Articles

Generation of Functionally Substituted Cyclopentadienyl Ligands in Osmium(IV) Chemistry†

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Several types of substituted cyclopentadienyl osmium(IV) complexes can be obtained by reaction of $OsH(\eta^5\text{-}C_5H_5)Cl(EPh_3)(P^iPr_3)$ (E = Ge (**1**), Si (**2**)) with LiNu reagents. Both **1** and **2** react with $LiCH_2CN$. The reactions give $OsH_2(\eta^5\text{-}C_5H_4EPh_3)(CH_2CN)(P^iPr_3)$ (E = Ge (**3**), Si (**4**)). The reaction of the perdeuterated cyclopentadienyl complex $OsH(\eta^5\text{-}C_5D_5)Cl(SiPh_3)(P^iPr_3)$ (**2-d$_5$**) with $LiCH_2CN$ affords $Os(H)(D)(\eta^5\text{-}C_5D_4SiPh_3)(CH_2CN)(P^iPr_3)$ (**4-d$_5$**). Complex **4** reacts with CD_3OD to give $OsH_2(\eta^5\text{-}C_5H_4SiPh_3)(CD_2CN)(P^iPr_3)$ (**4-d$_2$**), which can be also obtained by addition of $LiCD_2CN$ to **2**. The treatment of **1** with RLi leads to $OsH_2(\eta^5\text{-}C_5H_4R)(GePh_3)(P^iPr_3)$ (R = CH_3 (**5**), ^{n}Bu (**6**), ^{sec}Bu (**7**)). Under the same conditions, the addition of ^{n}BuLi to $OsH(\eta^5\text{-}C_5D_5)Cl(GePh_3)(P^iPr_3)$ (**1-d$_5$**) affords $Os(H)(D)(\eta^5\text{-}C_5D_4{}^n\text{Bu})(GePh_3)(P^iPr_3)$ (**6-d$_5$**). Complex **2** also reacts with CH_3Li and ^{n}BuLi. In both cases, complex $OsH_2\{\eta^5\text{-}C_5H_4\text{-}Si(C_6H_4)Ph_2\}(P^iPr_3)$ (**8**) is obtained. The structure of **8** has been determined by X-ray diffraction analysis. The distribution of ligands around the metallic center can be described as a four-legged piano stool geometry with the phosphine and the metalated phenyl group mutually *transoid*. The treatment at room temperature of **2-d$_5$** with ^{n}BuLi leads to a mixture of $OsH_2(\eta^5\text{-}C_5D_4Si(C_6H_4)Ph_2\}(P^iPr_3)$ (**8-d$_4$**) and $Os(H)(D)(\eta^5\text{-}C_5D_4{}^n\text{Bu})(SiPh_3)(P^iPr_3)$ (**9-d$_5$**) in a 2:1 molar ratio. The reaction of **2** with ^{sec}BuLi also gives a mixture. In this case, it is formed by $OsH_2(\eta^5\text{-}C_5H_4{}^{sec}\text{Bu})(SiPh_3)(P^iPr_3)$ (**10**) and **8** in a 1:4 molar ratio. The addition of $LiCH_2C(O)CH_3$ to **2** leads to $OsH(\eta^5\text{-}C_5H_5)(SiPh_2C_6H_4)(P^iPr_3)$ (**11**). The reactions of **1** with $LiNR_2$ afford $OsH_2(\eta^5\text{-}C_5H_4NR_2)(GePh_3)(P^iPr_3)$ (R = Et (**12**), allyl (**13**)), while under the same conditions **2** gives mixtures of **8** and $OsH_2(\eta^5\text{-}C_5H_4NR_2)(SiPh_3)(P^iPr_3)$ (R = Et (**14**), allyl (**15**)). The structure of **13** has been also determined by X-ray diffraction analysis. The distribution of ligands around the metallic center is also a four-legged piano stool geometry, but in this case, the phosphine is *transoid* to $GePh_3$. Both **1** and **2** react with $LiPPh_2$. The reactions give the cyclopentadienyl phosphine derivatives $OsH_2(\eta^5\text{-}C_5H_4PPh_2)(EPh_3)(P^iPr_3)$ (E = Ge (**16**), Si (**17**)).

Introduction

Transition metal complexes containing a η^5-cyclopentadienyl group and monodentate ligands undergo base-induced migration reactions of a monodentate ligand from the metal to a neighboring cyclopentadienyl carbon atom. It is widely accepted that such reactions involve the initial deprotonation of the cyclopentadienyl ring followed by the ligand migration. The produced anion is quenched by reaction with an electrophile (Scheme 1). The first example of this type of migration reaction was reported by Dean and Graham in 1977 for $M(\eta^5\text{-}C_5H_5)(GePh_3)(CO)_3$ (M = Mo, W).[1] Since then, several types of migrations have been observed: silyl from rhenium[2] and iron,[3] germyl, stannyl, and plumbyl from molybdenum, tungsten, and iron,[3e,4] acyl from rhenium[5] and iron,[6] hydride from rhenium[7] and iron,[8] acetylide from iron,[9] and phosphorus ligands from iron[10] and ruthenium.[11]

In addition to these reactions, which provide potentially useful approaches to functionally substituted

† Dedicated to Prof. José Barluenga on the occasion of his 60th birthday.

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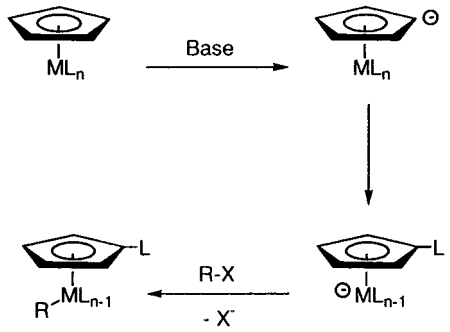
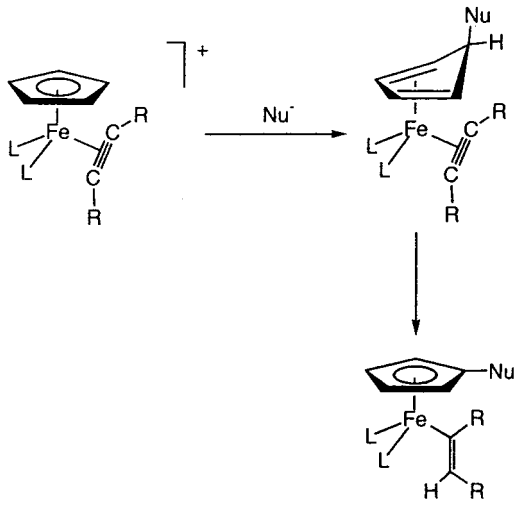
Scheme 1



Scheme 2



cyclopentadienyl complexes,[12] it has been observed that cyclopentadienyl iron π-alkyne complexes $[Fe(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2R_2)L_2]^+$ add nucleophiles to afford $Fe(\eta^5\text{-}C_5H_4Nu)(CR{=}CHR)L_2$ and/or $Fe(\eta^5\text{-}C_5H_5)\{CR{=}C(Nu)R\}L_2$ depending upon of the substituents of the alkyne and the nature of the nucleophile. The formation of the substituted cyclopentadienyl derivatives involves the intermolecular *exo*-addition of the nucleophile to the cyclopentadienyl ring followed by the intramolecular *cis*-addition to the alkyne of the *endo*-hydrogen of the cyclopentadiene formed in the first step (Scheme 2).[13] A similar type of cyclopentadienyl ring substitution, where a π-alkyne is not involved, has been reported in the reaction of a cyclopentadienyl cobalt complex with MeLi.[14]

The chemistry of the cyclopentadienyl−osmium complexes is a little-known field[15] due to the lack of convenient osmium synthetic precursors[16] and the higher kinetic inertia of the $Os(\eta^5\text{-}C_5H_5)L_3$ compounds in comparison with the related iron and ruthenium species.[17]

As a part of our study on the chemical properties of the six-coordinate osmium(IV) complex $OsH_2Cl_2(P^iPr_3)_2$, we have previously reported the synthesis of the cyclopentadienyl osmium compound $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$.[18] Despite the high kinetic inertia of the $Os(\eta^5\text{-}C_5H_5)L_3$ compounds, this complex is a labile starting material for the development of new cyclopentadienyl osmium chemistry.[19] Thus, in pentane and toluene, the dissociation of a phosphine ligand is favored, and the resulting metallic fragment $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)$ is capable of activating by oxidative addition HER_3 molecules. The reactions afford osmium(IV) hydride derivatives of the type $OsH(\eta^5\text{-}C_5H_5)Cl(ER_3)(P^iPr_3)$ (E = Si, Ge), with a distribution of ligands around the metallic center that can be described as a four-legged piano stool geometry. The thermodynamic stability of the Os−ER_3 bonds depends on the cone angle of the ER_3 group and increases in the sequence Os−Si ≪ Os−Sn < Os−Ge.[20]

In the search for novel cyclopentadienyl chemistry, we have now studied the reactivity of the complexes $OsH(\eta^5\text{-}C_5H_5)Cl(EPh_3)(P^iPr_3)$ (E = Si, Ge) toward LiNu nucleophillic reagents. This paper reports novel Nu(Os)/H(C_5H_5) exchange reactions, which afford substituted cyclopentadienyl osmium(IV) complexes.

Results and Discussion

1. Reactions of $OsH(\eta^5\text{-}C_5H_5)Cl(EPh_3)(P^iPr_3)$ (E = Ge, Si) with $LiCH_2CN$: EPh_3(Os)/H(C_5H_5) Exchange. Complexes $OsH(\eta^5\text{-}C_5H_5)Cl(EPh_3)(P^iPr_3)$ (E = Ge (**1**), Si (**2**)) react with $LiCH_2CN$ in tetrahydro-

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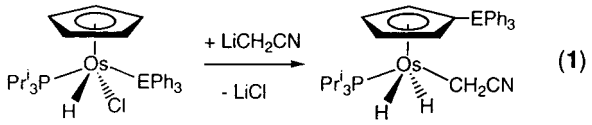
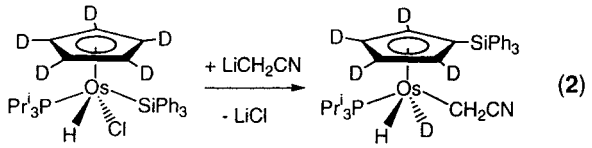
furan at room temperature to give the substituted cyclopentadienyl derivatives $OsH_2(\eta^5\text{-}C_5H_4EPh_3)(CH_2CN)(P^iPr_3)$ (E = Ge (**3**), Si (**4**)), according to eq 1.



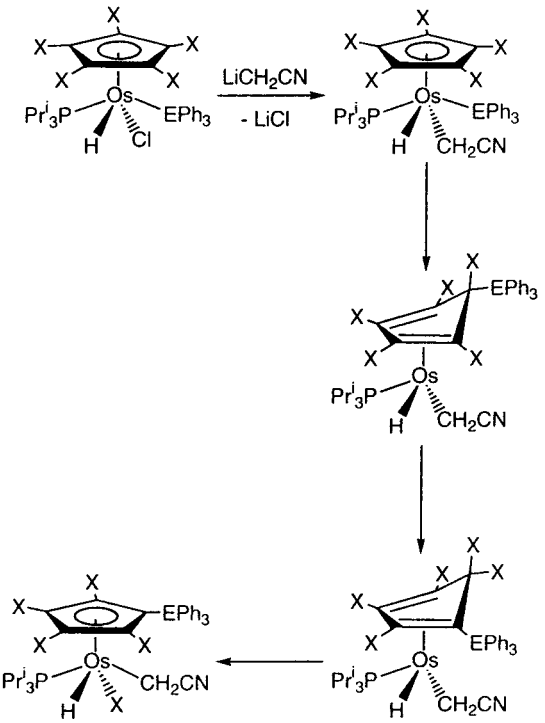
The new compounds were isolated as white solids in about 60% yield. In agreement with the presence of the substituted cyclopentadienyl ligands, the resonances of the C_5H_4 protons in the ^1H NMR spectra appear between 4.80 and 4.30 ppm as AA′BB′ spin systems. In addition, the spectra show singlets at 2.10 (**3**) and 1.87 (**4**) ppm, corresponding to the CH_2CN protons, and doublets at −14.49 (**3**) and −14.80 (**4**) ppm with H−P coupling constants of 28.8 and 27.0 Hz, respectively, due to the hydride ligands. The presence of only one signal for the hydrides and the values of the H−P coupling constants[21] are consistent with four-legged piano stool structures with the hydrides *transoid*. The ^1H NMR spectra show also only one ^{i}Pr−methyl chemical shift, suggesting that in solution the substituted cyclopentadienyl groups rotate around the osmium cyclopentadienyl axis. The $^{13}C\{^1H\}$ NMR spectra are in accordance with the ^1H NMR spectra; thus the cyclopentadienyl carbon atoms display three signals at about 91 ($CEPh_3$) and 81 and 78 (CH) ppm. The CH_2CN ligand gives rise to two singlets at 118.3 (CN, **3** and **4**) and 16.5 (CH_2, **3**) and 15.8 (CH_2, **4**) ppm. The $^{31}P\{^1H\}$ NMR spectra contain singlets at about 41 ppm, which are split into triplets under off-resonance conditions, by spin coupling with two equivalent hydrides.

To investigate the mechanism of the process shown in eq 1, we have carried out the reaction of the perdeuterated cyclopentadienyl complex $OsH(\eta^5\text{-}C_5D_5)Cl(SiPh_3)(P^iPr_3)$ (**2-d$_5$**) with $LiCH_2CN$. Treatment of **2-d$_5$** with $LiCH_2CN$ under the same conditions as those mentioned for the formation of **3** and **4** leads selectively to $Os(H)(D)(\eta^5\text{-}C_5D_4SiPh_3)(CH_2CN)(P^iPr_3)$ (**4-d$_5$**), containing a deuteride ligand at the osmium atom (eq 2).



The presence of a deuterium atom bonded to the metallic center of **4-d$_5$** is strongly supported by the ^2H NMR spectrum of the complex, which shows an AA′BB′ spin system centered at 4.34 ppm (C_5D_4) and a broad singlet at −14.89 ppm (Os−D) with a 4:1 intensity ratio.

