 (d, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 20.72 (d, J_{PC} = 22 Hz), 23.02 (dvt, J_{PC} = 2.3, N_{PC} = 33 Hz), 27.95 (d, J_{PC} = 32 Hz), 112.58 (q, $^1J_{CF}$ = 31 Hz, *C*F$_3$), 116.82 (s), 119.95 (s), 126.63 (q, $^2J_{CF}$ = 3.0), 174.25 (d, ^3J = 5.0 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −36.66 (dd, 2P, J_{PP} = 19, 16 Hz), −41.73 (dt, 1P, J_{PP} = 6, 19 Hz, trans to OsH), −49.94 (dt, 1P, J_{PP} = 6, 16 Hz, cis to OsH). Anal. Calcd for $C_{19}H_{41}OP_4F_3Os$: C, 34.75; H, 6.29. Found: C, 34.02; H, 6.31.

$L_4Os(H)(OC_6H_4NH_2)$ (6d). 6d was prepared using 19 mg (0.18 mmol) of *p*-aminophenol and 100 mg (0.2 mmol) of **1**; yield 55 mg, 61%. ^{1}H NMR (C_6D_6): δ −7.81 (dq, 1H, J_{PH} = 80, 24 Hz, Os*H*), 1.24 (d, 9H, J = 8 Hz, P(C*H*$_3$)$_3$), 1.27 (d, 9H, J =

7 Hz, P(CH_3)$_3$), 1.33 (vt, 18H, N = 6 Hz, *trans*-P(CH_3)$_3$), 2.62 (s, NH_2), 6.70 (d, 2H, J = 9 Hz), 7.06 (d, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 20.71 (d, J_{PC} = 22 Hz), 23.12 (dvt, J_{PC} = 2.4, N_{PC} = 31 Hz), 28.41 (d, J_{PC} = 31 Hz), 117.90 (s), 119.73 (d, $^4J_{PC}$ = 1.6), 132.50 (s), 164.52 (d, $^3J_{PC}$ = 5.7 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −35.96 (dd, 2P, J_{PP} = 19, 16 Hz), −41.89 (dt, 1P, J_{PP} = 6, 19 Hz, trans to OsH), −50.74 (dt, 1P, J_{PP} = 6, 16 Hz, cis to OsH).

L$_4$Os(H)(OC$_6$H$_4$CN) (6e). 6e was prepared using 21 mg (0.18 mmol) of *p*-cyanophenol and 100 mg (0.2 mmol) of **1**; yield 92 mg, 83%. ^{1}H NMR (C_6D_6): δ −8.15 (dq, 1H, J_{PH} = 78, 23 Hz, Os*H*), 1.13 (m, 36H, P(CH_3)$_3$)), 6.87 (d, 2H, J = 8 Hz), 7.40 (d, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 20.68 (d, J_{PC} = 21 Hz), 22.95 (dvt, J_{PC} = 2.7, N_{PC} = 32 Hz), 27.85 (d, J_{PC} = 32 Hz), 120.65 (d, ^4J = 2.6), 133.64 (s), *C*−CN, *C*−O and *C*≡N not found. ^{31}P-{^{1}H} NMR (C_6D_6): δ −36.92 (dd, 2P, J_{PP} = 19, 17 Hz), −41.75 (dt, 1P, J_{PP} = 6, 19 Hz, trans to OsH), −49.75 (dt, 1P, J_{PP} = 6, 17 Hz, cis to OsH).

