Indenyl Hemilability: Unveiling a Masked (η^5-C_5Me_5)Ru(κ^2-*P*,*C*arbene) Zwitterion Via Facile and Reversible Ru−C(sp^3) Bond Cleavage

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Data obtained from dynamic NMR investigations and reactivity studies revealed that the isolable, 18-electron Cp*Ru(κ^3-*P*,*C*,*C*′) complex **3** provides access to the reactive, coordinatively unsaturated Cp*Ru(κ^2-*P*,*C*) zwitterionic intermediate **4** by way of an unprecedented and reversible Ru−C(sp^3) bond cleavage process that can be described as 'indenyl hemilability'. Indirect support for the reversible generation of **4** from **3** was obtained through the isolation of adducts of the type **4**·**L** upon treatment of **3** with various L-donor substrates (L = CO, PPh_3, $PHPh_2$, 4-dimethylaminopyridine, NH_3, piperidine, and 2,6-dimethylaniline). The reactivity observed upon treatment of **3** with E−H containing substrates (H_2, ^{i}PrOH, Ph_3SiH, Ph_2SiH_2, $PhNH_2$, and pyrrole) can be rationalized in terms of net cooperative substrate activation involving the Lewis acidic metal fragment and the Lewis basic indenide unit in the reactive intermediate **4**. In the apparent reaction of **4** with $PHPh_2$ and PH_2Ph, an unusual ancillary ligand rearrangement involving the net metathesis of P−H and C−N bonds was observed, resulting in the formation of zwitterionic Cp*Ru(=CH(NHMe))(κ^2-*P*,*P*) complexes that feature the first examples of κ^2-*P*,*P*-indenide ligation.

Introduction

The design and construction of new and reactive classes of coordinatively unsaturated platinum-group metal (PGM) complexes represents a crucial step toward addressing challenging stoichiometric and/or catalytic substrate transformations. In moving beyond traditional ancillary ligand design themes,[1] considerable research effort is being directed toward the pursuit of complexes supported by ancillary ligands featuring added functionality that are capable of: (a) providing stability to a resting state of a complex while also providing access to reactive, coordinatively unsaturated species by way of a reversible ligand binding/reorganization process (e.g., cyclometalation,[2a−c] β-hydride elimination,[2b−e] hemilabile chelation,[2f,g] and other[2h,i]); and/or (b) promoting substrate bond activation processes through cooperative metal−ligand interactions.[1,3] In the context of Ru-mediated E−H (E = main group element) bond activation chemistry, landmark studies by Noyori and co-workers on the application of coordinatively unsaturated amido-Ru complexes in hydrogenation catalysis,[4] as well as by Milstein and co-workers on the use of hemilabile (κ^3-*P*,*N*,*N*)Ru species in both the dehydrogenation of alcohols into esters[5a] and the dehydrogenative synthesis of amides from alcohols and amines,[5b] exemplify the way in which new and unusual reactivity manifolds can be accessed by use of coordinatively unsaturated metal complexes supported by appropriately designed ancillary ligands that feature a reactive (nondative) Lewis basic functionality.

In keeping with these themes, we have initiated a research program focused on the synthesis and reactivity of coordinatively unsaturated platinum-group metal complexes supported by donor-substituted indenide ligands (including κ^2-2-*N*Me_2-3-*P*^{i}Pr_2-indenide) that feature a formally cationic metal fragment counterbalanced by a sequestered, uncoordinated 10π-electron carbanion built into the backbone of the bidentate ancillary ligand.[6] We view such zwitterions as being appealing candidates for applications in E−H bond activation chemistry owing to the potential for net cooperative reactivity involving the Lewis acidic metal fragment and the Lewis basic indenide unit in these formally charge-separated complexes. Although we have yet to document unambiguously such cooperativity in stoichiometric E−H activation studies involving (κ^2-2-*N*R_2-3-*P*R'_2-

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(4) Selected examples: (a) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008. (b) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1997**, *36*, 285. (c) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521.

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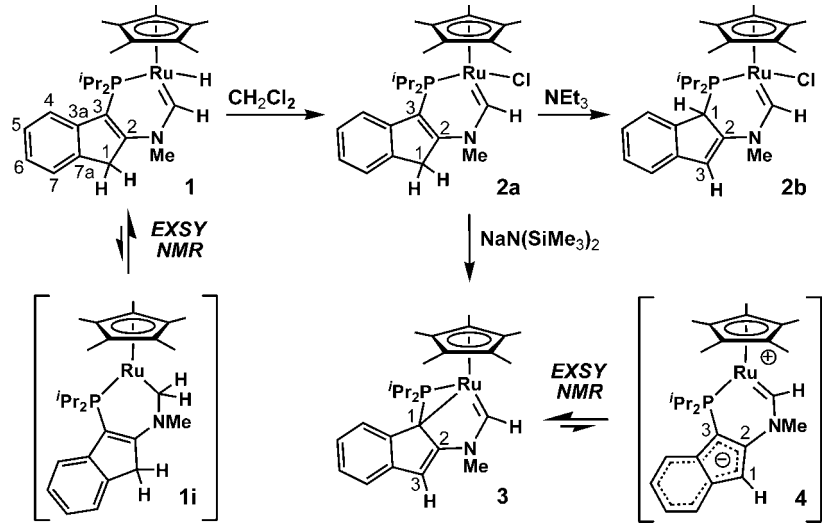
Scheme 1. Synthesis of 3 and the Reversible Formation of 4 (the Atomic Numbering Scheme Is Provided for Representative Complexes)



indenide)ML_n zwitterions, this behavior may contribute to the remarkable activity afforded by the zwitterionic precatalyst (η^6-*p*-cymene)Ru(Cl)(κ^2-2-*N*Me_2-3-*P*^{i}Pr_2-indenide) in ketone transfer hydrogenation.[6b]

In the course of our investigations of the coordinatively unsaturated zwitterion Cp*Ru(κ^2-2-*N*Me_2-3-*P*^{i}Pr_2-indenide) (Cp* = η^5-C_5Me_5), we observed that in the presence of a stabilizing ligand it is possible to isolate 18-electron species of the type Cp*Ru(L)(κ^2-2-*N*Me_2-3-*P*^{i}Pr_2-indenide) (e.g., L = CH_3CN).[6d] However, in the absence of such a stabilizing ligand Cp*Ru(κ^2-2-*N*Me_2-3-*P*^{i}Pr_2-indenide) rapidly rearranges to the Cp*Ru(H)(κ^2-*P*, *C*) hydridocarbene complex (**1**, Scheme 1) via double geminal C−H bond activation involving a ligand NMe group; dynamic NMR data for **1** provided evidence for the first documented interconversion of Ru(*H*)═C*H* (**1**) and Ru−CH_2 (**1i**) groups by way of reversible α-hydride elimination.[6d] We report herein on the use of **1** as a synthetic precursor to the 18-electron Cp*Ru(κ^3-*P*,*C*,*C*′) species **3**. Notably, dynamic NMR data reveal that **3** provides access to the coordinatively unsaturated Cp*Ru(κ^2-*P*,*C*) zwitterionic intermediate **4** by way of an unusual new mode of ancillary ligand hemilability involving reversible Ru−C(sp^3) bond cleavage. Furthermore, reactivity studies confirm that **3** behaves as a masked source of **4**, both in reactions with L-donors (to give **4**·**L**), as well as in reactions with a range of E−H containing substrates to give products corresponding to the net heterolytic cleavage of E−H bonds by the Lewis acidic metal fragment and the Lewis basic indenide unit in **4**.[7]

Results and Discussion

Pursuit of the Zwitterion 4. In viewing the hydridocarbene **1** as a starting point in the synthesis of the coordinatively unsaturated Cp*Ru(κ^2-*P*,*C*) zwitterion **4**,[8] the former was dissolved in CH_2Cl_2 in an effort to prepare the Cp*Ru(Cl)(κ^2-*P*,*C*) complex **2a** (Scheme 1). Upon dissolution of the bright orange **1** in CH_2Cl_2, a gradual color change of the solution from red-orange to dark brown was observed over the course of 6 h, at which point ^{31}P NMR analysis of the reaction mixture indicated the clean conversion to **2a**; in turn this product was isolated as an analytically pure orange-brown powder in 96% yield and characterized. The observation of diagnostic Ru═*CH* NMR signals for **2a** (δ ^{1}H = 12.60, δ ^{13}C = 246.9; *cf* 12.09 and 244.1 for **1**[6d]) confirmed that the carbene portion of the κ^2-*P*,*C* ligand in **1** remained intact during conversion to **2a**. In solution, the slow conversion of **2a** to **2b** in CH_2Cl_2 was detected (^{31}P NMR) in the absence of observable intermediates (ca. 75% conversion after 2 weeks). This isomerization process was found to be accelerated in the presence of excess NEt_3, thereby enabling the isolation of analytically pure **2b** in 91% yield.

In an effort to exploit the chlorocarbene **2a** as a precursor to **4** via dehydrohalogenation, **2a** was treated with $NaN(SiMe_3)_2$ and the progress of the reaction was monitored by use of ^{31}P NMR methods. Complete conversion to a new phosphorus-containing product was observed over the course of 45 min, which in turn was isolated in 81% yield. While elemental analysis data for this new product were found to be consistent with the dehydrohalogenation of **2a**, NMR spectroscopic and X-ray crystallographic data confirmed the identity of this species as the C_1-symmetric, 18-electron Cp*Ru(κ^3-*P*,*C*,*C*′) complex **3**. An ORTEP[9] diagram of one of the two crystallographically independent molecules of **3** is provided in Figure 1, while crystallographic data and selected interatomic distances for all of the crystallographically characterized compounds reported herein are collected in Tables 1 and 2, respectively. Some of the core structural features in **3** can be compared with a related (η^6-arene)Ru(Cl)(κ^2-^{i}Pr_2*P*−*C*HCO_2Me) complex reported by

(6) Complexes of donor-substituted indenide ligands are described as zwitterionic in that they lack conventional resonance structures that would enable the indenide anionic charge to be delocalized onto the pendant donor atoms. For (κ^2-P, N)-PGM complexes, see: (a) Lundgren, R. J.; Rankin, M. A.; McDonald, R.; Stradiotto, M. *Organometallics* **2008**, *27*, 254. (b) Lundgren, R. J.; Rankin, M. A.; McDonald, R.; Schatte, G.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4732. (c) Cipot, J.; McDonald, R.; Ferguson, M. J.; Schatte, G.; Stradiotto, M. *Organometallics* **2007**, *26*, 594. (d) Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2005**, *24*, 4981.

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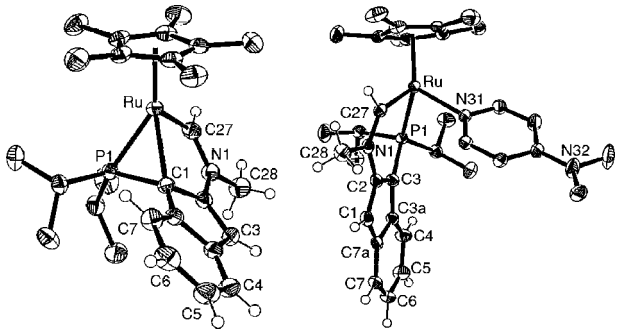
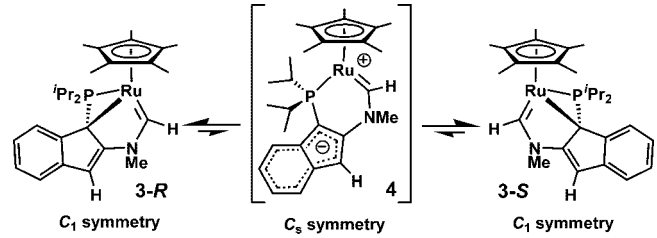


Figure 1. ORTEP diagrams for **3** (left) and **4·DMAP** (right), shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; only one of the two crystallographically independent molecules of **3** is presented, and selected H-atoms have been omitted for clarity (DMAP = 4-dimethylaminopyridine).