Scheme 3



The formation of **4-d$_5$** suggests that the processes shown in eqs 1 and 2 proceed via the elemental steps collected in Scheme 3. The reactions initially involve the replacement of the Cl^- anion by the CH_2CN group. The spontaneous migration of EPh_3 from the osmium atoms into the cyclopentadienyl ligands should afford substituted cyclopentadiene osmium(II) species, with the EPh_3 groups in *endo* position. Subsequently, these intermediates could evolve by *exo*-1,5-hydride (deuteride) shift to place a hydrogen (deuterium) atom in *endo* position. The *exo*-1,5-hydride shift in $\eta^4\text{-}C_5H_6$ is precedented.[7a,8] Finally the migration of this *endo*-hydrogen (deuterium) atom from the dienes into the osmium atoms should give **3**, **4**, and **4-d$_5$**.

Although there are not precedents for the spontaneous migration of ligands from the metals to coordinated cyclopentadienyl groups, it has been observed that the irradiation of $Fe(\eta^5\text{-}C_5H_5)\{CH(OSiMe_3)Ph\}(CO)_2$ in the presence of triphenylphophine leads to $Fe\{\eta^4\text{-}C_5H_5CH(OSiMe)Ph\}(CO)_2(PPh_3)$, with the alkyl substituent in *exo* position.[22] Similarly, the irradiation of $Fe(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}CH_2Ph)(CO)_2$ under carbon monoxide atmosphere affords $Fe\{\eta^4\text{-}C_5(Me)_5CH_2Ph\}(CO)_3$ with the benzyl group also in *exo* position.[23]

In solution H/D exchanges between the metal and the cyclopentadienyl and CH_2CN ligands of **4-d$_5$** are not observed. However, the CH_2CN group of **4** undergoes intermolecular H/D exchange with methanol-d_4, without affecting the hydride positions. Thus, the stirring of **4** in methanol-d_4 at room temperature leads to $OsH_2(\eta^5\text{-}C_5H_4SiPh_3)(CD_2CN)(P^iPr_3)$ (**4-d$_2$**) in 37% yield after 3 days. This deuterated species could be formed via the CH_2CN−methanol-d_4 interaction shown in eq 3.

(21) They are typical values for this arrangement: see for example refs 18 and 19d, and (a) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Chem. Commun.* **1992**, 1201. (b) Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5527. (c) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267. (d) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980. (e) Grumbine, S. K.; Mitchell, G. P.; Strauss, D. A.; Tilley, T. D.; Rheingold, A. L. *Organometallics* **1998**, *17*, 5607.

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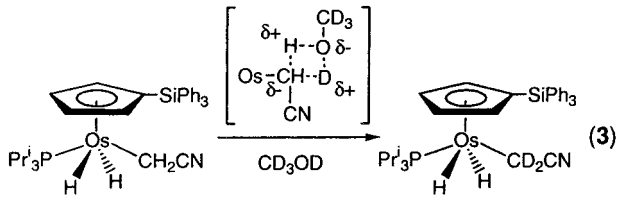
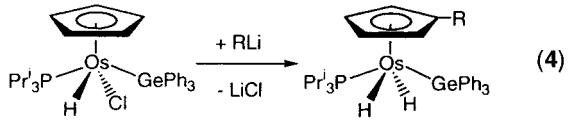


4 **4-d_2**

The most noticeable spectroscopic feature of **4-d_2**, which is also obtained by reaction of **2** with $LiCD_2CN$, is a singlet at 2.15 ppm in the ^2H NMR spectrum.

2. Reactions of $OsH(\eta^5\text{-}C_5H_5)Cl(GePh_3)(P^iPr_3)$ with RLi (R = CH_3, ^{n}Bu, ^{sec}Bu): R(Os)/H(C_5H_5) Exchange. Treatment of tetrahydrofuran solutions of **1** with MeLi, ^{n}BuLi, and ^{sec}BuLi at room temperature affords the substituted cyclopentadienyl derivatives $OsH_2(\eta^5\text{-}C_5H_4R)(GePh_3)(P^iPr_3)$ (R = CH_3 (**5**), ^{n}Bu (**6**), ^{sec}Bu (**7**)), which were isolated as white solids in good yield (eq 4).

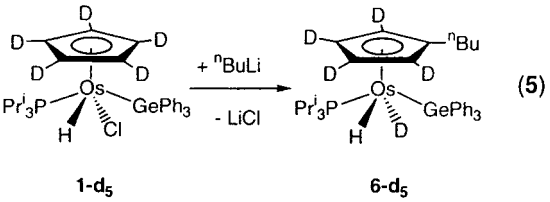


1 R = CH_3 (**5**), ^{n}Bu (**6**), ^{sec}Bu (**7**)

In the ^1H NMR spectra of **5** and **6**, the most noticeable features are AA′BB′ spin systems between 4.80 and 4.40 ppm, corresponding to the C_5H_4 protons, and at about −14.5 ppm doublets with H−P coupling constants of about 29 Hz, due to the hydride ligands. The presence of the alkyl substituents at the cyclopentadienyl groups is strongly supported by the APT $^{13}C\{^1H\}$ NMR spectra, which show singlets at 14.4 (+, CH_3, **5**) and 35.3 (−, CH_2, **6**) ppm. The $^{31}P\{^1H\}$ NMR spectra contain singlets at about 42 ppm, which under off-resonance conditions are split into triplets by spin coupling with the two equivalent hydrides.

The ^1H NMR spectrum of **7** reveals the asymmetry of the alkyl group, which gives rise to two ^{i}Pr−methyl chemical shifts, and inequivalent hydride ligands. Thus, in the high-field region, the spectrum shows two double doublets at −14.46 and −14.56 ppm with H−P and H−H coupling constants of 29.4 and 3.3 Hz, respectively. Furthermore the spectrum contains between 4.80 and 4.40 ppm a complex resonance corresponding to the cyclopentadienyl protons, two multiplets at 1.62 (CH) and 1.19 (CH_2) ppm, a doublet at 1.08 (J(HH) = 6.9 Hz, CH_3) ppm, and a triplet at 0.70 (J(HH) = 7.5 Hz, CH_3) ppm due to the *sec*-butyl group. In the APT $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonance is a singlet at 33.3 (+) ppm, corresponding to the CH carbon atom of the alkyl group. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 41.3 ppm.

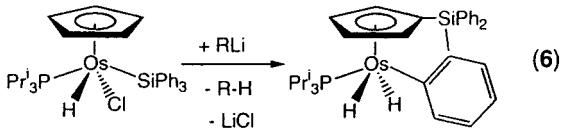
The formation of **5**−**7** involves a sequence of reactions similar to that shown in Scheme 3, where on $OsH(\eta^5\text{-}C_5H_5)(alkyl)(GePh_3)(P^iPr_3)$ intermediates, the spontaneous migration of the alkyl group (instead EPh_3) from the osmium atom to the cyclopentadienyl group has taken place. This is supported by the reaction of the perdeuterated cyclopentadienyl complex $OsH(\eta^5\text{-}C_5D_5)Cl(GePh_3)(P^iPr_3)$ (**1-d_5**) with ^{n}BuLi, which leads to $Os(H)(D)(\eta^5\text{-}C_5D_4{}^nBu)(GePh_3)(P^iPr_3)$ (**6-d_5**), according to eq 5.



1-d_5 **6-d_5**

In agreement with the presence of a deuterium atom bonded to the osmium atom of **6-d_5**, the ^2H NMR spectrum of this compound shows an AA′BB′ spin system centered at 4.61 ppm (C_5D_4) and a broad singlet at −14.33 ppm (Os-D) with a 4:1 intensity ratio.

3. Reactions of $OsH(\eta^5\text{-}C_5H_5)Cl(SiPh_3)(P^iPr_3)$ with RLi (R = CH_3, ^{n}Bu, ^{sec}Bu): $SiPh_3$(Os)/H(C_5H_5) Exchange and Subsequent C−H Activation of a Phenyl Group. Treatment of tetrahydrofuran solutions of **2** with MeLi and ^{n}BuLi at room temperature affords $OsH_2\{\eta^5\text{-}C_5H_4Si(C_6H_4)Ph_2\}(P^iPr_3)$ (**8**), which is a result of a $SiPh_3$(Os)/H(C_5H_5) exchange and subsequent C−H activation of a phenyl of the silyl group. Complex **8** was isolated as a white solid in 61% yield, according to eq 6.



2 R = CH_3, ^{n}Bu **8**

A view of the molecular geometry of **8** is shown in Figure 1. Selected bond distances and angles are listed in Table 1. The hydride ligands H(01) and H(02) were located in the difference Fourier maps and refined as isotropic atoms together with the rest of the non-hydrogen atoms of the structure, giving Os−H(01) and Os−H(02) distances of 1.54(8) and 1.56(7) Å, respectively.

The distribution of ligands around the osmium atom can be described as a four-legged piano stool geometry with the hydride ligands disposed mutually *transoid* (H(01)−Os−H(02) = 116(4)°) and the metalated phenyl group disposed *transoid* to the triisopropylphosphine ligand (P−Os−C(6) = 90.9(3)°). In agreement with this disposition, the ^1H NMR spectrum shows at −12.76 ppm a doublet with an H−P coupling constant of 36.3 Hz, for the hydride ligands, and the $^{13}C\{^1H\}$ NMR spectrum contains at 140.6 ppm a doublet with a C−P coupling constant of 6 Hz, due to C(6).

The Os−C(6) bond length of 2.106(7) Å is typical for an Os−C(aryl) single bond and agrees well with the values previously found in the complexes $OsH\{C_6H_4\text{-}2\text{-}(E\text{-}CH{=}CHPh)\}(CO)(P^iPr_3)_2$ (2.136(7) Å),[24] $[OsH(\eta^5\text{-}C_5H_5)\{NH{=}C(Ph)C_6H_4\}(P^iPr_3)]BF_4$ (2.10(2) and 2.137(19) Å), $[OsH(\eta^5\text{-}C_5H_5)(PPh_2C_6H_4)(P^iPr_3)]BF_4$ (2.180(9) and 2.136(9) Å),[19d] $Os(C_2Ph)\{NH{=}C(Ph)C_6H_4\}(CO)$-

(24) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Sola, E. *J. Am. Chem. Soc.* **1996**, *118*, 89.

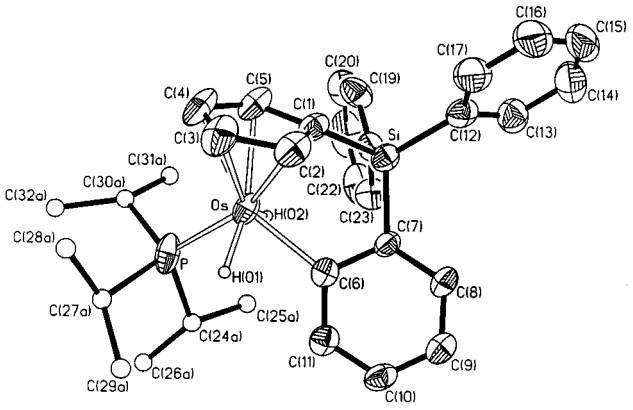


Figure 1. Molecular diagram of complex $OsH_2\{\eta^5\text{-}C_5H_4Si(C_6H_4)Ph_2\}(P^iPr_3)$ (**8**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $OsH_2\{\eta^5\text{-}C_5H_4Si(C_6H_4)Ph_2\}(P^iPr_3)$ (8)

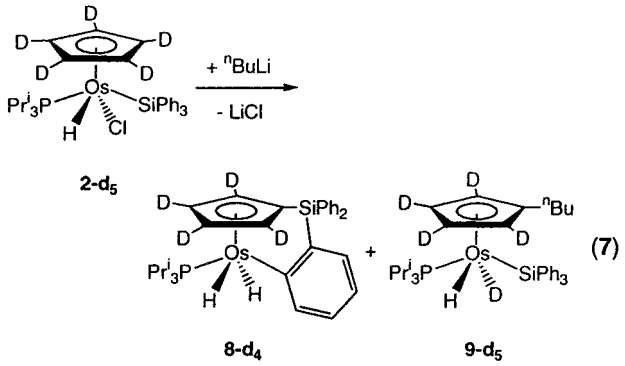
Os−P	2.290(2)	Si−C(1)	1.867(8)
Os−C(1)	2.215(7)	Si−C(7)	1.869(7)
Os−C(2)	2.205(8)	Si−C(12)	1.887(8)
Os−C(3)	2.315(8)	Si−C(18)	1.884(7)
Os−C(4)	2.350(8)	C(6)−C(7)	1.444(10)
Os−C(5)	2.243(9)	C(6)−C(11)	1.410(10)
Os−C(6)	2.106(7)	C(7)−C(8)	1.414(9)
Os−H(01)	1.54(8)	C(8)−C(9)	1.389(11)
Os−H(02)	1.56(7)	C(9)−C(10)	1.383(11)
		C(10)−C(11)	1.388(10)
P−Os−M(1)[a]	133.6(3)	Os−C(6)−C(7)	116.1(5)
P−Os−C(6)	107.29(19)	Si−C(1)−C(2)	123.8(5)
P−Os−H(01)	71(3)	Si−C(1)−C(5)	126.4(6)
P−Os−H(02)	71(2)	Si−C(7)−C(6)	114.8(5)
M(1)−Os−C(6)	118.9(3)	C(1)−Si−C(7)	102.8(3)
M(1)−Os−H(01)	126(3)	C(1)−Si−C(12)	111.9(3)
M(1)−Os−H(02)	118(3)	C(1)−Si−C(18)	109.1(3)
C(6)−Os−H(01)	72(3)	C(7)−Si−C(12)	114.1(3)
C(6)−Os−H(02)	73(3)	C(7)−Si−C(18)	111.1(3)
H(01)−Os−H(02)	116(4)	C(12)−Si−C(18)	107.8(3)
C(6)−C(7)−C(8)	120.8(6)		

[a] M(1) is the midpoint of the C(1)−C(5) Cp carbon atoms.