L$_4$Os(H)(HNC$_6$H$_5$) (7a). In the glovebox, 100 mg (0.2 mmol) of **1** (cooled to −20 °C prior to weighing for ease of handling) and aniline (17 mg, 0.18 mmol) were added to a 9 mm NMR tube fused to a 14/20 ground-glass joint. Approximately 3 mL of THF was added, and the tube was removed from the glovebox, sealed on the vacuum line, and heated in an oil bath at 110 °C. The reaction, monitored by ^{31}P NMR, was complete after 60 h. The tube was broken in the glovebox, and the contents were transferred to a Schlenk flask. Solvent was removed under vacuum, and the residue was washed with hexanes (5 × 10 mL) at −78 °C to separate any residual **1**. The bright yellow, powdery residue weighed 89 mg, 84%. ^{1}H NMR (C_6D_6): δ −8.67 (dq, 1H, J_{PH} = 74, 23 Hz, Os*H*), 1.07 (d, 9H, J = 6 Hz, P(CH_3)$_3$), 1.26 (d, 9H, J = 7 Hz, P(CH_3)$_3$), 1.30 (vt, 18H, N = 6 Hz, *trans*-P(CH_3)$_3$), 2.32 (brd, 1H, J_{PH} = 6, N*H*), 6.57 (d, 1H, J = 8 Hz), 6.91 (dd, 1H, J = 8, 3.5 Hz), 7.19 (dd, 1H, J = 6, 8 Hz), 7.31 (d, 1H, J = 8 Hz), 7.63 (dd, 1H, J = 6, 3.5 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.80 (d, J_{PC} = 21 Hz), 23.42 (dvt, J_{PC} = 2.3, N_{PC} = 31 Hz), 28.45 (d, J_{PC} = 29 Hz), 108.15 (s), 115.14 (s), 117.02 (d, $^4J_{PC}$ = 3.8), 129.12 (s), 129.51 (s), 160.64 (d, $^3J_{PC}$ = 6 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −42.15 (dd, 2P, J_{PP} = 18, 16 Hz), −51.02 (dt, 1P, J_{PP} = 9, 18 Hz, trans to OsH), −52.81 (dt, 1P, J_{PP} = 9, 16 Hz, cis to OsH). Anal. Calcd for $C_{18}H_{43}NP_4Os$: C, 36.79; H, 7.38. Found: C, 36.59; H, 7.25.

L$_4$Os(H)(HNC$_6$H$_4$OMe) (7b). The same procedure as for **7a** was used with 100 mg (0.2 mmol) of **1** and 22 mg (0.18 mmol) of *p*-methoxyaniline in ca. 3 mL of THF at 110 °C for 80 h; yield 93.4 mg, 84%. ^{1}H NMR (C_6D_6): δ −8.33 (dq, 1H, J_{PH} = 75, 23 Hz, Os*H*), 1.09 (d, 9H, J = 6 Hz, P(CH_3)$_3$), 1.28 (d, 9H, J = 7 Hz, P(CH_3)$_3$), 1.33 (vt, 18H, N = 6 Hz, *trans*-P(CH_3)$_3$), 1.87 (brd, 1H, 7 Hz, N*H*), 3.61 (s, OCH_3), 6.49 (brs, 1H), 6.95 (brs, 1H), 7.08 (brs, 1H), 7.21 (brs, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.81 (d, J_{PC} = 22 Hz), 23.40 (dvt, J_{PC} = 3.6, N_{PC} = 34 Hz), 28.57 (d, J_{PC} = 29 Hz), 55.27 (O*C*H$_3$), 114.56 (s), 115.01 (s), 116.20 (s), 120.94 (s), 141.54 (s), 152.81 (s). ^{31}P{^{1}H} NMR (C_6D_6): δ −41.51 (dd, 2P, J_{PP} = 18, 16 Hz), −50.34 (dt, 1P, J_{PP} = 9, 18 Hz, trans to OsH), −52.38 (dt, 1P, J_{PP} = 9, 16 Hz, cis to OsH). Anal. Calcd for $C_{19}H_{45}ONP_4Os$: C, 36.95; H, 7.34. Found: C, 37.21; H, 7.35.