Werner and co-workers.[10] While each of the Ru−P distances in **3** is shorter than that of the comparator complex, the corresponding Ru−C1 and $^{i}Pr_2P-C$ distances in **3** are significantly longer, suggesting less P=C character in **3** possibly resulting from the structural requirements of the tridentate κ^3-*P*,*C*,*C*′ ligand.[11]

Dynamic Behavior of 3. Given the somewhat unusual connectivity in **3**, we sought to explore the dynamic properties of this complex in solution. In this regard, data from 1D- and 2D-EXSY ^{1}H NMR[12] experiments provided definitive spectroscopic evidence for the operation of an unprecedented and reversible Ru−C(sp^3) bond cleavage process involving **3**. In the case of 1D-EXSY experiments, irradiation of either of the diastereotopic P(C*H*Me$_2$)$_2$ resonances resulted in significant positively phased enhancement of the other methine signal, in keeping with chemical exchange involving these two environments. Moreover, the 2D-EXSY spectra of **3** featured positively phased off-diagonal exchange cross-peaks that correlate the two diastereotopic P(C*H*Me$_2$)$_2$ environments, as well as pairs of P(CH*Me*$_2$)$_2$ resonances. Collectively, these spectroscopic observations can be rationalized in terms of the reversible cleavage of the Ru−C1 linkage in **3**, thereby providing access to the coordinatively unsaturated, C_S-symmetric zwitterionic intermediate **4** (Schemes 1 and 2). It is noteworthy that this dynamic process is distinct from conventional cyclometalation or β-hydride elimination reactions commonly associated with the breaking and reforming of M-C(sp^3) linkages; given that the reversible Ru−C(sp^3) bond cleavage process in **3** occurs without a change in formal oxidation state at Ru, this novel dynamic process is perhaps best described as "indenyl hemilability".[13] Each of the Ru−C1 distances in **3** (2.250(2) Å, 2.245(2) Å) is not unusually long, exhibiting values that fall between those of the related tridentate complexes Cp*Ru(κ^3-H*C*(PPh$_2$*N*Ph)$_2$) (2.273(2) Å)[14a] and (η^6-*p*-cymene)Ru(κ^3-H*C*(PPh$_2$*N*Ph)$_2$) (2.224(3) Å).[14b] As such, the remarkable ease with which the Ru−C1 linkage undergoes formal heterolytic cleavage in the reversible transformation of **3** into **4** may be attributable in part to the relief of ring strain in the κ^3-*P*,*C*,*C*′ complex **3**, as well as to the energetic favorability of generating a Hückel aromatic indenide anion within the zwitterion **4**, upon ring opening.

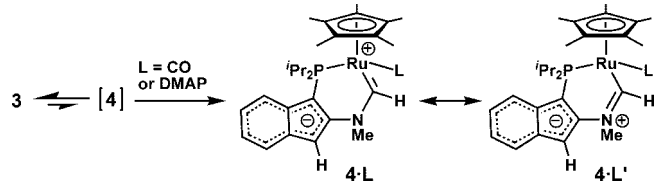
Scheme 2. Proposed Interconversion of Enantiomeric Forms of 3 via the C_s-Symmetric Intermediate 4[a]



[a] "*R*" and "*S*" refer to the configuration at C-1.

Reaction of 3 with CO and DMAP. Intrigued by the possibility that the dynamic behavior of **3** might allow for this complex to serve as a reactive source of the originally targeted coordinatively unsaturated zwitterion **4**, we sought to canvas the stoichiometric reactivity of **3** with a range of small molecule substrates. In initial investigations employing simple L-donors, a solution of **3** was exposed to either an equivalent of 4-dimethylaminopyridine (DMAP) or an atmosphere of CO (Scheme 3). In each case the clean formation of the corresponding adduct **4·L** (L = DMAP, 95%; L = CO, 96%) provided indirect support for the ability of **3** to provide access to **4** *in situ*. The facile Ru−C(sp^3) bond cleavage observed in the course of transforming **3** into **4·CO** contrasts the chemistry exhibited by Cp*Ru(κ^3-H*C*(PPh$_2$*N*Ph)$_2$) upon exposure to CO, whereby a Cp*Ru(CO)(κ^2-*N*,*C*,N) adduct arising from net substitution of an ancillary ligand N-donor arm is produced.[14a]

Scheme 3. Preparation of 4·L and an Important Resonance Contributor (4·L′) for This Class of Complexes[a]



[a] L = CO or 4-Dimethylaminopyridine, DMAP.

Both **4·CO** and **4·DMAP** were characterized spectroscopically, and crystallographic data were also obtained for **4·DMAP**; an ORTEP[9] diagram of this complex is presented in Figure 1. The carbocyclic backbone in **4·DMAP** (as well as in the related adducts **4·NC$_8$H$_{11}$** and **4·PPh$_3$**, *vide infra*; NC$_8$H$_{11}$ = 2,6-dimethylaniline) exhibits C−C distances that are consistent with a delocalized 10π-electron indenide unit, as has been observed for other crystallographically characterized donor-substituted indenide complexes.[6] However, while the formally zwitterionic **4·DMAP** lacks a conventional resonance structure that places the anionic charge onto either the carbene or phosphine donor fragments, the relatively short P−C3 and C1−C2 distances in this adduct (1.779(3) and 1.390(5) Å) indicate that a less-conventional non-zwitterionic resonance contributor featuring a *P*=C3 bond, which places the anionic charge on phosphorus, may also figure prominently in **4·DMAP**

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Table 1. Crystallographic Data for 3, 4·DMAP, 4·NC$_8$H$_{11}$(2.5NC$_8$H$_{11}$), 4·PPh$_3$(C$_6$H$_6$), 8, 12(C$_6$H$_6$)$_{2.5}$, and 13

	3	**4·DMAP**	**4·NC$_8$H$_{11}$** (2.5NC$_8$H$_{11}$)	**4·PPh$_3$** (C$_6$H$_6$)	**8**	**12**(C$_6$H$_6$)$_{2.5}$	**13**
Empirical formula	$C_{27}H_{38}NPRu$	$C_{34}H_{48}N_3PRu$	$C_{55}H_{76.5}N_{4.5}PRu$	$C_{51}H_{59}NP_2Ru$	$C_{39}H_{50}NPRuSi$	$C_{54}H_{64}NP_2Ru$	$C_{33}H_{45}NP_2Ru$
Formula weight	508.62	670.79	932.75	849.00	692.93	890.07	619.72
Crystal dimensions	0.62 × 0.33 × 0.28	0.15 × 0.10 × 0.10	0.60 × 0.57 × 0.14	0.30 × 0.20 × 0.20	0.10 × 0.08 × 0.08	0.20 × 0.20 × 0.20	0.15 × 0.15 × 0.10
Crystal system	triclinic	triclinic	triclinic	orthorhombic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.3256(5)	8.8300(3)	10.9510 (9)	15.9860(2)	9.4870(17)	12.9030(16)	8.8150(4)
b (Å)	15.1105(10)	10.9600(4)	14.3673 (12)	22.7080(4)	11.844(2)	12.9220(10)	10.6730(4)
c (Å)	21.0117(14)	17.1350(5)	16.7877 (13)	23.8110(2)	16.851(4)	15.8990(12)	18.0270(8)
α (deg)	84.0995(9)	87.246(2)	84.2967 (11)	90	98.505(10)	74.415(3)	76.406(2)
β (deg)	79.3200(9)	83.675(2)	77.9902 (10)	90	101.400(8)	71.476(5)	75.879(3)
γ (deg)	78.8049(9)	69.536(2)	73.5579 (10)	90	107.029(9)	70.052(4)	69.245(2)
V (Å^3)	2542.0(3)	1544.08(9)	2475.5 (3)	8643.6(2)	1731.4(6)	2324.2(4)	1517.25(11)
Z	4	2	2	8	2	2	2
ρ_{calcd} (g cm^{-3})	1.329	1.357	1.251	1.305	1.329	1.272	1.354
μ (mm^{-1})	0.693	0.587	0.389	0.472	0.561	0.442	0.644
Range of transmission	0.8296−0.6732	0.9437−0.9173	0.9475−0.8000	0.9115−0.8713	0.9565−0.9460	0.9167−0.9011	0.9384−0.9095
2θ limit (deg)	52.78	54.96	54.86	60.06	43.94	56.38	52.74
Index ranges	$-10 \le h \le 10$ $-18 \le k \le 18$ $-26 \le l \le 26$	$-11 \le h \le 11$ $-14 \le k \le 14$ $-22 \le l \le 22$	$-13 \le h \le 14$ $-18 \le k \le 18$ $-21 \le l \le 21$	$-22 \le h \le 22$ $-31 \le k \le 31$ $-33 \le l \le 33$	$0 < h < 9$ $-12 \le k \le 11$ $-17 \le l \le 16$	$-16 < h < 17$ $-17 \le k \le 17$ $-20 \le l \le 20$	$-11 < h < 10$ $-12 \le k \le 13$ $-22 \le l \le 22$
Total data collected	19436	11746	21645	24114	4135	19505	10370
Independent reflections	10336	7037	11137	12615	4135	11368	6164
R_{int}	0.0170	0.0473	0.0156	0.0387	na	0.0532	0.0508
Observed reflections	9377	5714	9997	9406	3036	9493	4947
Data/restraints/parameters	10336/0/553	7037/0/364	11137/9/544	12615/0/506	4135/145/402	11638/0/536	6164/0/348
Goodness-of-fit	1.089	1.043	1.060	1.029	1.045	1.021	1.061
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0247	0.0459	0.0370	0.0405	0.0631	0.0413	0.0428
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0691	0.1020	0.1016	0.0974	0.1436	0.0906	0.1009
Largest peak, hole (e Å^{-3})	0.316 and −0.670	0.793 and −0.785	1.284 and −0.561	0.663 and −0.604	0.602 and −0.579	0.611 and −1.106	0.754 and −0.587

Table 2. Selected Interatomic Distances (Å) for 3, 4·DMAP, 4·NC$_8$H$_{11}$(2.5NC$_8$H$_{11}$), 4·PPh$_3$(C$_6$H$_6$), 8, 12(C$_6$H$_6$)$_{2.5}$, and 13