$(P^iPr_3)_2$ (2.089(7) Å),[25] $Os(\eta^5\text{-}C_5H_5)\{C_6H_4[C(OH)(Ph)\text{-}CH{=}CHOC(O)CH_3]\}(P^iPr_3)$ (2.108(11) Å),[19b] and $OsCl\{NH{=}C(Ph)C_6H_4\}(\eta^5\text{-}H_2)(P^iPr_3)_2$ (2.069(4) Å).[26]

To rationalize the formation of **8**, we have carried out the reaction of the perdeuterated cyclopentadienyl complex **2-d$_5$** with ^{n}BuLi. At room temperature, under the same conditions as those mentioned for the formation of **8**, the addition of a hexane solution of ^{n}BuLi to **2-d$_5$** leads to a mixture of the deuterated compounds $OsH_2[\eta^5\text{-}C_5D_4Si(C_6H_4)Ph_2\}(P^iPr_3)$ (**8-d$_4$**) and $Os(H)(D)(\eta^5\text{-}C_5D_4{}^nBu)(SiPh_3)(P^iPr_3)$ (**9-d$_5$**) in a 2:1 molar ratio (eq 7). At low temperature, the formation of **9-d$_5$** is favored. Thus, when the reaction is carried out at −78 °C, a 2:3 molar ratio is obtained.

The presence of two hydride ligands in **8-d$_4$** is supported by the ^{1}H and ^{2}H NMR spectra of this compound.



The ^{1}H NMR spectrum contains at −12.76 ppm a doublet with an H−P coupling constant of 36.3 Hz, which shows an intensity ratio with regard to the CH resonance of the phosphine of 2:3, whereas the ^{2}H NMR spectrum does not contain any resonance in the high-field region. The ^{2}H NMR spectrum shows an AA′BB′ spin system centered at 5.38 ppm corresponding to the deuterium atoms of the cyclopentadienyl group.

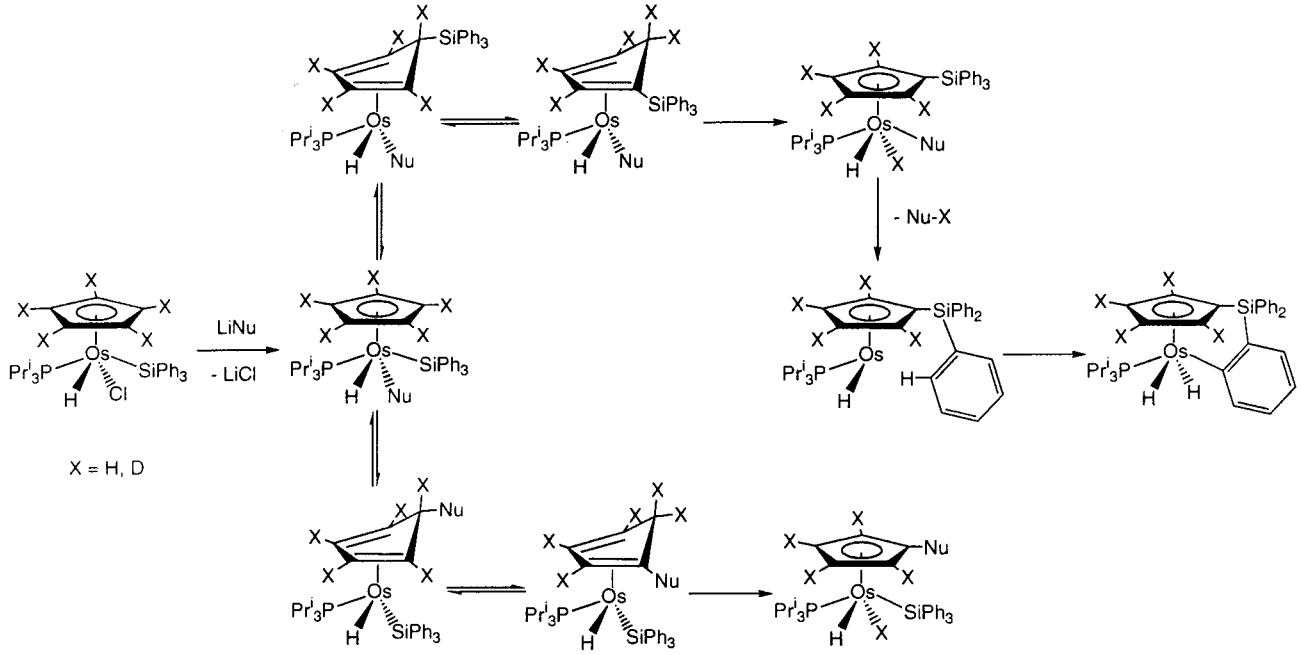
The ^{1}H and ^{2}H NMR spectra of **9-d$_5$** also support the distribution of deuterium atoms shown in eq 7. In the high-field region, the ^{1}H NMR spectrum contains at −14.83 ppm a doublet with an H−P coupling constant of 29.4 Hz. The intensity of this signal with regard to the $C_5D_4{-}CH_2$ resonance of the ^{n}Bu group is 0.5. The ^{2}H NMR spectrum shows at −14.78 ppm a doublet with a D−P coupling constant of 2.6 Hz, corresponding to the deuteride ligand, and the characteristic AA′BB′ spin system due to the deuterium atoms of the cyclopentadienyl group, centered at 4.73 ppm.

The reactions shown in eqs 6 and 7 can be rationalized according to Scheme 4 (Nu = R). The formation of both **8-d$_4$** and **9-d$_5$** (eq 7) suggests that on $OsH(\eta^5\text{-}C_5X_5)(R)(SiPh_3)(P^iPr_3)$ (X = H, D; R = alkyl) intermediates two competitive spontaneous migrations from the osmium atom to the cyclopentadienyl group can take place: the migration of the silyl group, which affords **8-d$_4$**, and the migration of the alkyl group, which leads to **9-d$_5$** by a pathway similar to that described for the formation of **5**−**7** and **6-d$_5$**.

According to Scheme 3, the silyl migration should give $OsH(X)(\eta^5\text{-}C_5X_4SiPh_3)(R)(P^iPr_3)$ intermediates, which should be unstable toward the reductive elimination of alkane (R−X). Thus, the formation of unsaturated $OsH(\eta^5\text{-}C_5X_4SiPh_3)(P^iPr_3)$ species could afford **8** and **8-d$_4$** by C−H activation of a phenyl of the silyl group. The activation of the phenyl instead an isopropyl group of the phosphine in the unsaturated $OsH(\eta^5\text{-}C_5X_4SiPh_3)(P^iPr_3)$ intermediates agrees well with the aryl C−H activation observed in the complex $Os(\eta^5\text{-}C_5H_5)Cl(PPh_3)(P^iPr_3)$[19d] and the thermodynamically favored aromatic C−H activation of tertiary phosphines attached to the $Ru(\eta^6\text{-}C_6H_6)$ unit.[27] In addition, it should be noted the absence of some deuterium atom at the metallic center of **8-d$_4$**, which indicates kinetic and/or thermodynamic preference by the deuteride ligand during the reductive elimination of alkane from $Os(H)(D)(\eta^5\text{-}C_5D_4SiPh_3)(R)$-

(25) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 2496.
(26) Barea, G.; Esteruelas, M. A.; Lledós, A.; López, A. M.; Oñate, E.; Tolosa, J. I. *Organometallics* **1998**, *17*, 4065.
(27) Bennett, M. A.; Huang, T.-N.; Latten, J. L. *J. Organomet. Chem.* **1984**, *272*, 189.

Scheme 4



(P^iPr_3), in agreement with the higher strength of the alkyl−D bond in comparison with the alkyl−H bond.[28]

Complexes **8-d$_4$** and **9-d$_5$** do not undergo H/D exchange processes between the osmium atom and the cyclopentadienyl group at rates comparable to their rates of formation. This suggests that the migration of X from the dienes η^4-C_5X_5R and η^4-$C_5X_5SiPh_3$ to the osmium atom, in the intermediates $OsH(SiPh_3)(\eta^4$-$C_5X_5R)(P^iPr_3)$ and $Os(H)(R)(\eta^4$-$C_5X_5SiPh_3)(P^iPr_3)$, is an irreversible step. So, the exclusive formation of **8**, according to the eq 6, suggests that the $SiPh_3$(Os)/$H(C_5H_5)$ exchange is kinetically favored with regard to the R(Os)/$H(C_5H_5)$ exchange.

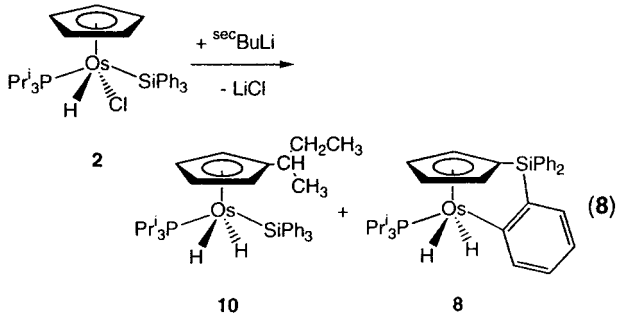
The formation of **9-d$_5$**, according to eq 7, proves that the R(Os)/$D(C_5D_5)$ exchange with regard to the $SiPh_3$-(Os)/$D(C_5D_5)$ exchange is more favored than the R(Os)/$H(C_5H_5)$ exchange with regard to the $SiPh_3$(Os)/$H(C_5H_5)$ exchange. These exchange processes involve: (i) the migration of R or $SiPh_3$ from the osmium atom to the cyclopentadienyl group, (ii) the *exo*-1,5-X shift within the resulting η^4-C_5X_5R or η^4-$C_5X_5SiPh_3$ ligands, and (iii) the migration of X from the diene to the osmium atom. The steps i and ii should not be affected by the nature of X, hydrogen, or deuterium, the first of them because X is not directly involved, and the second one because the necessary energy to break the C−X bonds should be compensated with the energy of formation of the C−X bonds. However, step iii must be highly dependent upon the nature of X because it involves the breaking of C−X bonds and the formation of Os−X bonds. According to the expected primary isotope effect for this step,[28] the substitution of hydrogen by deuterium should produce an increase of the energy barriers for the migrations of X from η^4-$C_5X_5SiPh_3$ and η^4-C_5X_5R to the osmium atoms, similar in both cases, with the corresponding decrease in the X migration rates. So, the substitution of hydrogen by deuterium should not affect the result of the reaction shown in eq 6, if the rate-determining steps for the $SiPh_3$(Os)/$X(C_5X_5)$ and R(Os)/$X(C_5X_5)$ exchanges were the same, since the substitution affects in the same manner the energy barriers of each step of both processes. Neither should one expect the formation of **9-d$_5$**, according to eq 7, if the rate-determining step for the $SiPh_3$(Os)/$X(C_5X_5)$ exchange was step i or ii and the rate-determining step for the R(Os)/$X(C_5X_5)$ exchange was step iii, since the $SiPh_3$(Os)/$H(C_5H_5)$ exchange is kinetically favored with regard to the R(Os)/$H(C_5H_5)$ exchange, and the substitution of hydrogen by deuterium should give rise to an increase of the energy barrier for the R(Os)/$X(C_5X_5)$ exchange without affecting the energy barrier for the $SiPh_3$(Os)/$X(C_5X_5)$ exchange. However, if the rate-determining step for the $SiPh_3$(Os)/$X(C_5X_5)$ exchange was step iii and the rate-determining step for the R(Os)/$X(C_5X_5)$ exchange was step i or ii, the substitution of the hydrogen by deuterium should lead to an increase of the energy barrier for the $SiPh_3$(Os)/$X(C_5X_5)$ exchange without affecting the energy barrier for the R(Os)/$X(C_5X_5)$ exchange, compensating the initial difference between them. So, the comparison of eqs 6 and 7 suggests that for the $SiPh_3$(Os)/$X(C_5X_5)$ exchange the migration of X from the diene of $Os(H)(R)(\eta^4$-C_5X_5-$SiPh_3)(P^iPr_3)$ to the osmium atom is the rate-determining step of the process, whereas for the R(Os)/$X(C_5X_5)$ exchange the migration of R from the osmium atom of $OsH(\eta^5$-$C_5X_5)(R)(SiPh_3)(P^iPr_3)$ to the cyclopentadienyl group or, alternatively, the *exo*-1,5-X shift in the resulting diene should be the rate-determining step of the process.

The formation of both **8-d$_4$** and **9-d$_5$** by reaction of **2-d$_5$** with ^{n}BuLi suggests that the difference between the energy barriers for the $SiPh_3$(Os)/$X(C_5X_5)$ and R(Os)/$X(C_5X_5)$ exchanges is not very high. So, if for the R(Os)/$X(C_5X_5)$ exchange the rate-determining step was the 1,5-X shift (the highest energy barrier for the process), the ratio between the exchanges should be affected by the elimination of R−X from $Os(H)(X)(\eta^5$-$C_5X_4SiPh_3)$-

(28) Connors, K. A. *Chemical Kinetics. The Study of Reaction Rates in Solution*; VCH Publisher: New York, 1990.

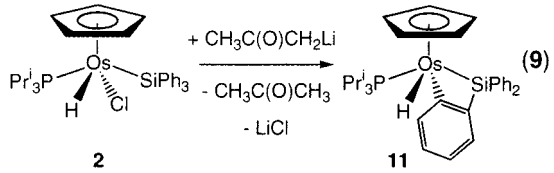
(R)(P^iPr_3). This reductive elimination should shift the equilibria toward the formation of Os(H)(X)(η^5-C_5X_4-$SiPh_3$)(R)(P^iPr_3) and, in this way, toward the formation of the aryl C−H activation product. However, this does not appear to be the case: the reductive elimination of R−D is more favored than the reductive elimination of R−H (note that **8-d$_4$** does not contain any deuterium atom at the metallic center) and the alkyl exchange is favored for X = D. So, the rate-determining step for the R(Os)/X(C_5X_5) exchange appears to be the alkyl migration (step i), and the reductive elimination of R−X from Os(H)(X)(η^5-$C_5X_4SiPh_3$)(R)(P^iPr_3) appears to occur once the exchanges have taken place. When decreasing the reaction temperature, the formation of **9-d$_5$** is slightly favored with regard to **8-d$_4$** (3:2 molar ratio), at −78 °C. This suggests that the R(Os)/D(C_5D_5) exchange is slightly favored with regard to the $SiPh_3$(Os)/D(C_5D_5) exchange, from a kinetic point of view, and that the energy barrier for the migration of the silyl group from the osmium atom of OsH(η^5-C_5D_5)(^{n}Bu)($SiPh_3$)(P^iPr_3) to the cyclopentadienyl ligand is lower than that for the ^{n}Bu migration.