L$_4$Os(H)(HNC$_6$H$_4$CF$_3$) (7c). The same procedure as for **7a** was used with 100 mg (0.2 mmol) of **1** and 22.8 μL (0.18 mmol) of *p*-trifluoromethylaniline in ca. 3 mL of THF at 110 °C for 40 h; yield 100 mg, 85%. ^{1}H NMR (C_6D_6): δ −8.61 (dq, 1H, J_{PH} = 75, 23 Hz, Os*H*), 1.01 (d, 9H, J = 6 Hz, P(CH_3)$_3$), 1.19 (vt, 18H, N = 6 Hz, *trans*-P(CH_3)$_3$), 1.20 (d, 9H, J = 7 Hz, P(CH_3)$_3$), 2.96 (brd, 1H, 6 Hz, N*H*), 6.27 (d, 1H, J = 9 Hz), 7.20 (d, 1H, J = 8 Hz), 7.37 (d, 1H, J = 8 Hz), 7.62 (d, 1H, J = 9 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 21.64 (d, J_{PC} = 22 Hz), 23.34 (dvt, J_{PC} = 3.2, N_{PC} = 31 Hz), 28.07 (d, J_{PC} = 29 Hz), 107.88 (q, $^1J_{CF}$ = 31 Hz, *C*F$_3$), 113.99 (s), 114.3 (s), 116.06 (s), 126.13 (d, $^3J_{PC}$ = 2.5 Hz), 126.93 (d, $^3J_{PC}$ = 3.8 Hz), 163.22 (brs). ^{31}P-{^{1}H} NMR (C_6D_6): δ −41.77 (dd, 2P, J_{PP} = 18, 17 Hz), −50.45 (dt, 1P, J_{PP} = 9, 18 Hz, trans to OsH), −51.72 (dt, 1P, J_{PP} = 9, 17 Hz, cis to OsH). ^{19}F{^{1}H} NMR (C_6D_6): δ −57.88 (s). Anal. Calcd for $C_{19}H_{42}NF_3P_4Os$: C, 34.81; H, 6.46. Found: C, 35.15; H, 6.20.

L$_4$Os(H)(SC$_6$H$_5$) (8a). The same procedure as for **7a** was used with 100 mg (0.2 mmol) of **1** and 20 mg (0.18 mmol) of thiophenol in ca. 3 mL of THF, except that no heating was necessary. After the sample warmed to room temperature the ^{31}P NMR revealed complete reaction. The pale green, powdery residue weighed 85 mg, 78%. ^{1}H NMR (C_6D_6): δ −9.50 (dq, 1H, J_{PH} = 64, 23 Hz, Os*H*), 1.27 (d, 9H, J = 6 Hz, P(CH_3)$_3$), 1.30 (d, 9H, J = 7 Hz, P(CH_3)$_3$), 1.43 (vt, 18H, N = 6 Hz, *trans*-P(CH_3)$_3$), 6.88 (t, 1H, J = 7 Hz), 7.20 (t, 2H, J = 7 Hz), 8.27 (d, 2H, J = 7 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 22.83 (d, J_{PC} = 24 Hz), 23.61 (dvt, J_{PC} = 2.5, N_{PC} = 35 Hz), 28.58 (dd, J_{PC} = 27, 2.8 Hz), 119.82 (s), 131.57 (d, $^4J_{PC}$ = 3.1), 150.43 (d, $^3J_{PC}$ = 10), one *C* not found (under solvent?). ^{31}P{^{1}H} NMR (C_6D_6): δ −49.61 (dd, 2P, J_{PP} = 18, 13 Hz), −50.86 (dt, 1P, J_{PP} = 13, 18 Hz, trans to OsH), −53.83 (dt, 1P, J_{PP} = 13, 18 Hz, cis to OsH). Anal. Calcd for $C_{19}H_{42}SP_4Os$: C, 35.75; H, 7.00. Found: C, 35.78; H, 6.98.