	3[a]	**3**[b]	**4·DMAP**[c]	**4·NC$_8$H$_{11}$**[d]	**4·PPh$_3$**	**8**[e]	**12**[f]	**13**[g]
Ru−P1	2.2158(5)	2.2206(5)	2.3011(9)	2.3139(5)	2.3242(6)	2.295(2)	2.3362(6)	2.3160(9)
Ru−P2	−	−	−	−	2.3297(5)	−	2.2899(6)	2.2639(9)
Ru=C	1.941(2)	1.936(2)	1.949(3)	1.946(2)	1.963(2)	−	1.964(2)	1.980(4)
Ru*C*−*N*	1.346(2)	1.355(3)	1.329(4)	1.328(3)	1.323(3)	1.47(1)	1.311(3)	1.306(5)
N−*C*H$_3$	1.463(2)	1.461(3)	1.472(4)	1.471(3)	1.478(3)	1.46(1)	1.458(3)	1.455(5)
N−C2	1.397(2)	1.389(3)	1.425(4)	1.427(3)	1.424(3)	1.37(1)	−	−
^{i}Pr$_2$*P*−*C*ind	1.805(2)	1.802(2)	1.779(3)	1.790(2)	1.776(2)	1.889(7)	1.781(2)	1.779(3)
C1−C2	1.468(2)	1.462(3)	1.390(5)	1.391(3)	1.392(3)	1.52(1)	1.400(3)	1.394(5)
C1−C7a	1.475(3)	1.482(3)	1.420(5)	1.412(3)	1.411(3)	1.50(1)	1.415(3)	1.420(5)
C2−C3	1.361(3)	1.365(3)	1.423(4)	1.428(3)	1.433(3)	1.37(1)	1.424(3)	1.435(5)
C3−C3a	1.445(3)	1.432(4)	1.434(4)	1.433(3)	1.433(3)	1.44(1)	1.434(3)	1.427(5)
C3a−C4	1.392(3)	1.411(4)	1.407(5)	1.413(3)	1.412(3)	1.38(1)	1.413(3)	1.407(5)
C4−C5	1.380(3)	1.374(6)	1.374(5)	1.381(3)	1.380(3)	1.37(1)	1.380(3)	1.377(5)
C5−C6	1.394(3)	1.372(6)	1.406(5)	1.404(4)	1.406(3)	1.38(1)	1.401(4)	1.399(6)
C6−C7	1.394(3)	1.388(4)	1.370(5)	1.373(4)	1.372(4)	1.40(1)	1.372(4)	1.376(5)
C7−C7a	1.388(3)	1.390(4)	1.404(5)	1.402(3)	1.407(3)	1.37(1)	1.412(3)	1.403(5)
C3a−C7a	1.428(3)	1.419(4)	1.445(4)	1.445(3)	1.446(3)	1.41(1)	1.450(3)	1.440(5)

[a] In the first crystallographically independent molecule of **3**, Ru−C1 = 2.250(2) Å. [b] In the second crystallographically independent molecule of **3**, Ru−C1 = 2.245(2) Å. [c] Ru−N31 = 2.147(3) Å. [d] Ru−N2 = 2.256(2) Å. [e] Ru−Si = 2.391(2) Å; Ru−H = 1.48(9) Å; Ru−CH$_2$ = 2.169(8) Å; Si−C1 = 1.958(8) Å; Ru−*H*−*Si* = 1.90(8) Å. [f] P2−C2 = 1.798(2) Å. [g] P2−C2 = 1.796(3) Å; P−H = 1.35(4) Å.

(as well as in **4·NC$_8$H$_{11}$** and **4·PPh$_3$**).[15] Furthermore, the planarity of the N1 atom ($\Sigma_{angles\ at\ N1}$ ca. 360°) and the relatively short Ru−C27 (Ru=C, 1.949(3) Å) and N−C27 (Ru*C*−*N*, 1.329(4) Å; *cf N*−*C*H$_3$, 1.472(4) Å) distances in **4·DMAP** point to significant π-bonding interactions along the Ru−C−N fragment, thereby underscoring the potential importance of resonance contributors of the type **4·L′** (Scheme 3) in describing the electronic structure of **4·DMAP** and related **4·L** adducts.

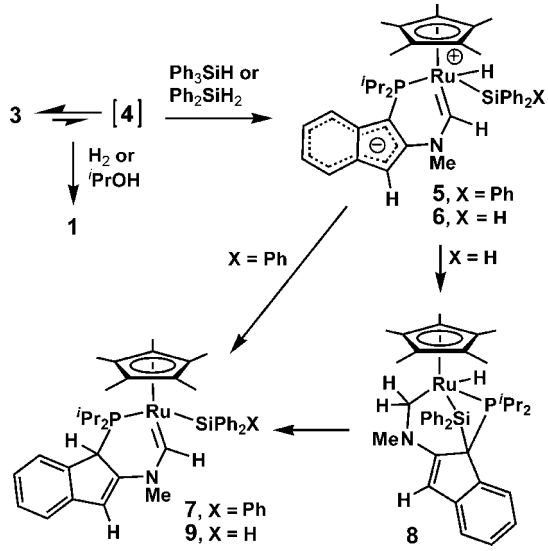
Reaction of 3 with H$_2$, ^{i}PrOH, and Organosilanes. Encouraged by the apparent ability of **3** to behave as a masked source of the zwitterion **4** in reacting with the L-donors CO and DMAP, we proceeded to examine the reactivity of **3** with E−H containing substrates. Exposure of **3** in C$_6$D$_6$ to H$_2$ (ca. 1 atm) resulted in the clean conversion to **1** after 10 min, in the absence of observable (^{1}H and ^{31}P NMR) intermediates (Scheme 4). Similarly, treatment of a C$_6$D$_6$ solution of **3** with excess ^{i}PrOH afforded quantitatively the allylic isomer of **1** (i.e., **1b** - the Ru−H variant of **2b**) after 30 min; in turn **1b** was observed to isomerize cleanly to **1** over the course of 24 h (^{1}H and ^{31}P NMR).[16] While in the absence of mechanistic data we are hesitant to comment conclusively regarding the mechanism of these chemical transformations, each corresponds to the net addition of H$^-$ and H$^+$ to the Lewis acidic Ru and Lewis basic indenide fragments (respectively) in **4**.

In turning our attention to Si−H containing substrates, a solution of **3** in C$_6$D$_6$ was treated with an equivalent of Ph$_3$SiH, and the progress of the reaction was monitored by use of NMR methods (Scheme 4). After 45 min, the **3**:**5** ratio was ca. 1:1 (^{31}P NMR), and after 24 h a mixture of **3**:**5**:**7** (ca. 2:2:1) was detected spectroscopically. Continued monitoring of the solution revealed that a total reaction time of three weeks was needed

(15) Izod, K. *Coord. Chem. Rev.* **2002**, *227*, 153.

(16) The clean isomerization of **1b** into **1** has been documented previously; see ref 6d herein.

Scheme 4. Reactions Involving H_2, ^{i}PrOH, and Organosilanes



in order to achieve the quantitative formation of **7**, and on a preparative scale this compound was obtained as an analytically pure solid in 93% isolated yield. The spectroscopically identified first-formed product **5** can be viewed as arising from Si−H oxidative addition to Ru in the reactive intermediate **4**, followed by slow net transfer of H^+ from Ru to the indenide fragment to give **7**. An analogous intermediate **6** was identified spectroscopically as a kinetic product upon treatment of **3** with Ph_2SiH_2. However, unlike the direct transformation of **5** into **7**, the intermediate **6** was observed to rearrange quantitatively to an alternative, isolable intermediate **8** over the course of 24 h. Compound **8** was isolated in 91% yield and characterized by use of spectroscopic and X-ray crystallographic techniques; an ORTEP[9] diagram of **8** is presented in Figure 2. We are reluctant to comment definitively regarding the location of the hydride in **8**; however, the final refined crystallographic parameters, as well as the experimentally determined $^2J_{SiH}$ value (21.0 Hz), point to an unsymmetrical Ru−H···Si bridging interaction in this complex.[17] While additional mechanistic data are lacking, the rearrangement of **6** to **8** can be viewed as proceeding via net 1,3-H transfer from Si to Ru=*C*, accompanied by intramolecular nucleophilic attack of the indenide unit on silicon. Overall, the transformation of **4** into **8** corresponds to the net extrusion of diphenylsilylene (Ph_2Si:) from Ph_2SiH_2, in which the cationic Ru fragment and the anionic κ^2-*P*,*C* ligand in **4** each play a role in the silane activation process.[18] Efforts to prepare a base-stabilized zwitterionic Ru=$SiPh_2$ complex via heterolytic cleavage of the Si-indenyl linkage in **8** upon treatment with DMAP were unsuccessful.[19] Periodic monitoring of a C_6D_6 solution of **8** (stored at ambient temperature under N_2) revealed the incomplete conversion to **9** (the $SiPh_2H$ variant of **7**); after 1 week the ratio of **8**:**9** was 10:1, while after 5 months the ratio was observed to be 1:8, with no subsequent conversion noted. Attempts to accelerate the rearrangement of **8** to **9** upon heating at 60 °C for 48 h resulted in decomposition, and we have thus far been unsuccessful in our efforts to isolate **9** in analytically pure form. Nonetheless, the unambiguous characterization of **9** (in the presence of **8** as an impurity) was made possible through the use of 1D- and 2D-NMR spectroscopic techniques. Analogous reactions involving the treatment of **3** in C_6D_6 with an equivalent of $PhSiH_3$, pinacolborane, catecholborane, water (5 equiv in THF), or phenylacetylene (24 or 60 °C) each resulted in the formation of an intractable product mixture.

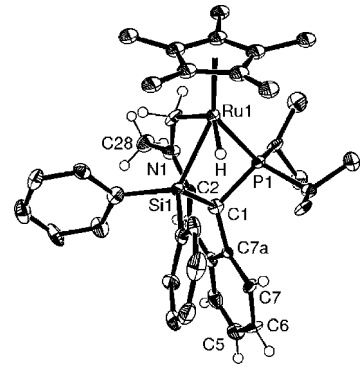


Figure 2. ORTEP diagram for **8**, shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected H-atoms have been omitted for clarity.

Reaction of 3 with Amines. In building upon the aforementioned reactivity studies, we sought to evaluate the reactivity of **3** with group 15 L-donor substrates that also feature E−H bonds. Treatment of a solution of **3** in C_6H_6 with an excess of NH_3 (0.5 M in dioxane) or piperidine (NC_5H_{11}) afforded cleanly the corresponding **4**·**L** adduct (Scheme 5); upon workup each of **4**·$\mathbf{NH_3}$ (75% yield) and **4**·$\mathbf{NC_5H_{11}}$ (82% yield) was obtained as an analytically pure solid. While dissolution of **4**·$\mathbf{NH_3}$ (0.023 g) in C_6D_6 (0.8 mL) resulted in negligible dissociation to give **3** and free NH_3 (^{1}H and ^{31}P NMR), dissolution of **4**·$\mathbf{NC_5H_{11}}$ (0.019 g) in C_6D_6 (0.8 mL) produced a mixture of **4**·$\mathbf{NC_5H_{11}}$ and **3** (ca. 9:1 on the basis of ^{31}P NMR data), as well as a stoichiometric equivalent of free piperidine (relative to **3**; ^{1}H NMR). In keeping with this trend, when **3** was treated with an excess of the more sterically demanding substrate 2,6-dimethylaniline (NC_8H_{11}) under similar conditions, ^{31}P NMR data revealed a mixture of **4**·$\mathbf{NC_8H_{11}}$ and **3** (ca. 2:1). Upon concentrating the solution *in vacuo* only **4**·$\mathbf{NC_8H_{11}}$(δ ^{31}P = 58.9) was observed, and treatment of this mixture with pentane followed by storage at −35 °C allowed for the isolation of solid **4**·$\mathbf{NC_8H_{11}}$, including some crystals of **4**·$\mathbf{NC_8H_{11}}$($2.5NC_8H_{11}$) that proved to be suitable for X-ray diffraction analysis; an ORTEP[9] diagram of **4**·$\mathbf{NC_8H_{11}}$($2.5NC_8H_{11}$) is presented in Figure 3. The salient structural features of **4**·$\mathbf{NC_8H_{11}}$ mirror those found in **4**·**DMAP** (*vide supra*). Upon dissolution in C_6D_6 (0.8 mL), **4**·$\mathbf{NC_8H_{11}}$ (0.022 g) was observed to produce significant quantities of **3** (ca. 80%, ^{31}P NMR), as well as free 2,6-dimethylaniline (^{1}H NMR).