As expected from the fact that the rate-determining step for the R(Os)/X(C_5X_5) exchange is the migration of the alkyl group to the osmium atom (step i), the molar ratio between the exchanges is also affected by the nature of the alkyl group. Thus, we have also observed that the reaction of **2** with *sec*-butyllithium, in contrast to that shown in eq 6, leads to a mixture of **8** and OsH_2(η^5-$C_5H_4{}^{sec}Bu$)($SiPh_3$)(P^iPr_3) (**10**) in a 4:1 molar ratio (eq 8). The formation of **10** can be rationalized on the basis of the steric hyndrance of the *sec*-butyl group, which favors the migration of the alkyl group from the osmium atom to the cyclopentadienyl ligand.



The ^{1}H NMR spectrum of **10** agrees well with that of **7**. In accordance with the asymmetry of the alkyl substituent of the cyclopentadienyl ligand, the spectrum contains two ^{i}Pr−methyl chemical shifts and two hydride resonances at −14.72 and −14.91 ppm, with H−P and H−H coupling constants of 27.6 and 3.9 Hz, in both cases. Furthermore, the spectrum shows a complex resonance between 4.90 and 4.30 ppm, corresponding to the cyclopentadienyl protons, and two multiplets at 1.40 (CH) and 1.15 (CH_2) ppm, a doublet at 1.05 (J(HH) = 6.6 Hz, CH_3) ppm, and a triplet at 0.69 (J(HH) = 7.2 Hz, CH_3) ppm, due to the *sec*-butyl group. The presence of the *sec*-butyl substituent at the cyclopentadienyl group is supported by the APT ^{13}C{^{1}H} NMR spectrum, which shows at 32.5 ppm an up-singlet, corresponding to the CH carbon atom. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 40.6 ppm.

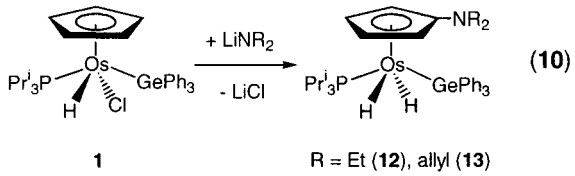
4. Reaction of OsH(η^5-C_5H_5)Cl($SiPh_3$)(P^iPr_3) with $CH_3C(O)CH_2Li$: C−H Activation of a Phenyl Group. The reactions shown in eqs 1−8 take place because the OsH(η^5-C_5H_5)(Nu)(EPh_3)(P^iPr_3) intermediates are stable toward the reductive elimination of Nu−H and/or the formation of the substutituted cyclopentadienyl derivatives is faster than the loss of Nu−H. In contrast to the nucleophile previously studied, the enolate $CH_3C(O)CH_2$-Li does not afford substituted cyclopentadienyl compounds. Thus, the reaction of **2** with this nucleophile gives OsH(η^5-C_5H_5)($SiPh_2C_6H_4$)(P^iPr_3) (**11**) and acetone (eq 9).



The formation of **11** probably involves the initial replacement of the chlorine ligand by the enolate, followed by the reductive elimination of acetone to give an unsaturated Os(η^5-C_5H_5)($SiPh_3$)(P^iPr_3) intermediate. The intramolecular C−H activation of a phenyl group of the silyl of this intermediate should afford **11**. The C−H activation of the phenyl group instead an isopropyl group of the phosphine is in agreement with the previously mentioned arene preference in the Os(η^5-C_5H_5)(LPh)(P^iPr_3) fragments.[19d]

Complex **11** was isolated as a white solid in 65% yield and characterized by MS, elemental analysis, and IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies. In the ^{1}H NMR spectrum, the most noticeable resonance is a doublet at −13.71 ppm, with an H−P coupling constant of 29.7 Hz, corresponding to the hydride ligand. In the ^{13}C{^{1}H} NMR spectrum, the resonance due to the metalated carbon atom is observed at 165.2 ppm as a singlet. The ^{31}P{^{1}H} NMR spectrum contains at 21.8 ppm a singlet, which under off-resonance conditions is split into a doublet by spin coupling with a hydride ligand.

5. Reactions of OsH(η^5-C_5H_5)Cl($GePh_3$)(P^iPr_3) with $LiNR_2$ (R = Et, allyl): NR_2(Os)/H(C_5H_5) Exchange. Treatment of tetrahydrofuran solutions of **1** with $LiNR_2$ (R = Et, allyl) at room temperature leads to OsH_2(η^5-$C_5H_4NR_2$)($GePh_3$)(P^iPr_3) (R = Et (**12**), allyl (**13**)), where the substituent of the cyclopentadienyl group contains a nitrogen atom (eq 10). The formation of these derivatives can be rationalized as the initial replacement of the chlorine ligand of **1** by the amide followed by an NR_2(Os)/H(C_5H_5) exchange.



Complexes **12** and **13** were isolated as white solids in 56% (**12**) and 53% (**13**) yield and characterized by MS, elemental analysis, and IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies. Furthermore, complex **13** was characterized by X-ray diffraction analysis. A view of its molecular geometry is shown in Figure 2. Selected bond distances and angles are listed in Table 2. The

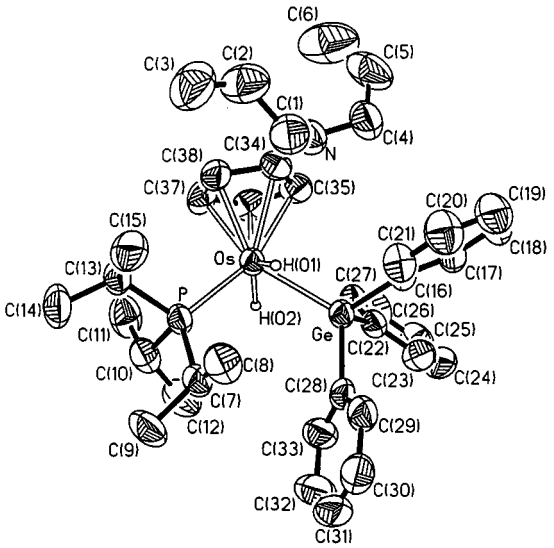


Figure 2. Molecular diagram of complex $OsH_2\{\eta^5\text{-}C_5H_4\text{-}N(CH_2CH{=}CH_2)_2\}(GePh_3)(P^iPr_3)$ (**13**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex $OsH_2\{\eta^5\text{-}C_5H_4N(CH_2CH{=}CH_2)_2\}(GePh_3)(P^iPr_3)$ (13).

Os−Ge	2.4596(7)	N−C(1)	1.448(8)
Os−P	2.2988(13)	N−C(4)	1.419(8)
Os−C(34)	2.354(5)	N−C(34)	1.383(8)
Os−C(35)	2.280(5)	C(1)−C(2)	1.493(10)
Os−C(36)	2.235(5)	C(2)−C(3)	1.297(11)
Os−C(37)	2.221(5)	C(4)−C(5)	1.461(11)
Os−C(38)	2.241(6)	C(5)−C(6)	1.283(15)
Os−H(01)	1.30(5)	C(34)−C(35)	1.432(8)
Os−H(02)	1.59(5)	C(35)−C(36)	1.428(9)
		C(36)−C(37)	1.414(8)
		C(37)−C(38)	1.400(9)
Ge−Os−P	108.89(4)	N−C(1)−C(2)	113.6(6)
Ge−Os−M(1)[a]	122.9(2)	N−C(4)−C(5)	115.7(7)
Ge−Os−H(01)	66(2)	N−C(34)−C(35)	125.4(5)
Ge−Os−H(02)	68.0(18)	N−C(34)−C(38)	127.4(5)
P−Os-M(1)	128.3(2)	C(1)−N−C(4)	120.0(6)
P−Os−H(01)	88.4(18)	C(1)−N−C(34)	119.0(5)
P−Os−H(02)	82.7(15)	C(4)−N−C(34)	119.9(5)
M(1)−Os−H(01)	111(2)	C(1)−C(2)−C(3)	127.3(9)
M(1)-Os−H(02)	115(2)	C(4)−C(5)−C(6)	126.1(9)
H(01)−Os−H(02)	127(3)		

[a] M(1) is the midpoint of the C(1)−C(5) Cp carbon atoms.

distribution of ligands around the osmium atom can be described as a piano stool geometry, with the cyclopentadienyl ligand occupying the three-membered face, while the four monodentate ligands lie in the other face. The bulky ligands, triisopropylphosphine and triphenylgermyl, are mutually *transoid* disposed, with a Ge−Os−P angle of 108.89(4)°. This stereochemistry is similar to that found in the diphenylsilyl derivative $OsH(\eta^5\text{-}C_5H_5)Cl(SiHPh_2)(P^iPr_3)$ and appears to be thermodynamically favored. The basis of this preference isprobably steric and involves minimizing interaction between the ER_3 ligand and the isopropyl groups of the phophine.[20] The Os−Ge distance is 2.4596(7) Å.

The amino group of the substituted cyclopentadienyl ligand is planar with angles around the nitrogen atom of about 120°. This indicates that the nitrogen lone pair is largely delocalized into the aromatic ring and allyl systems, as has been previously observed in other

Table 3. Crystal Data and Data Collection and Refinement for $OsH_2\{\eta^5\text{-}C_5H_4Si(C_6H_4)Ph_2\}(P^iPr_3)$ (8) and $OsH_2\{\eta^5\text{-}C_5H_4N(CH_2CH{=}CH_2)_2\}(GePh_3)(P^iPr_3)$ (13)

	8	13
	Crystal Data	
formula	$C_{32}H_{41}SiPOs$	$C_{38}H_{52}NPGeOs$
molecular wt	674.91	816.17
color and habit	colorless block	colorless, prismatic
symmetry, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$
a, Å	10.677(1)	12.345(2)
b, Å	11.171(2)	20.975(2)
c, Å	13.241(2)	13.932(2)
α, deg	85.53(1)	
β, deg	72.32(1)	91.07(2)
γ, deg	80.04(1)	
V, Å^3	1481.5(4)	3606.9(9)
Z	2	4
D_{calc}, g cm^{-3}	1.513	1.504
data collection and refinement		
diffractometer	Brucker-Siemens P4	Bruker Siemens-STOE AED-2
λ(Mo Kα), Å	0.71073	
monochromator	graphite oriented	
μ, mm^{-1}	4.42	4.42
scan type	$\omega/2\theta$	$\omega/2\theta$
2θ range, deg	$5° \le 2\theta \le 50°$	$5° \le 2\theta \le 50°$
temp, K	200.0(2)	298.0(2)
no. of data collected	6101 (h: −12, 1; k: −13, 13; l: −15, 15)	10 617 (h: −14, 14; k: 0, 24; l: −16, 7)
no. of unique data	5185 (merging R factor 0.0484)	6330 (merging R factor 0.0475)
no. of params refined	318	392
R_1[a] [$F^2 > 2\sigma(F^2)$]	0.0439	0.0317
wR_2[b] [all data]	0.1240	0.0875
S[c] [all data]	1.022	0.994

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] Goof $= S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections, and p is the number of refined parameters.

cyclopentadienyl amino complexes.[29] The delocalization produces the shortening of the N−C distances (1.383(8), 1.419(8), and 1.448(8) Å), which are shorter than those expected for N−C(sp^2) (about 1.44 Å) and N−C(sp^3) (about 1.50 Å) single bonds.[30]

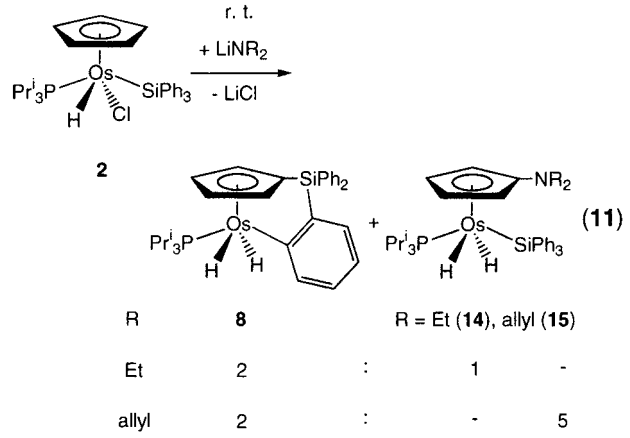
In agreement with the structure shown in Figure 2, the ^{1}H NMR spectra of **12** and **13** show AA′BB′ spin systems between 4.5 and 4.0 ppm, for the hydrogen atoms of the cyclopentadienyl group, only one ^{i}Pr−methyl chemical shift, and in the high-field region doublets at −14.10 (**12**) and −14.12 (**13**) ppm with H−P coupling constants of about 29 Hz, corresponding to the equivalent hydride ligands. The carbon atoms of the cyclopentadienyl rings display three signals, at about 132 (CN), 68 and 63 (C−H) ppm, in the ^{13}C{^{1}H} NMR spectra. The ^{31}P{^{1}H} NMR spectra contain singlets at 40.2 (**12**) and 39.8 (**13**) ppm, which under off-resonance

(29) (a) Stahl, K.-P.; Boche, G.; Massa, W. *J. Organomet. Chem.* **1984**, *277*, 113. (b) Morrow, J. R.; Templeton, J. L.; Bandy, J. A.; Bannister, C.; Prout, C. K. *Inorg. Chem.* **1986**, *25*, 1923. (c) Brun, P.; Vierling, P.; Riess, J. G.; Le Borgne, G. *Organometallics* **1987**, *6*, 1032. (d) Luttikhedde, H. J. G.; Leino, R. P.; Wilén, C.-E.; Näsman, J. H.; Ahlgrén, M. J.; Pakkanen, T. A. *Organometallics* **1996**, *15*, 3092. (e) Barsties, E.; Schaible, S.; Prosenc, M.-H.; Rief, U.; Röll, W.; Weyand, O.; Dorer, B.; Brintzinger, H.-H. *J. Organomet. Chem.* **1996**, *520*, 63. (f) Knüppel, S.; Fauré, J.-L.; Erker, G.; Kehr, G.; Nissinen, M.; Fröhlich, R. *Organometallics* **2000**, *19*, 1262.

(30) Bernad, D. J.; Esteruelas, M. A.; López, A. M.; Modrego, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4995.

conditions are split into triplets by spin coupling with the hydride ligands.

6. Reactions of OsH(η^5-C_5H_5)Cl($SiPh_3$)(P^iPr_3) with $LiNR_2$ (R = Et, allyl): NR_2(Os)/H(C_5H_5) Exchange versus $SiPh_3$(Os)/H(C_5H_5) Exchange. Treatment at room temperature of tetrahydrofuran solutions of **2** with $LiNR_2$ (R = Et, allyl) in contrast to the reactions shown in eq 10 leads to mixtures of **8** and the cyclopentadienyl amino complexes $OsH_2(\eta^5$-$C_5H_4NR_2)(SiPh_3)(P^iPr_3)$ (R = Et (**14**), allyl (**15**)). The molar ratios of the reaction products depend on the substituents of the amide (eq 11).