L$_4$Os(H)(SC$_6$H$_4$OMe) (8b). The same procedure as for **8a** was used with 100 mg (0.2 mmol) of **1** and 22.4 μL (0.18 mmol) of *p*-methoxythiophenol in ca. 3 mL of THF; yield 91 mg, 80%. ^{1}H NMR (C_6D_6): δ −9.50 (dq, 1H, J_{PH} = 64, 23 Hz, Os*H*), 1.26 (d, 9H, J = 6 Hz, P(CH_3)$_3$), 1.31 (d, 9H, J = 8 Hz, P(CH_3)$_3$), 1.40 (vt, 18H, N = 6 Hz, *trans*-P(CH_3)$_3$), 3.59 (s, OCH_3), 7.19 (d, 2H, J = 7 Hz), 8.10 (d, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 22.27 (d, J_{PC} = 20 Hz), 22.64 (dvt, J_{PC} = 2.5, N_{PC} = 35 Hz), 27.52 (dd, J_{PC} = 27, 2.8 Hz), 55.95 (s, O*C*H$_3$), 119.19 (s), 130.52 (d, $^4J_{PC}$ = 3.1), 149.47 (d, $^3J_{PC}$ = 10), one *C* not found (under solvent?). ^{31}P{^{1}H} NMR (C_6D_6): δ −50.37 (t, 2P, J_{PP} = 18 Hz), −51.54 (dt, 1P, J_{PP} = 12, 18 Hz, trans to OsH), −54.42 (dt, 1P, J_{PP} = 12, 18 Hz, cis to OsH). Anal. Calcd for $C_{19}H_{42}OSP_4Os$: C, 35.95; H, 6.99. Found: C, 35.80; H, 6.83.

P(CD$_3$)$_3$−P(CH$_3$)$_3$ Exchange Kinetics. A typical phosphine exchange experiment was as follows. Approximately 10 mg of L$_4$Os(H)(XC$_6$H$_4$Z) was weighed in the drybox and added to a 5 mm NMR tube fused to a vacuum valve. Benzene-d_6 (0.3 mL) was added to the tube to form a clear solution that ranged from colorless (phenoxides), to yellow (amides), to pale green (thiophenoxides). The sample was freeze−pump−thaw degassed three times, and at least 20 equiv per osmium of L′ (P(CD$_3$)$_3$) was condensed into the tube. Kinetic data were obtained from ^{31}P NMR spectra using an inverse-gated, proton-decoupling pulse sequence used to minimize nuclear Overhauser enhancements. The average phosphorus T_1 value for these compounds is 10−12 s, so a relaxation delay of 55 s was used. Integrations against standard materials revealed errors of less than 5%. Progress of the reaction was monitored either by continuous data acquisition in the NMR probe at the designated temperature or by heating the sample in a constant-temperature bath with periodic measurement of the ^{31}P{^{1}H} NMR spectra at room temperature. R^2 values from the kinetic plots were usually greater than 0.99.

Kinetic Modeling of L/L′ Exchange. The Weigert program[17] was used to iteratively calculate time/concentration curves for particular exchange schemes. For example, the model for the exchange of L$_4$Os(H)(NHCHOMe) given in the results section interconverts 16 isotopic substitutional isomers of **9** (including enantiomers), 16 of **12**, and 10 of **13**, using 89 equations and 5 distinct rate constants, some multiplied by statistical factors. The concentration numbers for the isotopomers of **9** were converted to phosphorus integral values, and the rate constants $k_{L_aL_a}$, k_{L_b}, and k_{L_c} were calculated. For the rate constants $k_{ion} = 4 \times 10^{-4}$, $k_{assoc} = 1 \times 10^6$, $k_{L'} = 1 \times 10^4$, $k_{-L} = 1 \times 10^{-3}$, and $k_{isom} = 1 \times 10^8$, calculated rates were $k_{L_aL_a} = 1.99 \times 10^{-6}$ and $k_{L_b} = k_{L_c} = 7.11 \times 10^{-7}$; that is, $L_aL_a/L_b/L_c$ = 1:0.36:0.36.

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