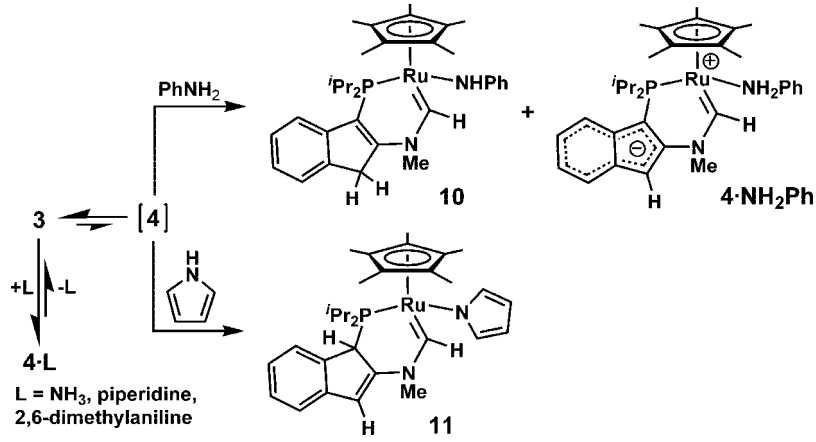
In an effort to observe σ-bond activation chemistry, the reactivity of **3** with alternative N−H containing substrates was examined. Treatment of **3** with $PhNH_2$ in C_6D_6 afforded after 10 min a 1:4 mixture of the apparent N−H activation product **10** (δ ^{31}P = 76.2), and a second product tentatively assigned as **4**·$\mathbf{NH_2Ph}$ (δ ^{31}P = 64.0) on the basis ^{1}H NMR data (by comparison to **4**·$\mathbf{NH_3}$ and **4**·$\mathbf{NC_5H_{11}}$). In monitoring further the progress of the reaction, ^{31}P NMR analysis after 72 h revealed the presence of **10** and an as-yet-unidentified species (broad, 62.1 ppm) in a ratio of ca. 10:1. While we have yet to obtain **10** in the absence of this unknown complex, the identity of **10** was determined on the basis of 1D- and 2D-NMR spectroscopic data. The observation of five distinct N−Ph C−*H*

(17) (a) Lachaize, S.; Sabo-Etienne, S. *Eur. J. Inorg. Chem.* **2006**, 2115. (b) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

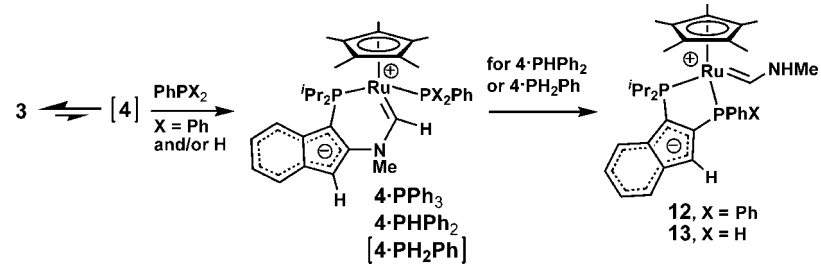
(18) Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 13640.

(19) We have reported recently zwitterionic Ru=Si complexes of this type that feature intramolecular base-stabilization: Rankin, M. A.; MacLean, D. F.; Schatte, G.; McDonald, R.; Stradiotto, M. *J. Am. Chem. Soc.* **2007**, *129*, 15855.

Scheme 5. Reactions Involving Amines



Scheme 6. Reactions Involving Phosphines



signals in the ^{1}H NMR spectrum of **10** indicates that rotation about the N−Ph axis is slow on the NMR time scale at 300K, as has been observed in related Ru(NHPh) complexes.[20,21] While N−H oxidative addition to the zwitterion **4** to give an intermediate analogous to **5** or **6** cannot be unequivocally ruled out in the absence of mechanistic data,[20] we view the formation of **10** as arising from the net deprotonation (either intra- or intermolecular) of the coordinated aniline ligand in **4·NH$_2$Ph** by indenide. In this vein, an adduct of the type **4·L** was not detected in analogous reactions with **3** employing the more acidic N−H substrate pyrrole. Rather, treatment of a solution of **3** in C_6H_6 with pyrrole afforded only **11** (^{31}P NMR) over the course of 10 min,[21] thereby allowing for the isolation of this product as an analytically pure solid in 95% yield. Periodic monitoring (^{1}H and ^{31}P NMR) of a solution of **11** (0.022 g) in C_6D_6 (0.8 mL) over the course of 6 h revealed ca. 20% conversion to a mixture containing what we assign as the vinylic isomer of **11** (i.e., the Ru-NC$_4$H$_4$ variant of **10**; δ ^{31}P = 61.6), **3**, and free pyrrole.

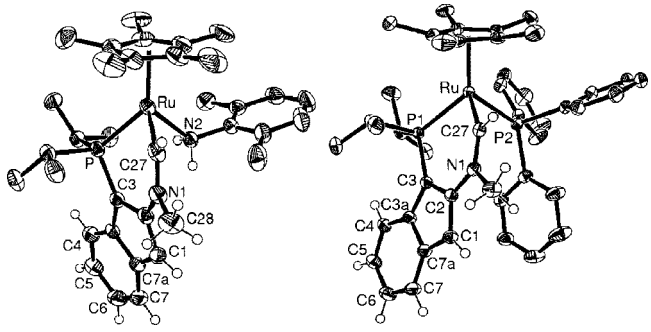


Figure 3. ORTEP diagrams for **4·NC$_8$H$_{11}$**(2.5NC$_8$H$_{11}$) (left) and **4·PPh$_3$**(C_6H_6) (right), shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected H-atoms, as well as the benzene and 2,6-dimethylaniline (NC$_8$H$_{11}$) solvates, have been omitted for clarity.

Reaction of 3 with Phosphines. Complex **3** was observed (^{31}P NMR) to react cleanly in C_6H_6 with an equivalent of PPh$_3$ over the course of 15 min to give a single product (**4·PPh$_3$**), which in turn was obtained in 96% isolated yield (Scheme 6). An ORTEP[9] diagram of **4·PPh$_3$**(C_6H_6) is presented in Figure 3. The core structural features of this complex are similar to those found in the related zwitterionic adducts **4·NC$_8$H$_{11}$** and **4·DMAP** (*vide supra*). Subsequently, we turned our attention to reactions involving PHPh$_2$ or PH$_2$Ph in an effort to assess the ability of the reactive intermediate **4** to promote P−H bond cleavage reactions.[22] Consistent with the formation of **4·PPh$_3$**, the adduct **4·PHPh$_2$** was generated initially upon combination of **3** and PHPh$_2$; **4·PHPh$_2$** was isolated in 94% yield, and characterized spectroscopically. However, in monitoring the stability of **4·PHPh$_2$** in C_6D_6 at ambient temperature (^{1}H and ^{31}P NMR), partial conversion to a new phosphorus-containing product (**12**) was detected after 36 h, accompanied by the gradual drop in intensity of the P−*H* signal in **4·PHPh$_2$**; after five weeks, this transformation was observed to proceed to completion. In raising the temperature to 50 °C, the clean conversion of **4·PHPh$_2$** into **12** was achieved in only one week, thereby allowing for the more convenient synthesis of **12** in 91% isolated yield. Whereas ^{1}H NMR data revealed that the coordinated secondary phosphine ligand in **4·PHPh$_2$** had undergone a P−H bond cleavage process in the formation of

(20) For an example of aniline N−H oxidative addition to Ru, see: Hartwig, J. F.; Anderson, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875.

(21) For pyrrole and related N−H activation by Ru, see: (a) Gunnoe, T. B. *Eur. J. Inorg. Chem.* **2007**, 1185. (b) Pittard, K. A.; Cundari, T. R.; Gunnoe, T. B.; Day, C. S.; Petersen, J. L. *Organometallics* **2005**, *24*, 5015.

(22) For some recent selected reports and reviews related to late metal-mediated P−H bond activation, see: (a) Han, L.-B.; Tilley, T. D. *J. Am. Chem. Soc.* **2006**, *128*, 13698. (b) Scriban, C.; Glueck, D. S. *J. Am. Chem. Soc.* **2006**, *128*, 2788. (c) Chan, C. S.; Stewart, I. C.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 2786. (d) Tanaka, M. *Top. Curr. Chem.* **2004**, *232*, 25. (e) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079.

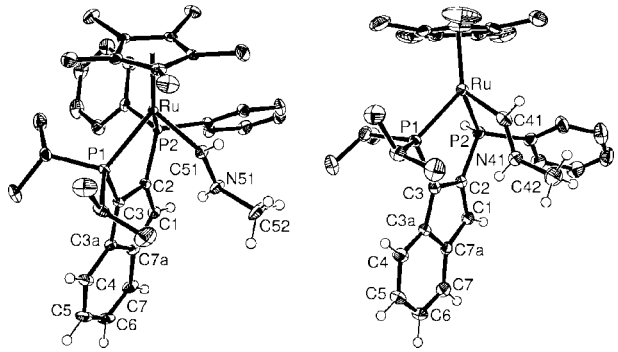
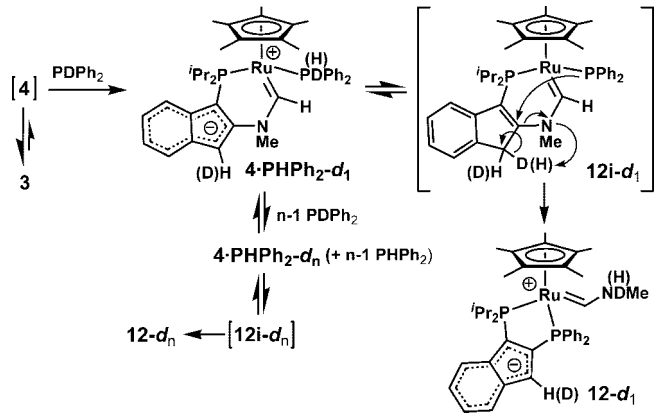


Figure 4. ORTEP diagrams for **12**$(C_6H_6)_{2.5}$ (left) and **13** (right) shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected H-atoms and the benzene solvates have been omitted for clarity.