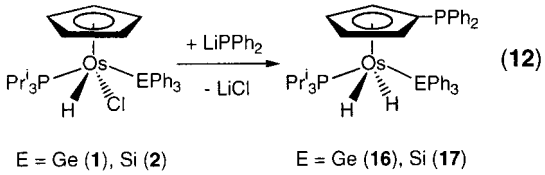
The reactions shown in eq 11 can be rationalized according to Scheme 4. That is, the migration of the amide from the osmium atom to the cyclopentadienyl ligand, to give **14** or **15**, competes with the silyl migration to afford $OsH_2(\eta^5$-$C_5H_4SiPh_3)(NR_2)(P^iPr_3)$ intermediates, which evolve into **8** by reductive elimination of amine and subsequent aryl C−H activation.

To establish the preference of the migration, we have carried out the reaction of **2** with $LiNEt_2$ at −78 °C. At this temperature, complex **14** is the only detected reaction product. Since the H(Os)/X(C_5X_4Nu) and H(Os)/X($C_5X_4SiPh_3$) exchanges do not appear to occur in these systems, the above-mentioned suggests that the NEt_2-(Os)/H(C_5H_5) exchange is slightly favored with regard to the $SiPh_3$(Os)/H(C_5H_5) exchange, from a kinetic point of view.

The comparison of eqs 10 and 11 suggests that in OsH(η^5-C_5H_5)(EPh_3)(Nu)(P^iPr_3) (E = Si, Ge) intermediates the migration of the $SiPh_3$ group from the osmium atom to the cyclopentadienyl ligand is favored with regard to the migration of the $GePh_3$ group not only when Nu is alkyl (eqs 4 and 6) but also when Nu is amide. In this context, it should be mentioned that spectroscopic studies on OsH(η^5-C_5H_5)Cl(EPh_3)(P^iPr_3) (E = Ge, Si) complexes show that Os−Ge bonds are significantly stronger than the Os−Si bonds.[20]

The spectroscopic data of **14** and **15** agree with those of **12** and **13**. The ^{1}H NMR spectra show AA′BB′ spin systems between 4.5 and 4.0 ppm for the hydrogen atoms of the cyclopentadienyl group, only one ^{i}Pr−methyl chemical shift, and in the high-field region doublets at −14.45 ppm (both compounds) with H−P coupling constants of about 28 Hz, corresponding to the hydride ligands. The $^{13}C\{^1H\}$ NMR spectra contain three resonances for the carbon atoms of the cyclopentadienyl rings, at about 134 (CN), 71 and 63 (CH) ppm. The $^{31}P\{^1H\}$ NMR spectra show singlets at about 39 ppm, which under off-resonance conditions are split into triplets.

7. Reactions of OsH(η^5-C_5H_5)Cl(EPh_3)(P^iPr_3) (E = Ge, Si) with $LiPPh_2$: PPh_2(Os)/H(C_5H_5) Exchange. Treatment of tetrahydrofuran solutions of **1** and **2** with $LiPPh_2$ at room temperature leads to the cyclopentadienyl phosphine derivatives $OsH_2(\eta^5$-C_5H_4-$PPh_2)(EPh_3)(P^iPr_3)$ (R = Ge (**16**), Si (**17**)), according to eq 12. The formation of these derivatives can be rationalized as the initial replacement of the chlorine ligand of the starting compounds by the phosphide group, followed by a PPh_2(Os)/H(C_5H_5) exchange.



Complexes **16** and **17** were isolated as white solids in about 60% yield. In agreement with the related compounds previously described, the ^{1}H NMR spectra of **16** and **17** show AA′BB′ spin systems between 4.8 and 4.4 ppm for the hydrogen atoms of the cyclopentadienyl group, only one ^{i}Pr−methyl chemical shift, and in the high-field region double doublets at −14.40 (**16**) and −14.65 (**17**) ppm, with H−P coupling constants of about 29 and 3 Hz, corresponding to the hydride ligands.

The presence of a cyclopentadienyl−P bond in the complexes is strongly supported by the $^{13}C\{^1H\}$ NMR spectra, which show at 93.4 (**16**) and 91.8 (**17**) doublets, with C−P coupling constants of about 18 Hz, corresponding to the C−P carbon atoms of the cyclopentadienyl groups. The $^{31}P\{^1H\}$ NMR spectra also support the structures shown in eq 12. Thus, they contain two singlets at about 39 (P^iPr_3) and −18 ($C_5H_4PPh_2$) ppm. Under off-resonance conditions, the triisopropylphosphine resonances are split into triplets, whereas the $C_5H_4PPh_2$ resonances remain unchanged.

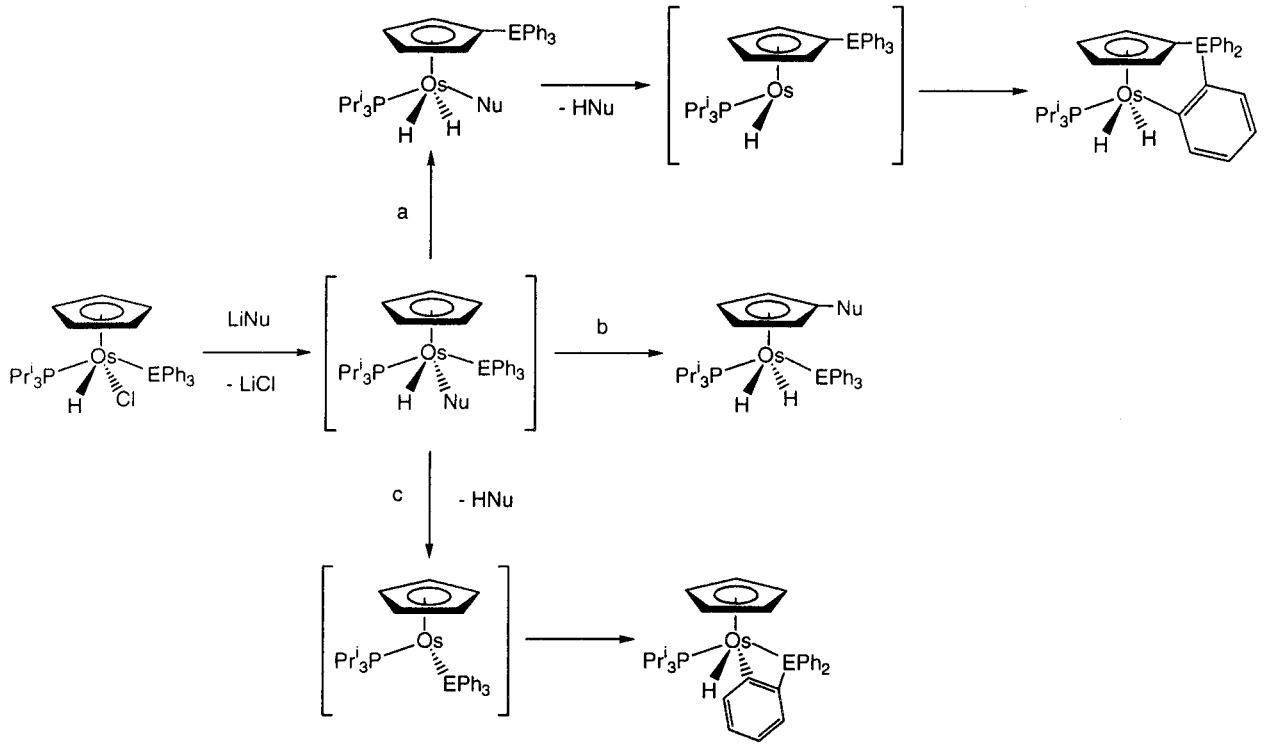
8. Generalization of the Reactivity of OsH(η^5-C_5H_5)Cl(EPh_3)(P^iPr_3) (E = Ge, Si) toward LiNu, and Conclusion. Scheme 5 sumarizes the behavior of **1** and **2** in the presence of LiNu (Nu = R, NR_2, PPh_2) reagents. Treatment of tetrahydrofuran solutions of both species with these reagents produces the replacement of the chlorine ligand of **1** and **2** by the Nu group to afford OsH(η^5-C_5H_5)(EPh_3)(Nu)(P^iPr_3) intermediates, which are unstable and evolve in three different manners depending on the nature of E and the Nu group.

(a) EPh_3(Os)/H(C_5H_5) Exchange. This process affords $OsH_2(\eta^5$-$C_5H_4EPh_3)(Nu)(P^iPr_3)$ derivatives, which have been isolated when the atom E is Ge and Si and the Nu group is CH_2CN (eq 1).

(b) Nu(Os)/H(C_5H_5) Exchange. This behavior is observed when the atom E is Ge and the Nu group is alkyl, amide, and phosphide and when the atom E is Si and the Nu group is phosphide. In this case, the dihydride germyl $OsH_2(\eta^5$-$C_5H_4Nu)(GePh_3)(P^iPr_3)$ (Nu = CH_3, ^{n}Bu, ^{sec}Bu, NEt_2, N(allyl)$_2$, PPh_2) and dihydride silyl $OsH_2(\eta^5$-$C_5H_4PPh_2)(SiPh_3)(P^iPr_3)$ derivatives are formed (eqs 4, 10, and 12).

(c) Reductive Elimination of H−Nu. This occurs in the reaction of **2** with $LiCH_2C(O)CH_3$. The loss of

Scheme 5



acetone from $OsH(\eta^5\text{-}C_5H_5)(SiPh_3)\{CH_2C(O)CH_3\}(P^iPr_3)$ affords the $Os(\eta^5\text{-}C_5H_5)(SiPh_3)(P^iPr_3)$ intermediate, which has the same behavior as the previously reported $Os(\eta^5\text{-}C_5H_5)(P^iPr_3)(LPh)$ systems[19d] and evolves by aryl C−H activation into $OsH(\eta^5\text{-}C_5H_5)(SiPh_2C_6H_4)(P^iPr_3)$ (eq 9).

Similarly to the complex $OsH_2(\eta^5\text{-}C_5H_5)(Sn^nBu_3)(P^iPr_3)$ previously reported,[20] the derivatives $OsH_2(\eta^5\text{-}C_5H_4Nu)(EPh_3)(P^iPr_3)$ (E = Ge, Nu = CH_3, ^{n}Bu, ^{sec}Bu, NEt_2, $N(allyl)_2$, PPh_2; E = Si, Nu = PPh_2) are stable toward the reductive elimination of $HEPh_3$. However, the stability of the $OsH_2(\eta^5\text{-}C_5H_4EPh_3)(Nu)(P^iPr_3)$ species depends on the nature of the Nu group. Thus, the reactions shown in eqs 8 and 11, where mixtures of $OsH_2\{\eta^5\text{-}C_5H_4Si(C_6H_4)Ph_2\}(P^iPr_3)$ and $OsH_2(\eta^5\text{-}C_5H_4Nu)(SiPh_3)(P^iPr_3)$ (Nu = ^{sec}Bu, NEt_2, $N(allyl)_2$) are obtained, suggest the following:

(i) For E = Si and Nu = ^{sec}Bu, NEt_2, and $N(allyl)_2$, the $OsH(\eta^5\text{-}C_5H_5)(EPh_3)(Nu)(P^iPr_3)$ intermediates undergo both EPh_3(Os)/H(C_5H_5) and Nu(Os)/H(C_5H_5) exchanges in a competitive manner.

(ii) The species $OsH_2(\eta^5\text{-}C_5H_4SiPh_3)(Nu)(P^iPr_3)$ (Nu = ^{sec}Bu, NEt_2, $N(allyl)_2$) resulting from the $SiPh_3$(Os)/H(C_5H_5) exchange, in contrast to the complexes $OsH_2(\eta^5\text{-}C_5H_4EPh_3)(CH_2CN)(P^iPr_3)$ (E = Ge, Si), are unstable toward the reductive elimination of H−Nu. As a result, the metallic center of the formed unsaturated intermediate $OsH(\eta^5\text{-}C_5H_4SiPh_3)(P^iPr_3)$ is capable of a C−H activation reaction on one of the phenyl groups of the $SiPh_3$ fragment, to give $OsH_2\{\eta^5\text{-}C_5H_4Si(C_6H_4)Ph_2\}(P^iPr_3)$.

Although in the $OsH(\eta^5\text{-}C_5H_5)(NR_2)(SiPh_3)(P^iPr_3)$ intermediates both exchanges occur, the reaction of $OsH(\eta^5\text{-}C_5H_5)Cl(SiPh_3)(P^iPr_3)$ with $LiNEt_2$ at −78 °C, which gives $OsH_2(\eta^5\text{-}C_5H_4NEt_2)(SiPh_3)(P^iPr_3)$ as the only detected organometallic reaction product, suggests that NR_2(Os)/H(C_5H_5) exchange is slightly favored with regard to the $SiPh_3$(Os)/H(C_5H_5) exchange, from a kinetic point of view.

The reaction of $OsH(\eta^5\text{-}C_5H_5)Cl(SiPh_3)(P^iPr_3)$ with LiR (R = CH_3, ^{n}Bu) at room temperature leads to $OsH_2\{\eta^5\text{-}C_5H_4Si(C_6H_4)Ph_2\}(P^iPr_3)$ as the only organometallic reaction product (eq 6). At first glance, this could suggest that the $OsH(\eta^5\text{-}C_5H_5)(R)(SiPh_3)(P^iPr_3)$ (R = CH_3, ^{n}Bu) intermediates only undergo $SiPh_3$(Os)/H(C_5H_5) exchange. However, the reaction of $OsH(\eta^5\text{-}C_5D_5)Cl(SiPh_3)(P^iPr_3)$ with ^{n}BuLi, which affords a mixture of $OsH_2\{\eta^5\text{-}C_5D_4Si(C_6H_4)Ph_2\}(P^iPr_3)$ and Os(H)(D)$(\eta^5\text{-}C_5D_4{}^nBu)(SiPh_3)(P^iPr_3)$ (eq 7), indicates that the above-mentioned $OsH(\eta^5\text{-}C_5H_5)(R)(SiPh_3)(P^iPr_3)$ intermediates also undergo both $SiPh_3$(Os)/H(C_5H_5) and R(Os)/H(C_5H_5) exchanges in a competitive manner.

The comparison of the products from the reactions shown in eqs 1, 2, and 4−12 indicates that the trend of the ligands H, Nu, and EPh_3 for exchanging their positions with the hydrogen atoms of the cyclopentadienyl group in the $OsH(\eta^5\text{-}C_5H_5)(EPh_3)(Nu)(P^iPr_3)$ species decreases in the sequence PPh_2 > $N(allyl)_2$ > NEt_2 > $SiPh_3$ > ^{sec}Bu > CH_3, ^{n}Bu > $GePh_3$ > H, D, CH_2CN, $CH_2C(O)CH_3$.

In conclusion, the reactions of $OsH(\eta^5\text{-}C_5H_5)Cl(EPh_3)(P^iPr_3)$ (E = Ge, Si) with LiNu reagents can give rise to four different types of compounds: $OsH_2(\eta^5\text{-}C_5H_4EPh_3)(Nu)(P^iPr_3)$, $OsH_2(\eta^5\text{-}C_5H_4Nu)(EPh_3)(P^iPr_3)$, $OsH_2\{\eta^5\text{-}C_5H_4Si(C_6H_4)Ph_2\}(P^iPr_3)$, and $OsH_2(\eta^5\text{-}C_5H_5)(SiPh_2C_6H_4)(P^iPr_3)$. The formation of these derivatives can be rationalized on the basis of the trend of the EPh_3 and Nu ligands of $OsH(\eta^5\text{-}C_5H_5)(EPh_3)(Nu)(P^iPr_3)$ for ex-

changing their positions with the hydrogen atoms of the cyclopentadienyl group and on the basis of the stability of these species and $OsH_2(\eta^5\text{-}C_5H_4EPh_3)(Nu)(P^iPr_3)$ toward the reductive elimination of H−Nu.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials $OsH(\eta^5\text{-}C_5H_5)Cl(GePh_3)(P^iPr_3)$ (**1**) and $OsH(\eta^5\text{-}C_5H_5)Cl(SiPh_3)(P^iPr_3)$ (**2**) were prepared by the published methods.[20] The starting materials $OsH(\eta^5\text{-}C_5D_5)Cl(GePh_3)(P^iPr_3)$ (**1-d$_5$**) and $OsH(\eta^5\text{-}C_5D_5)Cl(SiPh_3)(P^iPr_3)$ (**2-d$_5$**) were prepared by using procedures similar to those of the non-deuterated counterparts. Their precursor $Os(\eta^5\text{-}C_5D_5)Cl(P^iPr_3)_2$ was prepared in the same way described for $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$, but using TlC_5D_5.[18] TlC_5D_5 was prepared as previously described.[31]

In the NMR spectra, chemical shifts are expressed in ppm downfield from Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, *J*, are given in hertz.

Preparation of $OsH_2(\eta^5\text{-}C_5H_4GePh_3)(CH_2CN)(P^iPr_3)$ (3). To a solution of $OsH(\eta^5\text{-}C_5H_5)Cl(GePh_3)(P^iPr_3)$ (211.2 mg, 0.28 mmol) in 10 mL of THF was first added acetonitrile (1 mL) and then *n*-buthyllithium (0.3 mL). The mixture was left to stir for 30 min, and methanol (1 mL) was added. After 1 min of stirring, the solution was vacuum-dried, and the resulting sticky residue was washed with methanol (2 × 4 mL), leading to a white solid. Yield: 115 mg (55%). Anal. Calcd for $C_{34}H_{44}GeNOsP$: C, 53.70; H, 5.83; N, 1.84. Found: C, 54.02; H, 6.29; N, 1.82. IR (Nujol, cm^{-1}): ν(C≡N) 2257 (m); ν(Os−H) 2135 (m), 2088 (m), 2069 (m). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.00−7.00 (15 H, −Ph); 4.70−4.40 (4 H, η^5-C_5H_4−, AA′BB′ system); 2.10 (s, 2 H, $-CH_2-$); 1.30 (m, 3 H, PCH); 0.83 (dd, 18 H, PCHCH_3, $^3J_{HP}$ = 13.5 Hz, $^3J_{HH}$ = 7.2 Hz); −14.49 (d, 2 H, Os−H, $^2J_{HP}$ = 28.8 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 149.0 (−, s, Cipso Ph); 136.3, 127.9 (+, s, Cortho, Cmeta Ph); 127.8 (+, s, Cpara Ph); 118.3 (−, s, −CN); 91.3 (−, s, quaternary C in η^5-C_5H_4−Ge); 80.1, 78.5 (+, s, tertiary C's in η^5-C_5H_4−Ge); 29.2 (+, d, PCH, $^1J_{CP}$ = 32.3 Hz); 19.8 (+, s, PCH−CH_3); 16.5 (−, s, $-CH_2-$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 293 K): δ 41.6 (s, t in off-resonance). MS (FAB$^+$): *m*/*z* = 761 (M$^+$), 684 (M$^+$ − Ph).

Preparation of $OsH_2(\eta^5\text{-}C_5H_4SiPh_3)(CH_2CN)(P^iPr_3)$ (4). To a solution of $OsH(\eta^5\text{-}C_5H_5)Cl(SiPh_3)(P^iPr_3)$ (167.6 mg, 0.24 mmol) in 10 mL of THF was first added acetonitrile (1 mL) and then *n*-buthyllithium (0.5 mL). The mixture was left to stir for 1 h, and methanol (1 mL) was added. After 1 min of stirring, the resulting solution was vacuum-dried, and the sticky residue was washed with methanol (2 × 4 mL), leading to a white solid. Yield: 98 mg (58%). Anal. Calcd for $C_{34}H_{44}NOsPSi$: C, 57.02; H, 6.21; N, 1.96. Found: C, 56.62; H, 5.87; N, 1.86. IR (Nujol, cm^{-1}): ν(C≡N) 2256 (m); ν(Os−H) 2117 (m), 2104 (m). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.00−7.00 (15 H, −Ph); 4.80−4.30 (4 H, η^5-C_5H_4−, AA′BB′ system); 1.87 (s, 2 H, $-CH_2-$); 1.23 (m, 3 H, PCH); 0.83 (dd, 18 H, PCHCH_3, $^2J_{HP}$ = 13.2 Hz, $^2J_{HH}$ = 6.9 Hz); −14.80 (d, 2 H, Os−H, $^2J_{HP}$ = 27.0 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 147.7 (−, s, Cipso Ph); 137.3, 127.5 (+, s, Cortho, Cmeta Ph); 128.0 (+, s, Cpara Ph); 118.3 (−, s, −CN); 92.9 (−, s, quaternary C in η^5-C_5H_4−Si); 81.6, 78.2 (+, s, tertiary C's in η^5-C_5H_4−Si); 28.1 (+, d, PCH, $^1J_{CP}$ = 29.0 Hz); 19.6 (+, s, PCH−CH_3); 15.8 (−, s, $-CH_2-$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 293 K): δ 40.9 (s, t in off-resonance). MS (FAB$^+$): *m*/*z* = 717 (M$^+$), 640 (M$^+$ − Ph).

Preparation of Os(H)(D)(η^5-$C_5D_4SiPh_3$)(CH_2CN)(P^iPr_3) (4-d$_5$). This product was synthesized by the same method as its analogue **4**, but using **2-d$_5$** as starting material. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.00−7.00 (15 H, −Ph); 1.88 (s, 2 H, $-CH_2-$); 1.23 (m, 3 H, PCH); 0.83 (dd, 18 H, PCHCH_3, $^2J_{HP}$ = 13.2 Hz, $^2J_{HH}$ = 6.9 Hz); −14.82 (d, 1 H, Os−H, $^2J_{HP}$ = 27.0 Hz). ^{2}H NMR (46.1 MHz, C_6H_6, 293 K): δ 4.51−4.17 (4 D, η^5-C_5D_4−, AA′BB′ system), −14.89 (br s, 1 D, Os−D). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 293 K): δ 41.0 (s).

Reaction of $OsH_2(\eta^5\text{-}C_5H_4SiPh_3)(CH_2CN)(P^iPr_3)$ with CD_3OD. A suspension of $OsH_2(\eta^5\text{-}C_5H_4SiPh_3)(CH_2CN)(P^iPr_3)$ in CD_3OD was left to stir for 3 days. The resulting suspension was vacuum-dried, leading to a white solid (**4-d$_2$**) which showed 37% deuteration on the $-CH_2-$ unit.

Preparation of $OsH_2(\eta^5\text{-}C_5H_4CH_3)(GePh_3)(P^iPr_3)$ (5). To a solution of $OsH(\eta^5\text{-}C_5H_5)Cl(GePh_3)(P^iPr_3)$ (167.5 mg, 0.22 mmol) in 10 mL of THF was added methyllithium (0.2 mL). The mixture was left to stir for 20 min, and methanol (1 mL) was added. After 1 min of stirring, the solution was vacuum-dried, and the resulting sticky residue was then washed with methanol (2 × 3 mL), leading to a white solid. Yield: 81 mg (49%). Anal. Calcd for $C_{33}H_{45}GeOsP$: C, 53.88; H, 6.18. Found: C, 53.53; H, 6.03. IR (Nujol, cm^{-1}): ν(Os−H) 2093 (m). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−7.10 (15 H, −Ph); 4.60−4.40 (4 H, η^5-C_5H_4−, AA′BB′ system); 1.85 (s, 3 H, η^5-C_5H_4−CH_3); 1.36 (m, 3 H, PCH); 0.83 (dd, 18 H, PCHCH_3, $^3J_{HP}$ = 13.5 Hz, $^3J_{HH}$ = 6.9 Hz); −14.45 (d, 2 H, Os−H, $^2J_{HP}$ = 29.1 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 149.8 (−, s, Cipso $SiPh_3$); 136.5, 127.6 (+, s, Cortho, C meta $GePh_3$); 127.4 (+, s, Cpara $GePh_3$); 100.2 (−, s, quaternary C in η^5-C_5H_4−CH_3); 81.8, 75.8 (+, s, tertiary C's in η^5-C_5H_4−CH_3); 29.6 (+, d, PCH, $^1J_{CP}$ = 29.4 Hz); 19.8 (+, s, PCH−CH_3); 14.4 (+, s, $-CH_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 293 K): δ 42.3 (s, t in off-resonance). MS (FAB$^+$): *m*/*z* = 657 (M$^+$ − Ph).

Preparation of $OsH_2(\eta^5\text{-}C_5H_4CH_2CH_2CH_2CH_3)(GePh_3)(P^iPr_3)$ (6). To a solution of $OsH(\eta^5\text{-}C_5H_5)Cl(GePh_3)(P^iPr_3)$ (179 mg, 0.24 mmol) in 10 mL of THF was added *n*-buthyllithium (0.5 mL), and the mixture was left to react for 1 h. Methanol (1 mL) was added, the mixture was stirred for 1 min and then vacuum-dried. The resulting residue was washed with methanol (2 × 4 mL), leading to a white solid. Yield: 108 mg (59%). Anal. Calcd for $C_{36}H_{51}GeOsP$: C, 55.61; H, 6.61. Found: C, 55.19; H, 6.41. IR (Nujol, cm^{-1}): ν(Os−H) 2118 (m). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−7.10 (15 H, −Ph); 4.60−4.40 (4 H, η^5-C_5H_4−, AA′BB′ system); 2.09 (t, 2 H, η^5-C_5H_4−CH_2−, $^3J_{HH}$ = 7.8 Hz); 1.37 (m, 3 H, PCH); 1.30 − 1.10 (m, 4 H, $-CH_2-CH_2-$); 0.85 (dd, 18 H, PCHCH_3, $^3J_{HP}$ = 13.5 Hz, $^3J_{HH}$ = 7.2 Hz); 0.79 (t, 3 H, $-CH_3$, $^3J_{HH}$ = 7.2 Hz); −14.52 (d, 2 H, Os−H, $^2J_{HP}$ = 29.4 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 149.5 (−, s, Cipso Ph); 136.1, 127.2 (+, s, Cortho, Cmeta Ph); 127.0 (+, s, Cpara Ph); 105.4 (−, s, quaternary C in η^5-C_5H_4−CH_2−); 80.5, 75.6 (+, s, tertiary C's in η^5-C_5H_4−CH_2−); 35.3 (−, s, η^5-C_5H_4-CH_2−CH_2−CH_2−); 29.4 (+, d, PCH, $^1J_{CP}$ = 29.4 Hz); 28.6, 22.6 (−, s, η^5-C_5H_4−CH_2−CH_2−CH_2−); 19.5 (+, s, PCH−CH_3); 14.0 (+, s, $-CH_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 293 K): δ 42.0 (s, t in off-resonance). MS (FAB$^+$): *m*/*z* = 778 (M$^+$), 701 (M$^+$ − Ph).

Preparation of Os(H)(D)(η^5-$C_5D_4CH_2CH_2CH_2CH_3$)(GePh$_3$)(P^iPr_3) (6-d$_5$). This product was synthesized by the same method as its analogue **6**, but using **1-d$_5$** as starting material. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−7.10 (15 H, −Ph); 2.10 (t, 2 H, η^5-C_5D_4−CH_2−, $^3J_{HH}$ = 7.8 Hz); 1.37 (m, 3 H, PCH); 1.30−1.10 (m, 4 H, $-CH_2-CH_2-$); 0.85 (dd, 18 H, PCHCH_3, $^3J_{HP}$ = 13.5 Hz, $^3J_{HH}$ = 7.2 Hz); 0.79 (t, 3 H, $-CH_3$, $^3J_{HH}$ = 7.2 Hz); −14.54 (d, 1 H, Os−H, $^2J_{HP}$ = 29.4 Hz). ^{2}H NMR (46.1 MHz, C_6H_6, 293 K): δ 4.61 (s, 4 D, η^5-C_5D_4−); −14.33 (br s, 1 D, Os−D). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 293 K): δ 42.2 (s).

Preparation of $OsH_2\{\eta^5\text{-}C_5H_4CH(CH_3)CH_2CH_3\}(GePh_3)(P^iPr_3)$ (7). To a solution of $OsH(\eta^5\text{-}C_5H_5)Cl(GePh_3)(P^iPr_3)$ (250.1 mg, 0.33 mmol) in 10 mL of THF was added *sec*-buthyllithium (1 mL), and the mixture was left to react for 20 min. Methanol (1 mL) was added, the mixture was stirred for

(31) Anderson, G. K.; Cross, R. J.; Phillips, I. G. *J. Chem. Soc., Chem. Commun.* **1978**, 709.