12, both ^{1}H and ^{13}C NMR data supported the presence of a Ru=CH fragment in this product, thereby precluding the assignment of **12** as being a product arising from P−H bond addition across the Ru=C fragment. Moreover, the absence of a Ru−H ^{1}H NMR resonance, and observation of a signal attributable to an N−H unit served to rule out **12** as being derived from net P−H oxidative addition to the reactive intermediate **4**. The identity of **12** as a new zwitterionic Cp*Ru(=CH(NHMe))(κ^2-*P*,*P*) complex derived from net metathesis of C−N and P−H bonds in the κ^2-*P*,*C* species **4·PHPh$_2$** was confirmed by use of X-ray crystallographic techniques (*vide infra*). Treatment of **3** with PH_2Ph in C_6H_6 at ambient temperature resulted in the complete consumption of **3** after 15 min, accompanied by the formation of a mixture of phosphorus-containing products. After a total reaction time of 24 h, ^{31}P NMR data obtained from an aliquot of the reaction mixture revealed the presence of two major phosphorus-containing products (2:1 ratio): the new zwitterionic Cp*Ru(=CH(NHMe))(κ^2-*P*,*P*) complex **13** (related to **12**), as well an as-yet-unidentified intermediate (possibly **4·PH$_2$Ph**).[23] Continued monitoring of the reaction mixture (^{31}P NMR) revealed the presence of only **13** after a total reaction time of 72 h, thereby enabling the isolation of this complex in 88% yield.

An ORTEP[9] diagram for each of **12**$(C_6H_6)_{2.5}$ and **13** is presented in Figure 4. The salient structural features associated with these new κ^2-*P*,*P* zwitterions compare well with previously reported metal complexes featuring κ^2-*P*,*N* or κ^2-*P*,*C* indenide ligands,[6] including those reported herein (*vide supra*); the contracted P1−C3 and P2−C2 distances suggest that nonzwitterionic resonance contributors featuring *P*=C linkages and a formal negative charge on P1 and/or P2 should be considered in describing the electronic structure of these complexes.[15] In contrast to the nearly identical Ru−P distances that are found in **4·PPh$_3$**, the Ru−P1 linkage in each of **12** and **13** is significantly longer than the corresponding Ru−P2 distance. We are unsure as to whether the source of such differing Ru−P bond lengths is primarily steric or electronic in nature. However, the observation that structurally related Ru zwitterions supported by κ^2-3-*P*^{i}Pr$_2$-2-*N*Me$_2$-indenide do not exhibit contracted Ru−N or N−Cind linkages[6b,d] may foreshadow important differences in the behavior of the carbanion unit in structurally related classes of zwitterionic complexes featuring κ^2-*P*,*N*- and κ^2-*P*,*P*-indenide ancillary ligands. In light of the desirable bond activation behavior exhibited by cationic Cp*Ru(κ^2-*P*,*P*) species,[8] as well as alternative late metal zwitterions developed by Peters and co-workers[24] that feature $[\kappa^2\text{-}Ph_2B(CH_2PR_2)_2]^-$ ancillary ligands, we are currently in the process of establishing rational synthetic routes to substituted indenes that can serve as precursors to κ^2-*P*,*P*-indenide complexes. The results of such synthetic investigations will be reported elsewhere.

Scheme 7. Possible Mechanism for the Conversion of 4·PHPh$_2$ to 12 on the Basis of a Deuterium Labeling Study



In an effort to gain some insight into the mechanistic pathway linking **4·PHPh$_2$** and **12**, compound **3** (0.020 g) in benzene (0.8 mL) was treated with 1.0 or 1.5 equiv of $PDPh_2$ and the progress of the reaction was monitored by use of NMR methods (Scheme 7). Reactions employing 1.0 equiv of $PDPh_2$ afforded **4·PDPh$_2$** cleanly after 15 min. After 24 h at ambient temperature, ^{1}H and ^{2}H NMR analysis indicated partial conversion of **4·PDPh$_2$** to a new deuterium-containing species (i.e., **4·PHPh$_2$-*d*$_1$**), as evidenced by partial deuterium incorporation in the C3−H position, as well as the appearance of a ^{1}H NMR signal attributable to the P−H group in **4·PHPh$_2$**. When **3** was treated with 1.5 equivalents of $PDPh_2$ under similar conditions, **4·PDPh$_2$** once again was observed as the first formed product after 15 min, along with unreacted $PDPh_2$. However, NMR analysis of the reaction mixture after storage for 24 h at ambient temperature revealed the formation of **4·PHPh$_2$-*d*$_n$**, which exhibited more significant deuterium incorporation at the C3−H position than was observed when employing an equimolar amount of $PDPh_2$, as well as free $PHPh_2$ and $PDPh_2$. Such spectroscopic observations are consistent with the intermediacy of a Ru−PPh_2 complex such as **12i-*d*$_n$** (or **12i-*d*$_n$**), which could arise via reversible deprotonation of the P−D(H) unit (either intra- or intermolecular) by the indenide fragment in **4·PHPh$_2$-*d*$_n$** (or **4·PHPh$_2$-*d*$_n$**) (Scheme 7). After each mixture mentioned above was heated at 50 °C for 1 week, the quantitative formation of **12-*d*$_1$** (or **12-*d*$_n$**) was noted; in both cases NMR analyses indicated deuterium incorporation at the N−H and C3−H positions exclusively. Collectively, these qualitative observations are in keeping with a mechanism in which **4·PHPh$_2$** exists in equilibrium with an intermediate such as **12i** (similar to the amido complex **10**). Nucleophilic attack (either intramolecular as depicted in Scheme 7, or intermolecular) of the phosphido fragment on indene in this or a related intermediate, accompanied by net deprotonation of the indene moiety by nitrogen, affords **12**.[25]

(23) ^{31}P{^{1}H} NMR data for this intermediate (C_6D_6): δ 76.0 (d, J_{PP} = 35.3 Hz), 40.7 (d, J_{PP} = 35.3 Hz).

(24) Selected examples: (a) Lu, C. C.; Peters, J. C *J. Am. Chem. Soc.* **2004**, *126*, 15818. (b) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870. (c) Betley, T. A.; Peters, J. C. *Angew. Chem., Int. Ed.* **2003**, *42*, 2385.

(25) For a review of conceptually related transition metal-mediated P-C/X exchange at bound phosphine ligands, see: Macgregor, S. A. *Chem. Soc. Rev.* **2007**, *36*, 67.

Summary and Conclusions

In the pursuit of new classes of highly reactive, yet isolable, platinum-group metal complexes that are capable of mediating challenging substrate transformations, the identification of novel ancillary ligands whose dynamic coordination behavior renders the associated metal fragments operationally unsaturated[26] represents an important challenge. In this report we have demonstrated that the isolable 18-electron complex **3** provides access to the reactive, coordinatively unsaturated zwitterion **4** by way of an unprecedented and reversible Ru−C(sp^3) bond cleavage process, as evinced by data obtained from dynamic NMR investigations and reactivity studies. The apparent reactivity of **4** with E−H containing substrates (E = H, C, N, O, and Si) can be rationalized in terms of net cooperative substrate activation involving the Lewis acidic metal fragment and the Lewis basic indenide unit in **4**. Furthermore, in exploring the reactivity of the intermediate **4** with $PHPh_2$ and PH_2Ph, an unusual ancillary ligand rearrangement involving the net metathesis of P−H and C−N bonds was observed, resulting in the formation of zwitterionic Cp*Ru(=CH(NHMe))(κ^2-*P*,*P*) complexes (**12** and **13**) that feature the first examples of κ^2-*P*,*P*-indenide ligation. We anticipate that the unusual ancillary ligand design featured in **3** will serve as a general strategy for unveiling reactive, coordinatively unsaturated platinum-group metal zwitterions *in situ* by way of indenyl hemilability—what is perhaps the first example of a more general phenomenon (carbanion hemilability) that may be exploited in appropriately designed ligand systems. In this regard, we are currently evaluating the utility of this and related ligation strategies in combination with other platinum-group metals, in an effort to establish new classes of complexes for use in promoting a range of demanding stoichiometric and catalytic substrate transformations enabled by metal−ligand cooperative behavior. We will disclose our progress in these efforts in future reports.

Experimental Section

General Considerations. All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite (Aldrich) was oven-dried for 5 d and then evacuated for 24 h prior to use. The nondeuterated solvents dichloromethane, diethyl ether, benzene, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system purchased from mBraun Inc. Dichloromethane and diethyl ether were purified over two alumina-packed columns, while benzene and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. All solvents used within the glovebox were stored over activated 4 Å molecular sieves. Compound **1** was prepared employing literature procedures.[6d] Hydrogen (99.999%, UHP grade) and carbon monoxide gases (99.5%, chemically pure grade) were obtained from Air Liquide and were used as received. Purification of triethylamine was achieved by stirring over KOH for 7 d, followed by distillation; the distilled triethylamine was then refluxed over CaH_2 for 3 d under dinitrogen, followed by distillation. Purification of ^{i}PrOH (Aldrich, anhydrous 99.5%) was achieved by sparging with dinitrogen over a period of 0.25 h followed by storage over 4 Å molecular sieves (ca. 10 g/100 mL ^{i}PrOH) for a minimum of 24 h. C_6D_6 (Aldrich), Ph_2SiH_2 (Aldrich), and $PhSiH_3$ (Strem) were degassed by using three repeated freeze−pump−thaw cycles and then dried over 4 Å molecular sieves for 24 h prior to use. PH_2Ph (Aldrich) and $PHPh_2$ (Alpha Aesar) were stored over 4 Å molecular sieves for 24 h prior to use. Aniline, 2,6-dimethylaniline, piperidine, and pyrrole (all Aldrich) were degassed by using several freeze−pump−thaw cycles and stored over 4 Å molecular sieves for 24 h prior to use. NH_3 (0.5 M in dioxane, Aldrich) was used as received. All other commercial reagents were obtained from Aldrich and were used as received, with the exception that PPh_3, $NaN(SiMe_3)_2$, and 4-dimethylaminopyridine (DMAP) were dried *in vacuo* for 24 h prior to use. Unless otherwise stated NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1 (^{1}H), 125.8 (^{13}C), 99.4 (^{29}Si), and 202.5 (^{31}P) MHz with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^{1}H, ^{13}C, and ^{29}Si), or 85% H_3PO_4 in D_2O (for ^{31}P). ^{1}H and ^{13}C NMR chemical shift assignments are given on the basis of data obtained from ^{13}C-DEPT, ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC NMR experiments. EXSY spectra of **3** were acquired at 300 K using a mixing time of 0.5 s. ^{29}Si NMR chemical shift assignments and coupling constant data are given on the basis of data obtained from ^{1}H−^{29}Si HMBC/HMQC and ^{1}H-coupled ^{1}H−^{29}Si HMQC experiments. ^{1}H−^{15}N HMQC experiments were used to confirm N−H assignments. IR data were collected on a Bruker VECTOR 22 FT-IR instrument. Elemental analyses were performed either by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada or by Desert Analytics, Tucson, AZ.