1 min and then vacuum-dried. The subsequent residue was washed with methanol (2 × 4 mL), finally leading to a white solid. Yield: 157 mg (61%). Anal. Calcd for $C_{36}H_{51}GeOsP$: C, 55.60; H, 6.62. Found: C, 56.00; H, 6.35. IR (Nujol, cm^{-1}): ν(Os−H) 2100 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.00−7.10 (15 H, −Ph); 4.80−4.40 (4 H, η^5-C_5H_4−, ABCD system); 1.62 (m, 1 H, η^5-C_5H_4−C*H*−); 1.40 (m, 3 H, PCH); 1.19 (m, 2 H, η^5-C_5H_4−CH−CH_2−); 1.08 (d, 3 H, η^5-C_5H_4−CH−CH_3, $^3J_{HH}$ = 6.9 Hz); 0.87 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 12.9 Hz, $^3J_{HH}$ = 6.9 Hz); 0.85 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 12.9 Hz, $^3J_{HH}$ = 6.9 Hz); 0.70 (t, 3 H, η^5-C_5H_4−CH−CH$_2$−CH_3, $^3J_{HH}$ = 7.5 Hz); −14.46 (dd, 1 H, Os−H, $^2J_{HP}$ = 29.4 Hz, $^2J_{HH}$ = 3.3 Hz); −14.56 (d, 1 H, Os−H, $^2J_{HP}$ = 29.4 Hz, $^2J_{HH}$ = 3.3 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 150.0 (−, s, Cipso Ph); 136.5, 127.6 (+, s, Cortho, Cmeta Ph); 127.4 (+, s, Cpara Ph); 113.0 (−, s, quaternary C in η^5-C_5H_4−CH−); 81.6, 76.7, 76.2, 75.5 (+, s, tertiary C's in η^5-*C*$_5$H$_4$−CH−); 33.3 (+, s, η^5-C_5H_4-*C*H(CH$_3$)CH$_2$−CH$_3$); 32.3 (−, s, η^5-C_5H_4−CH−*C*H$_2$−); 29.8 (+, d, PCH, $^1J_{CP}$ = 29.7 Hz); 22.0, 12.5 (+, s, η^5-C_5H_4−CH(*C*H$_3$)CH$_2$−*C*H$_3$); 19.9, 19.7 (+, s, PCH−*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 41.3 (s, t in off-resonance). MS (FAB$^+$): m/z = 778 (M^+), 701 (M^+ − Ph).

Preparation of OsH$_2${η^5-C_5H_4Si(C_6H_4)Ph$_2$}(P^{i}Pr$_3$) (8). To a solution of OsH(η^5-C_5H_5)Cl(SiPh$_3$)(P^{i}Pr$_3$) (162 mg, 0.23 mmol) in 10 mL of THF was added *n*-buthyllithium (0.5 mL), and the mixture was left to react for 1 h. Methanol (1 mL) was added, and the mixture was stirred for 1 min and then vacuum-dried. The resulting residue was finally washed with methanol (2 × 4 mL), leading to a white solid. Yield: 94 mg (61%). Anal. Calcd for $C_{32}H_{41}OsPSi$: C, 56.77; H, 6.41. Found: C, 56.94; H, 6.13. IR (Nujol, cm^{-1}): ν(Os−H) 2144, 2111 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.90−6.90 (14 H, −Ph); 5.10−4.90 (4 H, η^5-C_5H_4−, AA′BB′ system); 1.73 (m, 3 H, PCH); 0.77 (dd, 18 H, CH$_3$, $^2J_{HP}$ = 13.8 Hz, $^2J_{HH}$ = 6.9 Hz); −12.76 (d, 2 H, Os−H, $^2J_{HP}$ = 36.3 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 159.2 (−, s, Os−C−*C*−Si); 147.8 (−, s, Cipso SiPh$_2$); 140.6 (−, d, Os−C, $^2J_{CP}$ = 6 Hz); 137.5, 135.3, 129.3, 121.1 (+, s, CH's in Os−C_6H_4−Si); 136.7, 128.4 (+, s, Cortho, Cmeta Ph); 129.8 (+, s, Cpara Ph); 89.3, 89.2 (+, s, tertiary C's in η^5-C_5H_4−Si); 75.6 (−, d, quaternary in η^5-C_5H_4−Si); 29.2 (+, d, PCH, $^1J_{CP}$ = 31.3 Hz); 19.9 (+, s, PCH−*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 47.6 (s, t in off-resonance). MS (FAB$^+$): m/z = 674 (M^+ − 2H), 598 (M^+ − H−Ph).

Reaction of OsH(η^5-C_5D_5)Cl(SiPh$_3$)(P^{i}Pr$_3$) with ^{n}BuLi. To a solution of OsH(η^5-C_5D_5)Cl(SiPh$_3$)(P^{i}Pr$_3$) (151 mg, 0.21 mmol) was added *n*-buthyllithium (0.4 mL), and the mixture was left to react for 7 min. Methanol (1 mL) was then added, and after 1 min of stirring, the solution was vacuum-dried. The resulting residue was washed with methanol (2 × 3 mL), leading to a white solid which was a mixture of the complexes OsH$_2${η^5-C_5D_4Si(C_6H_4)Ph$_2$}(P^{i}Pr$_3$) (**8-d$_4$**) and Os(H)(D)(η^5-C_5D_4^{n}Bu)(SiPh$_3$)(P^{i}Pr$_3$) (**9-d$_5$**) in a 2:1 molar ratio. Spectroscopic data for **8-d$_4$**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−6.90 (14 H, −Ph); 1.73 (m, 3 H, PCH); 0.77 (dd, 18 H, CH$_3$, $^2J_{HP}$ = 13.8 Hz, $^2J_{HH}$ = 6.9 Hz); −12.76 (d, 2 H, Os−H, $^2J_{HP}$ = 36.3 Hz). ^2H NMR (46.1 MHz, C_6H_6, 293 K): δ 5.63, 5.14 (s, η^5-C_5D_4−). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 47.6 (s). Spectroscopic data for **9-d$_5$**: ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−6.90 (15 H, −Ph); 2.01 (t, 2 H, η^5-C_5D_4−CH_2−, $^3J_{HH}$ = 7.2 Hz); 1.37 (m, 3 H, PCH); 1.40−1.10 (m, 4 H, −CH$_2$−CH$_2$−); 0.85 (dd, 18 H, PCHCH_3, $^3J_{HP}$ = 13.5 Hz, $^3J_{HH}$ = 7.2 Hz); 0.82−0.76 (3 H, −CH$_3$); −14.84 (d, 1 H, Os−H, $^2J_{HP}$ = 29.4 Hz). ^2H NMR (46.1 MHz, C_6H_6, 293 K): δ 4.82, 4.65 (s, 4 D, η^5-C_5D_4−); −14.78 (d, 1 D, Os-D, $^2J_{DP}$ = 2.6 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 41.4 (s).

Preparation of OsH$_2${η^5-C_5H_4CH(CH$_3$)CH$_2$CH$_3$}(SiPh$_3$)(P^{i}Pr$_3$) (10). To a solution of OsH(η^5-C_5H_5)Cl(SiPh$_3$)(P^{i}Pr$_3$) (195 mg, 0.27 mmol) in 10 mL of THF was added *sec*-buthyllithium (0.3 mL), and the mixture was left to react for 20 min. Methanol (1 mL) was added, and the mixture was stirred for 1 min and then vacuum-dried. The subsequent residue was washed with methanol (2 × 5 mL), leading to a white solid which was a (1:4) mixture of **10** and **8**. IR (Nujol, cm^{-1}): ν(Os−H) hidden by resonances of **8**. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.00−6.90 (15 H, −Ph); 4.90−4.30 (4 H, η^5-C_5H_4−, ABCD system); 1.40 (m, 1 H, η^5-C_5H_4−C*H*−); 1.32 (m, 3 H, PCH); 1.15 (m, 2 H, η^5-C_5H_4−CH−CH_2−); 1.05 (d, 3 H, η^5-C_5H_4−CH−CH_3, $^3J_{HH}$ = 6.6 Hz); 0.87 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 13.2 Hz, $^3J_{HH}$ = 6.9 Hz); 0.85 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 13.2 Hz, $^3J_{HH}$ = 6.9 Hz); 0.69 (t, 3 H, η^5-C_5H_4−CH−CH$_2$−CH_3, $^3J_{HH}$ = 7.2 Hz); −14.72 (dd, 1 H, Os−H, $^2J_{HP}$ = 27.6 Hz, $^2J_{HH}$ = 3.9 Hz); −14.91 (d, 1 H, Os−H, $^2J_{HP}$ = 27.6 Hz, $^2J_{HH}$ = 3.9 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 146.9 (−, s, Cipso Ph); 136.7, 127.2 (+, s, Cortho, Cmeta Ph); 127.6 (+, s, Cpara Ph); 112.9 (−, s, quaternary C in η^5-C_5H_4−CH−); 81.5, 78.8, 77.4, 76.3 (+, s, tertiary C's in η^5-*C*$_5$H$_4$−CH−); 32.5 (+, s, η^5-C_5H_4−*C*H(CH$_3$)CH$_2$−CH$_3$); 32.3 (−, s, η^5-C_5H_4−CH-*C*H$_2$−); 29.2 (+, d, PCH, $^1J_{CP}$ = 29.7 Hz); 21.8, 12.5 (+, s, η^5-C_5H_4−CH(*C*H$_3$)CH$_2$−*C*H$_3$); 19.9, 19.7 (+, s, PCH−*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 40.6 (s, t in off-resonance). MS (FAB$^+$): m/z = 734 (M^+).

Preparation of OsH(η^5-C_5H_5){Si(C_6H_4)Ph$_2$}(P^{i}Pr$_3$) (11). To a solution of OsH(η^5-C_5H_5)Cl(SiPh$_3$)(P^{i}Pr$_3$) (255 mg, 0.36 mmol) and acetone (0.5 mL) in 10 mL of THF was added *n*-buthyllithium (0.5 mL). The mixture was left to stir for 30 min, and methanol (1 mL) was added. After 1 min of stirring, the solution was vacuum-dried, and the sticky residue was washed with methanol (2 × 4 mL), leading to a white solid. Yield: 163 mg (67%). Anal. Calcd for $C_{32}H_{41}OsPSi$: C, 56.95; H, 6.12. Found: C, 56.53; H, 6.12. IR (Nujol, cm^{-1}): ν(Os−H) 2137 (m), 2104 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.30−7.00 (14 H, −Ph); 4.69 (s, 5 H, Cp); 1.91 (m, 3 H, PCH); 0.68 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 12.3 Hz, $^3J_{HH}$ = 7.2 Hz); 0.56 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 12.3 Hz, $^3J_{HH}$ = 7.2 Hz); −13.71 (d, 1 H, Os−H, $^2J_{HP}$ = 29.7 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, CCl_2D_2, 293 K, plus APT): δ 165.2 (−, s, Os−C−*C*−Si); 144.1, 142.1 (−, s, Cipso Ph); 140.1, 129.6, 128.5, 120.8 (+, s, tertiary C's in Os−C_6H_4−Si); 135.0, 133.9 (+, s, Cortho Ph); 127.8 (+, s, Cpara Ph); 127.4, 127.3 (+, s, Cmeta Ph); 126.3 (−, d, Os−*C*−C−Si, $^2J_{CP}$ = 13.7 Hz); 81.6 (+, s, Cp); 26.8 (+, d, PCH, $^1J_{CP}$ = 27.8 Hz); 20.2−20.0 (+, PCH−*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 21.8 (s, d in off-resonance). MS (FAB$^+$): m/z = 677 (M^+ + H).

Preparation of OsH$_2${η^5-C_5H_4N(CH$_2$CH$_3$)$_2$}(GePh$_3$)(P^{i}Pr$_3$) (12). To a solution of diethylamine (1.0 mL) in 10 mL of THF was first added *n*-buthyllithium (0.3 mL) and then OsH(η^5-C_5H_5)Cl(GePh$_3$)(P^{i}Pr$_3$) (140.1 mg, 0.19 mmol). The mixture was left to stir for 30 min, and methanol (1 mL) was added. After 1 min of stirring, the solution was vacuum-dried, and the resulting sticky residue was washed with methanol (2 × 3 mL), finally leading to a white solid. Yield: 82 mg (56%). Anal. Calcd for $C_{36}H_{52}GeNOsP$: C, 54.56; H, 6.61; N: 1.77. Found: C, 54.25; H, 6.76; N: 2.14. IR (Nujol, cm^{-1}): ν(Os−H) 2089 (m), 2066 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−7.10 (15 H, −Ph); 4.50−4.00 (4 H, η^5-C_5H_4−, AA′BB′ system); 2.52 (q, 4 H, N−CH$_2$−, $^3J_{HH}$ = 7.2 Hz); 1.46 (m, 3 H, PCH); 0.92 (dd, 18 H, PCHCH_3, $^3J_{HP}$ = 13.2 Hz, $^3J_{HH}$ = 7.2 Hz); 0.77 (t, 6 H, N−CH$_2$−CH_3, $^3J_{HH}$ = 7.2 Hz); −14.10 (d, 2 H, Os−H, $^2J_{HP}$ = 29.4 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 151.0 (−, s, Cipso GePh$_3$); 136.7, 127.5 (+, s, Cortho, Cmeta GePh$_3$); 134.0 (−, s, quaternary C in η^5-C_5H_4−N); 127.2 (+, s, Cpara GePh$_3$); 68.5, 63.0 (+, s, tertiary C's in η^5-C_5H_4−N); 45.7 (−, s, −N−CH$_2$−); 29.7 (+, d, PCH, $^1J_{CP}$ = 28.1 Hz); 20.1 (+, s, PCH−*C*H$_3$); 12.9 (+, s, −N−CH$_2$−*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 40.2 (s, t in off-resonance). MS (FAB$^+$): m/z = 793 (M^+), 716 (M^+ − Ph), 487 (M^+ − GePh$_3$ − 3H).

Preparation of OsH$_2${η^5-C_5H_4N(CH$_2$CH=CH$_2$)$_2$}(GePh$_3$)(P^{i}Pr$_3$) (13). To a solution of diallylamine (0.5 mL) in 10 mL of THF was first added *n*-buthyllithium (0.4 mL) and then

$OsH(\eta^5\text{-}C_5H_5)Cl(GePh_3)(P^iPr_3)$ (130 mg, 0.17 mmol). The mixture was left to stir for 30 min, and methanol (1 mL) was added. After 1 min of stirring, the solution was vacuum-dried, and the resulting sticky residue was washed with methanol (2 × 3 mL), leading to a white solid. Yield: 75 mg (53%). Anal. Calcd for $C_{38}H_{52}GeNOsP$: C, 55.88; H, 6.43; N: 1.72. Found: C, 56.27; H, 6.80; N: 2.00. IR (Nujol, cm^{-1}): ν(Os−H) 2083 (m), 2062 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−7.10 (15 H, −Ph); 5.60 (ddt, 2 H, $-CH_2-CH{=}CH_2$, $^3J_{HH} = 17.1$ Hz, $^2J_{HH} = 11.4$ Hz; $^2J_{HH} = 5.7$ Hz); 4.98 (dd, 2 H, H *trans* to $-CH_2-$ in $-CH{=}CH_2$, $^3J_{HH} = 17.1$ Hz, $^2J_{HH} = 1.5$ Hz); 4.93 (dd, 2 H, H *cis* to $-CH_2-$ in $-CH{=}CH_2$, $^3J_{HH} = 11.4$ Hz, $^2J_{HH} = 1.5$ Hz); 4.50−4.10 (4 H, η^5-C_5H_4-, AA′BB′ system); 3.15 (d, 4 H, $N-CH_2-$, $^3J_{HH} = 5.7$ Hz); 1.44 (m, 3 H, PCH); 0.91 (dd, 18 H, $PCHCH_3$, $^2J_{HP} = 13.2$ Hz, $^2J_{HH} = 7.2$ Hz); −14.12 (d, 2 H, Os−H, $^2J_{HP} = 29.7$ Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 150.5 (−, s, Cipso $GePh_3$); 136.3, 127.1 (+, s, Cortho, Cmeta $GePh_3$); 134.5 (+, s, $-CH{=}CH_2$); 131.2 (−, s, quaternary C in η^5-C_5H_4-N); 126.9 (+, s, Cpara $GePh_3$); 116.6 (−, s, $-CH{=}CH_2$); 68.6, 64.3 (+, s, tertiary C's in η^5-C_5H_4-N); 54.8 (−, s, $-N-CH_2-$); 29.3 (+, s, PCH); 19.4 (+, s, $PCH-CH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 39.8 (s, t in off-resonance). MS (FAB^+): $m/z = 817$ (M^+), 740 ($M^+ - Ph$), 513 ($M^+ - GePh_3 - H$).

Preparation of $OsH_2\{\eta^5\text{-}C_5H_4N(CH_2CH_3)_2\}(SiPh_3)(P^iPr_3)$ (14). To a cold solution of diethylamine (0.5 mL) in 10 mL of THF (−78 °C) was first added *n*-buthyllithium (0.2 mL) and then $OsH(\eta^5\text{-}C_5H_5)Cl(SiPh_3)(P^iPr_3)$ (216.5 mg, 0.30 mmol). The mixture was left to stir for 20 min, and methanol (1 mL) was added. After 1 min of stirring, the solution was vacuum-dried, and the resulting sticky residue was then washed with methanol (2 × 3 mL), leading to a white solid. Yield: 102 mg (45%). Anal. Calcd for $C_{36}H_{52}NOsPSi$: C, 57.79; H, 7.02; N: 1.87. Found: C, 57.40; H, 6.68; N: 2.01. IR (Nujol, cm^{-1}): ν(Os−H) 2095 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−7.10 (15 H, −Ph); 4.50−4.00 (4 H, η^5-C_5H_4-, AA′BB′ system); 2.52 (q, 4 H; $N-CH_2-$, $^3J_{HH} = 7.2$ Hz); 1.40 (m, 3 H, PCH); 0.93 (dd, 18 H, $PCHCH_3$, $^2J_{HP} = 13.2$ Hz, $^2J_{HH} = 7.2$ Hz); 0.75 (t, 6 H; $-CH_3$, $^3J_{HH} = 7.2$ Hz); −14.45 (d, 2 H, Os−H, $^2J_{HP} = 28.2$ Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 149.1 (−, s, Cipso $SiPh_3$); 137.4, 126.7 (+, s, Cortho, Cmeta $SiPh_3$); 134.6 (−, s, quaternary C in η^5-C_5H_4-N); 127.0 (+, s, Cpara $SiPh_3$); 70.8, 63.1 (+, s, tertiary C's in η^5-C_5H_4-N); 44.7 (−, s, $-N-CH_2-$); 28.3 (+, s, PCH); 19.7 (+, s, $PCH-CH_3$); 12.3 (+, s, $-N-CH_2-CH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 38.9 (s, t in off-resonance). MS (FAB^+): $m/z = 749$ (M^+), 672 ($M^+ - Ph$), 487 ($M^+ - SiPh_3 - 3H$).

Preparation of $OsH_2\{\eta^5\text{-}C_5H_4N(CH_2CH{=}CH_2)_2\}(SiPh_3)$-$(P^iPr_3)$ (15). To a solution of diallylamine (0.5 mL) in 10 mL of THF was first added *n*-buthyllithium (0.5 mL) and then $OsH(\eta^5\text{-}C_5H_5)Cl(SiPh_3)(P^iPr_3)$ (239 mg, 0.34 mmol). The mixture was left to stir for 1 h, and methanol (1 mL) was added. After 1 min of stirring, the solution was vacuum-dried, and the resulting sticky residue was washed with methanol (2 × 4 mL), leading to a white solid which was a (2:1) mixture of **15** and **8**. IR (Nujol, cm^{-1}): ν(Os−H) 2091 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−7.10 (15 H, −Ph); 5.59 (ddt, 2 H, $-CH_2-CH{=}CH_2$, $^3J_{HH} = 13.8$ Hz, $^2J_{HH} = 6.9$ Hz; $^2J_{HH} = 5.7$ Hz); 4.98 (dd, 2 H, H *trans* to $-CH_2-$ in $-CH{=}CH_2$, $^3J_{HH} = 13.8$ Hz, $^2J_{HH} = 1.5$ Hz); 4.93 (dd, 2 H, H *cis* to $-CH_2-$ in $-CH{=}CH_2$, $^3J_{HH} = 6.9$ Hz, $^2J_{HH} = 1.5$ Hz); 4.50−4.10 (4 H, η^5-C_5H_4-, AA′BB′ system); 3.13 (d, 4 H, $N-CH_2-$, $^3J_{HH} = 5.7$ Hz); 1.37 (m, 3 H, PCH); 0.91 (dd, 18 H, $PCHCH_3$, $^2J_{HP} = 12.9$ Hz, $^2J_{HH} = 7.2$ Hz); −14.45 (d, 2 H, Os−H, $^2J_{HP} = 27.9$ Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 149.5 (−, s, Cipso $SiPh_3$); 136.7, 127.2 (+, s, Cortho, Cmeta $SiPh_3$); 134.9 (+, s, $-CH{=}CH_2$); 133.7 (−, s, quaternary C in η^5-C_5H_4-N); 127.5 (+, s, Cpara $SiPh_3$); 117.0 (−, s, $-CH{=}CH_2$); 71.5, 64.9 (+, s, tertiary C's in η^5-C_5H_4-N); 54.5 (−, s, $-N-CH_2-$); 28.9 (+, d, PCH, $^1J_{CP} = 28.2$ Hz); 19.9 (+, s, $PCH-CH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 38.8 (s, t in off-resonance). MS (FAB^+): $m/z = 773$ (M^+).

Preparation of $OsH_2(\eta^5\text{-}C_5H_4PPh_2)(GePh_3)(P^iPr_3)$ (16). To a solution of diphenylphosphine (0.15 mL) in 10 mL of THF was first added *n*-buthyllithium (0.15 mL) and then $OsH(\eta^5\text{-}C_5H_5)Cl(GePh_3)(P^iPr_3)$ (211.2 mg, 0.28 mmol). The mixture was left to stir for 1 h, and methanol (1 mL) was added. After 1 min of stirring, the solution was vacuum-dried, and the resulting sticky residue was washed with methanol (2 × 4 mL), leading to a white solid. Yield: 147 mg (58%). Anal. Calcd for $C_{44}H_{52}GeOsP_2$: C, 58.35; H, 5.79. Found: C, 58.03; H, 5.45. IR (Nujol, cm^{-1}): ν(Os−H) 2168 (m), 2112 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.90−7.00 (25 H, −Ph); 4.80−4.50 (4 H, η^5-C_5H_4-, AA′BB′ system); 1.49 (m, 3 H, PCH); 0.87 (dd, 18 H, $PCHCH_3$, $^2J_{HP} = 13.5$ Hz, $^2J_{HH} = 7.2$ Hz); −14.40 (dd, 2 H, Os−H, $^2J_{HP} = 29.4$ Hz, $^3J_{HP} = 3.6$ Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 149.2 (−, s, Cipso $-GePh_3$); 139.4 (−, d, Cpara $-PPh_2$, $^1J_{CP} = 12.9$ Hz); 136.4, 127.7 (+, s, Cortho, Cmeta $-GePh_3$); 134.4 (+, d, Cortho $-PPh_2$, $^2J_{CP} = 19.8$ Hz); 129.4 (+, s, Cpara $-PPh_2$); 129.1 (+, d, Cmeta $-PPh_2$, $^3J_{CP} = 6.4$ Hz); 127.4 (+, s, Cpara $-GePh_3$); 93.4 (−, d, quaternary C in η^5-C_5H_4-P, $^1J_{CP} = 18.4$ Hz); 86.1 (+, d, one of the tertiary C's in η^5-C_5H_4-P, $^2J_{CP} = 15.2$ Hz); 79.5 (+, s, one of the tertiary C's in η^5-C_5H_4-P); 30.1 (+, d, PCH, $^1J_{CP} = 29.5$ Hz); 19.8 (+, s, $PCH-CH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 39.3 (s, P^iPr_3, t in off-resonance); −17.4 (s, $-PPh_2$, s in off-resonance). MS (FAB^+): $m/z = 906$ (M^+), 829 ($M^+ - Ph$).

Preparation of $OsH_2(\eta^5\text{-}C_5H_4PPh_2)(SiPh_3)(P^iPr_3)$ (17). To a solution of diphenylphosphine (0.15 mL) in 10 mL of THF was first added *n*-buthyllithium (0.20 mL) and then $OsH(\eta^5\text{-}C_5H_5)Cl(SiPh_3)(P^iPr_3)$ (301 mg, 0.42 mmol). The mixture was left to stir for 1 h, and methanol (1 mL) was added. After 1 min of stirring, the resulting solution was vacuum-dried, generating a sticky residue, which was washed with methanol (2 × 4 mL), finally leading to a white solid. Yield: 195 mg (54%). Anal. Calcd for $C_{44}H_{52}OsP_2Si$: C, 61.37; H, 6.09. Found: C, 61.62; H, 6.41. IR (Nujol, cm^{-1}): ν(Os−H) 2191 (m), 2137 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.00−7.00 (25 H, −Ph); 4.80−4.40 (4 H, η^5-C_5H_4-, AA′BB′ system); 1.46 (m, 3 H, PCH); 0.88 (dd, 18 H, $PCHCH_3$, $^2J_{HP} = 13.5$ Hz, $^2J_{HH} = 7.2$ Hz); −14.65 (dd, 2 H, Os−H, $^2J_{HP} = 28.2$ Hz, $^3J_{HP} = 2.7$ Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6, 293 K, plus APT): δ 147.9 (−, s, Cipso $-SiPh_3$); 139.6 (−, d, Cipso $-PPh_2$, $^1J_{CP} = 12.9$ Hz); 137.5, 127.3 (+, s, Cortho, Cmeta $-SiPh_3$); 134.4 (+, d, Cortho, $-PPh_2$, $^2J_{CP} = 20.3$ Hz); 129.3 (+, s, Cpara $-PPh_2$); 129.1 (+, d, Cmeta $-PPh_2$, $^1J_{CP} = 6.9$ Hz); 127.7 (+, s, Cpara $-SiPh_3$); 91.8 (−, d, quaternary C in η^5-C_5H_4-P, $^1J_{CP} = 18.4$ Hz); 87.7 (+, dd, one of the tertiary C's in η^5-C_5H_4-P, $^2J_{CP} = 12.5$ Hz, $^2J_{CP} = 2.8$ Hz); 80.9 (+, s, one of the tertiary C's in η^5-C_5H_4-P); 29.6 (+, d, PCH, $^1J_{CP} = 29.0$ Hz); 19.8 (+, s, $PCH-CH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 38.4 (s, P^iPr_3, t in off-resonance); −18.0 (s, $-PPh_2$, s in off-resonance). MS (FAB^+): $m/z = 862$ ($M^+ - H$), 785 ($M^+ - Ph$), 600 ($M^+ - SiPh_3 - H$).

X-ray Structure Analysis of Complexes $OsH_2\{\eta^5\text{-}C_5H_4$-$Si(C_6H_4)Ph_2\}(P^iPr_3)$ (8) and $OsH_2\{\eta^5\text{-}C_5H_4N(CH_2\text{-}CH{=}CH_2)_2\}(GePh_3)(P^iPr_3)$ (13). Crystals suitable for X-ray diffraction analysis were mounted onto a glass fiber and transferred to a Bruker-Siemens P-4 (8, $T = 200.0(2)$ K) and Bruker-Siemens-STOE AED-2 (13, $T = 298.0(2)$ K) automatic diffractometers (Mo Kα radiation, graphite monocromator, $\lambda = 0.71073$ Å). Accurate unit cell parameters were determined by least-squares fitting from the settings of high-angle reflections. Data were collected by the $\omega/2\theta$ Å scan method. Lorentz and polarization corrections were applied. Decay was monitored by measuring three standards throughout data collection. Corrections for decay and absorption (semiempirical ψ-scan method) were also applied.

The structures were solved by Patterson methods and

refined by full matrix least-squares on F^2 (**8** and **13**).[32] The triisopropylphosphine ligand of **8** was found to be disordered and refined with two moieties (a and b) with complementary occupancy factors and isotropic thermal parameters. The remaining non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were observed or included at idealized positions. Hydride ligands H(01) and H(02) (**8** and **13**) were located in the difference Fourier maps and refined isotropically.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **8** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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