Synthesis of 2a. To a glass vial containing freshly prepared **1** (0.15 g, 0.29 mmol) was added CH_2Cl_2 (5 mL). The vial was sealed with a PTFE-lined cap and magnetic stirring was initiated. Over the course of 1 h, the initial red-orange solution gradually darkened to deep red and then to dark brown. After 6 h, ^{31}P NMR data collected on an aliquot of this solution indicated clean conversion to **2a**. The CH_2Cl_2 solvent and other volatile materials were removed *in vacuo*, yielding an oily brown solid. The solid was triturated with pentane (1.5 mL) and the product was dried *in vacuo* to yield **2a** as an analytically pure, orange-brown powder (0.15 g, 0.28 mmol, 96%). Anal. calcd for $C_{27}H_{39}PNRuCl$: C 59.47; H 7.22; N 2.57. Found: C 59.16; H 7.21; N 2.57. ^{1}H NMR (C_6D_6): δ 12.60 (d, J = 2.5 Hz, 1H, Ru=CH), 7.68 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4−H or C7−H), 7.27 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 7.19−7.12 (m, 2H, aryl Hs), 3.28 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.92 (br. s, 2H, C(H_a)(H_b)), 2.85 (s, 3H, NMe), 1.77 (d of d, $^3J_{PH}$ = 10.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.69 (s, 15H, C_5Me_5), 1.56 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.22 (d of d, $^3J_{PH}$ = 19.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 1.03 (d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.76 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)); ^{13}C{^{1}H} (C_6D_6): δ 246.9 (d, $^2J_{PC}$ = 18.0 Hz, Ru=C), 159.4 (d, $^2J_{PC}$ = 10.4 Hz, C2), 147.2 (C3a or C7a), 137.5 (d, J_{PC} = 6.2 Hz, C7a or C3a), 126.8 (C5 or C6), 123.0−122.9 (m, 2 aryl CHs), 122.0 (C4 or C7), 108.0 (m, C3), 98.1 (C_5Me_5), 49.3 (NMe), 40.6 (d, $^3J_{PC}$ = 6.3 Hz, C1), 31.4 (d, $^1J_{PC}$ = 24.4 Hz, P(*C*HMe$_c$Me$_d$)), 26.5 (d, $^1J_{PC}$ = 26.3 Hz, P(*C*HMe$_a$Me$_b$)), 21.4 (P(CH*Me$_a$*Me$_b$)), 19.0 (d, $^2J_{PC}$ = 10.1 Hz, P(CHMe$_a$*Me$_b$*)), 18.7−18.5 (m, P(CH*Me$_c$Me$_d$*)), 10.2 (C_5Me_5); ^{31}P{^{1}H} NMR (C_6D_6): δ 59.0.

Synthesis of 2b. To a glass vial containing a magnetically stirred solution of freshly prepared **2a** (0.098 g, 0.18 mmol) in C_6H_6 (5 mL), was added NEt_3 (2 mL). The vial was then sealed with a PTFE-lined cap and the solution was magnetically stirred for 1 week. ^{31}P NMR data collected on an aliquot of this solution indicated quantitative conversion to **2b**. The C_6H_6 solvent and other volatile materials were then removed *in vacuo*, yielding a dark red-brown solid. The solid was then washed with cold pentane (2 × 1.5 mL, precooled to −35 °C) and the product was then dried *in vacuo* to yield **2b** as an analytically pure, reddish-brown powder (0.089 g, 0.16 mmol, 91%). Anal. calcd for $C_{27}H_{39}PNRuCl$: C 59.47; H 7.22; N 2.57. Found: C 59.26; H 7.60; N 2.53. ^{1}H NMR (C_6D_6): δ 12.29 (s, 1H, Ru=CH), 7.52 (d, $^3J_{HH}$ = 8.0 Hz, 1H,

(26) Johnson, T. J.; Folting, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488.

C4−H or C7−H), 7.35 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C7−H or C4−H), 7.25 (t,^{3} J_{HH} = 7.5 Hz, 1H, C5−H or C6−H), 7.12 (m, 1H, C6−H or C5−H), 6.59 (d, $^2J_{PH}$ = 15.5 Hz, 1H, C1−H), 5.94 (s, 1H, C3−H), 3.17 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.95 (s, 3H, NMe), 1.75 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.71 (s, 15H, C$_5$Me$_5$), 1.21 (m, 1H, P(C*H*Me$_c$Me$_d$)), 0.94 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.54 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.36 (d of d, $^3J_{PH}$ = 10.5 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHMe$_c$*Me$_d$*)); ^{13}C{^{1}H} (C$_6$D$_6$): δ 244.3 (d, $^2J_{PC}$ = 19.8 Hz, Ru=C), 152.1 (C2), 143.4 (d, J_{PC} = 2.0 Hz, C3a or C7a), 141.0 (d, J_{PC} = 8.8 Hz, C7a or C3a), 126.3 (C5 or C6), 124.3 (C4 or C7), 123.0 (C6 or C5), 120.4 (C7 or C4), 108.6 (d, $^3J_{PC}$ = 2.3 Hz, C3), 96.0 (*C*$_5$Me$_5$), 49.2 (NMe), 45.6 (d, $^1J_{PC}$ = 7.9 Hz, C1), 27.1−26.8 (m, P(*C*HMe$_c$Me$_d$) and P(*C*HMe$_a$Me$_b$)), 21.0 (d, $^2J_{PC}$ = 3.3 Hz, P(CH*Me$_a$*Me$_b$)), 18.5 (d, $^2J_{PC}$ = 3.3 Hz, P(CH*Me$_c$*Me$_d$)), 17.5 (d, $^2J_{PC}$ = 4.5 Hz, P(CHMe$_a$*Me$_b$*)), 16.8 (d, $^2J_{PC}$ = 6.4 Hz, P(CHMe$_c$*Me$_d$*)), 10.4 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 93.0.

Synthesis of 3. To a glass vial containing a magnetically stirred solution of **2a** (0.16 g, 0.29 mmol) in benzene (5 mL) was added solid NaN(SiMe$_3$)$_2$ (0.054 g, 0.29 mmol) all at once; alternatively, **2b** can be used in place of **2a**. The vial was sealed with a PTFE-lined cap and magnetic stirring was initiated. Over the course of several minutes, the reaction mixture evolved from dark brown to dark red. After 45 min, ^{31}P NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of **3**. The solution was filtered through Celite and the benzene solvent and other volatile materials were removed *in vacuo*, yielding an oily dark red solid. The residue was treated with pentane (2 × 2 mL), after which the dark-red supernatant solution was carefully removed via a Pasteur pipet, leaving a red solid. The pentane solution was stored at −35 °C in order to induce precipitation. After 12 h, a red-orange solid that had formed was isolated by transferring the supernatant solution to a new glass vial; this solution was concentrated *in vacuo* in order to induce further precipitation. After repeating this procedure, the isolated solids were combined and dried *in vacuo,* yielding **3** as an analytically pure, red-orange powder (0.12 g, 0.24 mmol, 81%). Anal. calcd for C$_{27}$H$_{38}$PNRu: C 63.74; H 7.53; N 2.75. Found: C 63.67; H 7.17; N 2.52. ^{1}H NMR (C$_6$D$_6$): δ 11.45 (s, 1H, Ru=CH), 7.56 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4−H or C7−H), 7.29 (m, 1H, C5−H or C6−H), 7.22 (m, 1H, C6−H or C5−H), 7.14 (m, 1H, C7−H or C4−H), 6.19 (s, 1H, C3−H), 2.84 (d, J = 2.0 Hz, 3H, NMe), 2.36 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.89−1.81 (m, 16H, C$_5$Me$_5$ and P(C*H*Me$_c$Me$_d$)), 1.18 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.02 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.98−0.94 (m, 6H, P(CHMe$_a$*Me$_b$*) and P(CHMe$_c$*Me$_d$*)); ^{13}C{^{1}H} (C$_6$D$_6$): δ 246.7 (d, $^2J_{PC}$ = 12.8 Hz, Ru=C), 166.4 (C2), 148.9 (C3a or C7a), 144.4 (d, J_{PC} = 3.5 Hz, C7a or C3a), 122.1 (C5 or C6), 121.1 (C4 or C7), 120.5 (C6 or C5), 120.4 (C7 or C4), 101.8 (C3), 90.7 (*C*$_5$Me$_5$), 40.8 (NMe), 30.5 (d, $^1J_{PC}$ = 21.1 Hz, P(*C*HMe$_a$Me$_b$)), 25.2 (d, $^1J_{PC}$ = 14.3 Hz, C1), 23.1 (d, $^2J_{PC}$ = 7.7 Hz, P(CH*Me$_c$*Me$_d$)), 21.4−21.2 (m, P(*C*HMe$_c$Me$_d$) and P(CHMe$_a$*Me$_d$*)), 19.6 (d, $^2J_{PC}$ = 8.3 Hz, P(CHMe$_a$*Me$_b$*)), 18.8 (d, $^2J_{PC}$ = 8.1 Hz, P(CH*Me$_a$*Me$_b$)), 11.5 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 78.8. Slow evaporation of a C$_6$D$_6$ solution of **3** produced a crystal suitable for single-crystal X-ray diffraction analysis.

Synthesis of 4·DMAP. To a glass vial containing a magnetically stirred solution of **3** (0.082 g, 0.16 mmol) in benzene (6 mL) was added solid DMAP (0.020 g, 0.16 mmol) all at once. An immediate lightening of the solution from dark red to a lighter red was observed upon the addition of DMAP. The vial was sealed with a PTFE-lined cap, and the solution was stirred for 45 min, after which time the solution was orange in color. ^{31}P NMR data collected on an aliquot of this solution indicated quantitative conversion to **4·DMAP**. The solvent and other volatile materials were removed *in vacuo*, yielding an oily dark yellow solid. The residue was triturated with pentane (2 × 1.5 mL), and the pentane was removed *in vacuo* to yield **4·DMAP** as an analytically pure, yellow powder (0.097 g, 0.15 mmol, 95%). Anal. calcd for C$_{34}$H$_{48}$PN$_3$Ru: C 64.72; H 7.67; N 6.66. Found: C 64.76; H 7.72; N 6.65. ^{1}H NMR (C$_6$D$_6$): δ 11.71 (s, 1H, Ru=CH), 8.03 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4−H or C7−H), 7.86 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7−H or C4−H), 7.73 (d, $^3J_{HH}$ = 7.0 Hz, 2H, DMAP-aryl Hs), 7.26 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C5−H or C6−H), 7.21 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C6−H or C5−H), 6.74 (d, J = 4.0 Hz, 1H, C1−H), 5.40 (d, $^3J_{HH}$ = 6.5 Hz, 2H, DMAP-aryl Hs), 3.80 (s, 3H, NMe), 3.76 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.74 (s, 6H, DMAP NMe$_2$), 1.71 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.62 (s, 15H, C$_5$Me$_5$), 1.30−1.23 (m, 6H, P(CH*Me$_a$*Me$_b$) and P(CH*Me$_c$*-Me$_d$)), 0.89−0.84 (apparent d of d, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe$_a$*Me$_b$*) and P(CHMe$_c$*Me$_d$*)); ^{13}C{^{1}H} (C$_6$D$_6$): δ 233.0 (d, $^2J_{PC}$ = 20.3 Hz, Ru=C), 156.4 (2 DMAP-aryl CHs), 152.4 (DMAP-aryl C), 145.0 (d, $^2J_{PC}$ = 15.1 Hz, C2), 133.5 (d, J_{PC} = 9.8 Hz, C3a or C7a), 133.2 (C7a or C3a), 119.9 (C4 or C7), 119.4 (C7 or C4), 117.4 (C5 or C6), 115.3 (C6 or C5), 106.4 (2 DMAP-aryl CHs), 93.5 (*C*$_5$Me$_5$), 92.6 (d, $^3J_{PC}$ = 6.5 Hz, C1), 71.1 (d, $^1J_{PC}$ = 59.0 Hz, C3), 53.0 (NMe), 37.8 (DMAP NMe$_2$), 31.2 (d, $^1J_{PC}$ = 25.5 Hz, P(*C*HMe$_c$Me$_d$)), 24.3 (d, $^1J_{PC}$ = 27.9 Hz, P(*C*HMe$_a$Me$_b$)), 19.7 (P(CHMe$_a$*Me$_b$*) or P(CHMe$_c$-*Me$_d$*)), 19.3 (d, $^2J_{PC}$ = 7.8 Hz, P(CH*Me$_a$*Me$_b$) or P(CH*Me$_c$*Me$_d$)), 18.8 (d, $^2J_{PC}$ = 4.2 Hz, P(CHMe$_a$*Me$_d$*) or P(CHMe$_a$*Me$_b$*)), 18.6 (d, $^2J_{PC}$ = 6.0 Hz, P(CH*Me$_c$*Me$_d$) or P(CH*Me$_a$*Me$_b$)), 10.5 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 55.3. Slow evaporation of a diethyl ether solution of **4·DMAP** produced a crystal suitable for single-crystal X-ray diffraction analysis.

Synthesis of 4·CO. Within a glovebox, a J. Young NMR tube was charged with **3** (0.015 g, 0.030 mmol) and 0.8 mL of C$_6$D$_6$. The tube was sealed and the solution was mixed by inversion of the tube several times. The resulting dark red solution was removed from the glovebox, connected to a Schlenk line, and degassed via three repeated freeze−pump−thaw cycles. An atmosphere of CO was introduced to the NMR tube, upon which the solution was observed to lighten gradually in color to red-orange over the course of several min. After 30 min, ^{31}P and ^{1}H NMR data collected on this reaction mixture indicated quantitative conversion to **4·CO**. Upon removal of solvent and other volatile materials *in vacuo*, followed by trituration with pentane (2 × 1.5 mL), **4·CO** was isolated as an analytically pure, bright-yellow powder (0.015 g, 0.028 mmol, 96%). Anal. calcd for C$_{28}$H$_{38}$PNORu: C 62.65; H 7.14; N 2.61. Found: C 62.26; H 7.04; N 2.56. ^{1}H NMR (C$_6$D$_6$): δ 9.95 (s, 1H, Ru=CH), 8.02 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4−H or C7−H), 7.92 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7−H or C4−H), 7.40 (m, 1H, C5−H or C6−H), 7.31 (m, 1H, C6−H or C5−H), 6.61 (d, J = 3.5 Hz, 1H, C1−H), 3.69 (m, 1H, P(C*H*Me$_a$Me$_b$)), 3.32 (s, 3H, NMe), 1.56 (d, J = 1.0 Hz, 15H, C$_5$Me$_5$), 1.52 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.32 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.10 (d of d, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.89 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.62 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)); ^{13}C{^{1}H} (C$_6$D$_6$): δ 221.9 (d, $^2J_{PC}$ = 15.9 Hz, Ru=C), 204.2 (d, $^2J_{PC}$ = 17.7 Hz, Ru−CO), 144.1 (d, $^2J_{PC}$ = 15.2 Hz, C2), 133.0 (d, J_{PC} = 11.2 Hz, C3a or C7a), 132.5 (C7a or C3a), 121.1 (C4 or C7), 118.9 (2 aryl CHs), 116.5 (C5 or C6), 98.4 (*C*$_5$Me$_5$), 96.7 (d, $^3J_{PC}$ = 7.0 Hz, C1), 72.8 (d, $^1J_{PC}$ = 72.3 Hz, C3), 53.4 (NMe), 30.2 (d, $^1J_{PC}$ = 22.8 Hz, P(*C*HMe$_c$Me$_d$)), 24.6 (d, $^1J_{PC}$ = 36.7 Hz, P(*C*HMe$_a$Me$_b$)), 19.8 (P(CH*Me$_a$*Me$_b$)), 17.9−17.8 (m, P(CH-Me$_a$*Me$_b$*) and P(CH*Me$_c$Me$_d$*)), 10.2 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 50.7. FTIR (CsI; cm^{-1}) ν(CO): 1940.

Synthesis of 4·NH$_3$. To a glass vial containing a mixture of **3** (0.099 g, 0.20 mmol) in benzene (3 mL) was added NH$_3$ (0.5 M in dioxane, 3.9 mL, 2.0 mmol) via Eppendorf micropipette, which resulted in the formation of a dark red-orange solution. The vial was then sealed with a PTFE-lined cap and stirred magnetically

for 48 h, after which the solution was brown-orange in color. Analysis of ^{31}P NMR data collected on an aliquot of this solution indicated quantitative conversion to **4·NH$_3$**. After removal of volatile materials *in vacuo*, the residue was triturated with pentane (1.5 mL), and then washed with pentane (2 × 1.5 mL). Residual volatile materials were then removed *in vacuo*, and **4·NH$_3$** was isolated as a analytically pure, brown-yellow powder (0.077 g, 0.15 mmol, 75%). Anal. calcd for $C_{27}H_{41}PN_2Ru$: C 61.67; H 7.87; N 5.33. Found: C 61.97; H 7.71; N 5.39. ^{1}H NMR (C_6D_6): δ 11.27 (d, J = 1.0 Hz, 1H, Ru=CH), 7.95 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4−H or C7−H), 7.90 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7−H or C4−H), 7.34 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C5−H or C6−H), 7.23 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C6−H or C5−H), 6.52 (d, J = 3.5 Hz, 1H, C1−H), 3.70 (m, 1H, P(C*H*Me$_a$Me$_b$)), 3.47 (s, 3H, NMe), 1.54 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.47 (s, 15H, C$_5$Me$_5$), 1.13 (d of d, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.04 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.86−0.79 (m, 6H, P(CHMe$_a$*Me$_b$*) and P(CHMe$_c$*Me$_d$*)), 0.51 (br. s, 3H, NH$_3$); ^{13}C{^{1}H} (C_6D_6): δ 234.3 (d, $^2J_{PC}$ = 19.4 Hz, Ru=C), 144.4 (d, $^2J_{PC}$ = 15.4 Hz, C2), 134.0 (C3a or C7a), 133.4 (d, J_{PC} = 9.2 Hz, C7a or C3a), 120.2 (C4 or C7), 118.3 (C7 or C4), 118.0 (C5 or C6), 115.8 (C6 or C5), 94.2 (d, $^3J_{PC}$ = 6.2 Hz, C1), 91.0 (*C*$_5$Me$_5$), 68.6 (d, $^1J_{PC}$ = 55.5 Hz, C3), 52.2 (NMe), 29.5 (d, $^1J_{PC}$ = 25.5 Hz, P(*C*HMe$_c$Me$_d$)), 23.7 (d, $^1J_{PC}$ = 28.1 Hz, P(*C*HMe$_a$Me$_b$)), 19.4 (d, $^2J_{PC}$ = 5.0 Hz, P(CHMe$_a$*Me$_b$*) or P(CHMe$_c$*Me$_d$*)), 18.8 (d, $^2J_{PC}$ = 4.9 Hz, P(CHMe$_c$*Me$_d$*) or P(CHMe$_a$*Me$_b$*)), 17.9 (d, $^2J_{PC}$ = 5.7 Hz, P(CH*Me$_a$*Me$_b$)), 17.3 (d, $^2J_{PC}$ = 6.0 Hz, P(CH*Me$_c$*Me$_d$)), 10.4 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (C_6D_6): δ 63.5.

Synthesis of 4·NC$_5$H$_{11}$. Piperidine (NC_5H_{11}, 0.10 mL, 1.01 mmol) was added via an Eppendorf micropipette to a glass vial containing a solution of **3** (0.082 g, 0.16 mmol) in benzene (6 mL), which resulted in a color change of the solution from dark red to brown-orange. The vial was then sealed with a PTFE-lined cap and mixed by inversion several times. After 30 min, ^{31}P NMR data collected on an aliquot of this solution indicated the quantitative formation of **4·NC$_5$H$_{11}$**. After removal of volatile materials *in vacuo*, the residue was triturated with pentane (1.5 mL), and then washed with pentane (2 × 1.5 mL). Residual volatile materials were then removed *in vacuo*, which left **4·NC$_5$H$_{11}$** as an analytically pure, yellow-orange powder (0.078 g, 0.13 mmol, 82%). Anal. calcd for $C_{32}H_{49}PN_2Ru$: C 64.71; H 8.32; N 4.72. Found: C 64.79; H 8.07; N 4.31. ^{1}H NMR (C_6D_6, pip = piperidine): δ 11.32 (d, J = 1.5 Hz, 1H, Ru=CH), 8.02 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4−H or C7−H), 7.87 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C7−H or C4−H), 7.40 (m, 1H, C5−H or C6−H), 7.26 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C6−H or C5−H), 6.54 (d, J = 3.5 Hz, 1H, C1−H), 3.72 (m, 1H, P(C*H*Me$_a$Me$_b$)), 3.62 (apparent br. t, J = 11.5 Hz, 1H, N−H), 3.38 (s, 3H, NMe), 2.81 (d, J = 13.0 Hz, 1H, pip-CH), 2.37 (d, J = 12.5 Hz, 1H, pip-CH), 1.97 (m, 1H, pip-CH), 1.70 (m, 1H, pip-CH), 1.60−1.54 (m, 16H, C$_5$Me$_5$ and P(C*H*Me$_c$Me$_d$)), 1.32 (d of d, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.14−1.08 (m, 6H, P(CHMe$_a$*Me$_b$*) and P(CH*Me$_c$*Me$_d$)), 0.92−0.84 (m, 5H, P(CHMe$_c$*Me$_d$*) and 2 pip-CHs), 0.74−0.67 (m, 3H, pip-CHs), 0.47 (m, 1H, pip-CH); ^{13}C{^{1}H} (C_6D_6): δ 235.2 (d, $^2J_{PC}$ = 20.3 Hz, Ru=C), 144.1 (d, $^2J_{PC}$ = 15.0 Hz, C2), 134.3 (C3a or C7a), 133.7 (d, J_{PC} = 9.3 Hz, C7a or C3a), 120.4 (C4 or C7), 118.5 (C7 or C4), 118.3 (C5 or C6), 116.1 (C6 or C5), 94.7 (d, $^3J_{PC}$ = 6.0 Hz, C1), 92.1 (*C*$_5$Me$_5$), 68.3 (d, $^1J_{PC}$ = 53.0 Hz, C3), 59.1 (pip-C), 57.6 (pip-C), 51.8 (NMe), 30.6 (d, $^1J_{PC}$ = 25.9 Hz, P(*C*HMe$_c$Me$_d$)), 28.6 (pip-C), 28.3 (pip-C), 23.9 (pip-C), 23.5 (d, $^1J_{PC}$ = 26.4 Hz, P(*C*HMe$_a$Me$_b$)), 21.0 (d, $^2J_{PC}$ = 4.3 Hz, P(CH*Me$_a$*Me$_b$)), 19.4 (d, $^2J_{PC}$ = 3.4 Hz, P(CHMe$_c$*Me$_d$*)), 19.1 (d, $^2J_{PC}$ = 5.8 Hz, P(CHMe$_a$*Me$_b$*) or P(CH*Me$_c$*Me$_d$)), 17.6 (d, $^2J_{PC}$ = 5.7 Hz, P(CH*Me$_c$*Me$_d$) or P(CHMe$_a$*Me$_b$*)), 11.1 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (C_6D_6): δ 61.1.

Formation of 4·NC$_8$H$_{11}$. To a glass vial containing a solution of **3** (0.11 g, 0.21 mmol) in benzene (7 mL) was added 2,6-dimethylaniline (NC_8H_{11}, 0.26 mL, 2.1 mmol) via Eppendorf micropipette. The addition caused an immediate color change of the solution from dark red to orange-brown. After 30 min, ^{31}P NMR data collected on an aliquot of this solution indicated the presence of a mixture of **4·NC$_8$H$_{11}$** and **3** (ca. 2:1 ratio). In an effort to induce further conversion of **3** to **4·NC$_8$H$_{11}$**, the solution was reduced in volume to ca. 2 mL *in vacuo*. ^{31}P NMR data collected on the resulting concentrated solution indicated the presence of only one phosphorus-containing product in solution (58.9 ppm, **4·NC$_8$H$_{11}$**). In order to induce precipitation of **4·NC$_8$H$_{11}$**, pentane (4 mL) was added to the solution, followed by storage of the solution at −35 °C. After 48 h, an orange-brown solid was isolated (0.055 g). Upon dissolution of this solid (0.022 g) in C_6D_6 (0.8 mL), a mixture of **4·NC$_8$H$_{11}$:3** (ca. 1:4) was detected by use of ^{31}P NMR methods; as well, significant amounts of free 2,6-dimethylaniline were detected in the broadened ^{1}H NMR spectra of this solution. Efforts to isolate **4·NC$_8$H$_{11}$** in analytically pure form were hampered by the dissociation of 2,6-dimethylaniline from **4·NC$_8$H$_{11}$**; as such we are unable to provide a proper yield determination, as well as comprehensive spectroscopic characterization data for this adduct. For characterization purposes, a solution of **3** (0.023 g, 0.045 mmol) in C_6D_6 (0.8 mL) was treated with a large excess of 2,6-dimethylaniline (0.20 mL, 1.6 mmol, ca. 36 equiv). The NMR spectra obtained on the resulting solution featured broadened signals, and exchange between free and bound amine precluded the definitive assignment of signals attributable to the coordinated 2,6-dimethylaniline ligand in **4·NC$_8$H$_{11}$**. Nonetheless, assignments of the other portions of **4·NC$_8$H$_{11}$** could be made. Data for **4·NC$_8$H$_{11}$**: ^{1}H NMR (C_6D_6): δ 11.59 (s, 1H, Ru=CH), 7.83 (br. m, 1H, aryl-H), 7.30 (br. t, $^3J_{HH}$ = 7.0 Hz, 1H, C5−H or C6−H), 7.15 (m, 1H, aryl-H), 7.04 (br. d, $^3J_{HH}$ = 7.0 Hz, 1H, C4−H or C7−H), 6.45 (br. s, 1H, C1−H), 3.75 (br. m, 1H, P(C*H*Me$_a$Me$_b$)), 3.48 (br. s, 3H, NMe), 1.65 (br. m, 1H, P(C*H*Me$_c$Me$_d$)), 1.33−1.21 (br. m, 18H, C$_5$Me$_5$ and P(CH*Me$_a$*Me$_b$)), 1.14−1.04 (br. m, 6H, P(CHMe$_a$*Me$_b$*) and P(CH*Me$_c$*Me$_d$)), 0.86 (br. d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)); ^{13}C{^{1}H} (C_6D_6): δ 234.5 (br. m, Ru=C), 120.0 (aryl-CH), 117.9 (C4 or C7), 117.3 (C5 or C6), 115.1 (aryl-CH), 93.5 (m, C1), 91.5 (*C*$_5$Me$_5$), 52.2 (NMe), 30.6 (m, P(*C*HMe$_c$Me$_d$)), 28.0 (m, P(*C*HMe$_a$Me$_b$)), 19.8 (P(CH*Me$_a$*Me$_b$)), 18.2 (P(CHMe$_c$*Me$_d$*)), 17.7 (P(CHMe$_a$*Me$_b$*)), 16.4 (P(CH*Me$_c$*Me$_d$)), 10.2 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (C_6D_6): δ 58.9. A crystal of **4·NC$_8$H$_{11}$**(2.5NC_8H_{11}) suitable for X-ray diffraction analysis was grown at −35 °C from a concentrated mixture in pentane/2,6-dimethylaniline (ca. 4:1) of the orange-brown solid isolated as above.

Synthesis of 4·PPh$_3$. To a glass vial containing a magnetically stirred solution of **3** (0.072 g, 0.14 mmol) in benzene (5 mL) was added PPh_3 (0.037 g, 0.14 mmol) all at once. An immediate lightening of the solution from dark red to a lighter red was observed upon the addition of PPh_3. The vial was sealed with a PTFE-lined cap, and the solution was stirred for 15 min, after which time the solution was red-orange in color. ^{31}P NMR data collected on an aliquot of this solution indicated quantitative conversion to **4·PPh$_3$**. The solvent and other volatile materials were removed *in vacuo*, affording an oily orange-yellow solid. The residue was triturated with pentane (2 × 3 mL), and the pentane was removed *in vacuo* to yield **4·PPh$_3$** as an analytically pure, bright orange-yellow powder (0.11 g, 0.14 mmol, 96%). Anal. calcd for $C_{45}H_{53}P_2NRu$: C 70.09; H 6.93; N 1.82. Found: C 69.98; H 6.87; N 1.73.^{1}H NMR (C_6D_6): δ 11.13 (s, 1H, Ru=CH), 7.84 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4−H or C7−H), 7.67 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C7−H or C4−H), 7.56−7.40 (br. m, 3H, P-aryl Hs), 7.29 (m, 1H, C5−H or C6−H), 7.24 (m, 1H, C6−H or C5−H), 7.08−6.92 (br. m, 6H, P-aryl Hs), 6.71−6.60 (br. m, 3H, P-aryl Hs), 6.43−6.32 (br. m, 3H, P-aryl Hs), 5.71 (d, J = 3.5 Hz, 1H, C1−H), 3.54 (m, 1H, P(C*H*Me$_a$Me$_b$)), 3.38 (s, 3H, NMe), 1.84 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.41 (s, 15H, C$_5$Me$_5$), 1.16−1.08 (m, 6H, P(CH*Me$_a$*Me$_b$) and P(CH*Me$_c$*Me$_d$)), 0.93 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHMe$_a$*Me$_b$*)),

0.66 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)); ^{13}C{^{1}H} (C_6D_6): δ 227.1 (apparent t, J = 18.6 Hz, Ru=C), 143.3 (d, $^2J_{PC}$ = 14.8 Hz, C2), 132.8 (d, J_{PC} = 10.2 Hz, C3a or C7a), 132.1 (C7a or C3a), 128.6−127.8 (br. m, P-aryl CHs), 120.2 (C4 or C7), 119.2 (C7 or C4), 117.6 (C5 or C6), 115.4 (C6 or C5), 97.1 (*C*$_5$Me$_5$), 94.9 (d, $^3J_{PC}$ = 6.4 Hz, C1), 72.5 (d, $^1J_{PC}$ = 60.3 Hz, C3), 53.6 (NMe), 33.3 (d, $^1J_{PC}$ = 25.2 Hz, P(*C*HMe$_c$Me$_d$)), 25.6 (d, $^1J_{PC}$ = 30.7 Hz, P(*C*HMe$_a$Me$_b$)), 20.7 (P(CHMe$_a$*Me$_b$*)), 19.7−19.4 (m, P(CH*Me$_a$*Me$_b$) and P(CH*Me$_c$*Me$_d$)), 18.5 (P(CHMe$_c$*Me$_d$*)), 10.8 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (C_6D_6): δ 55.6 (d, $^2J_{PP}$ = 28.3 Hz), 51.2 (d, $^2J_{PP}$ = 28.3 Hz). Slow evaporation of a C_6H_6 solution of **4·PPh$_3$** produced a crystal of **4·PPh$_3$**(C_6H_6) suitable for single-crystal X-ray diffraction analysis.

Synthesis of 4·PHPh$_2$. To a glass vial containing a magnetically stirred solution of **3** (0.093 g, 0.18 mmol) in benzene (6 mL) was added $PHPh_2$ (0.032 mL, 0.18 mmol) via Eppendorf micropipette. An immediate lightening of the solution from dark red to a lighter red was observed upon the addition of $PHPh_2$. The vial was sealed with a PTFE-lined cap, and the solution was stirred for 48 h, after which time the solution was orange in color. ^{31}P NMR data collected on an aliquot of this solution indicated quantitative conversion to **4·PHPh$_2$**. The solvent and other volatile materials were removed *in vacuo*, affording an oily yellow solid. The residue was triturated with pentane (2 × 3 mL), and the pentane was removed *in vacuo* to yield **4·PHPh$_2$** as an analytically pure, bright yellow powder (0.12 g, 0.17 mmol, 94%). Anal. calcd for $C_{39}H_{49}P_2NRu$: C 67.40; H 7.11; N 2.02. Found: C 67.30; H 7.16; N 2.13. ^{1}H NMR (C_6D_6): δ 10.21 (s, 1H, Ru=CH), 8.08 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4−H or C7−H), 7.91 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7−H or C4−H), 7.40 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C5−H or C6−H), 7.32 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C6−H or C5−H), 7.24−6.87 (m, 10H, P-aryl Hs), 6.85 (d of d, $^1J_{PH}$ = 380.0 Hz, $^3J_{PH}$ = 13.0 Hz, 1H, P−H), 6.35 (d, J = 3.5 Hz, 1H, C1−H), 3.65 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.94 (s, 3H, NMe), 1.77 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.56 (s, 15H, C$_5$Me$_5$), 1.33 (d of d, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.18 (d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.07 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.80 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)); ^{13}C{^{1}H} (C_6D_6): δ 229.5 (apparent t, J = 16.7 Hz, Ru=C), 142.6 (d, $^2J_{PC}$ = 14.1 Hz, C2), 142.2 (C3a or C7a), 138.9 (d, $^1J_{PC}$ = 52.7 Hz, P-aryl C), 134.3 (d, J_{PC} = 10.4 Hz, P-aryl CHs), 133.6 (m, C7a or C3a), 129.4 (P-aryl CH), 128.8 (P-aryl CH), 127.5 (d, J_{PC} = 9.4 Hz, P-aryl CHs), 120.6 (C4 or C7), 119.3 (C7 or C4), 118.1 (C5 or C6), 115.9 (C6 or C5), 96.2 (*C*$_5$Me$_5$), 95.0 (d, $^3J_{PC}$ = 6.5 Hz, C1), 72.5 (d, $^1J_{PC}$ = 64.8 Hz, C3), 52.5 (NMe), 31.3 (d, $^1J_{PC}$ = 24.8 Hz, P(*C*HMe$_c$Me$_d$)), 25.5 (d, $^1J_{PC}$ = 31.3 Hz, P(*C*HMe$_a$Me$_b$)), 19.9 (P(CH*Me$_a$*Me$_b$)), 18.8−18.6 (m, P(CHMe$_a$*Me$_b$*) and P(CH*Me$_c$*Me$_d$)), 18.4 (d, $^2J_{PC}$ = 3.4 Hz, P(CHMe$_c$*Me$_d$*)), 10.7 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (C_6D_6): δ 57.2 (d, $^2J_{PP}$ = 34.4 Hz), 33.6 (d, $^2J_{PP}$ = 34.4 Hz).

Reaction of 3 with H$_2$. A protocol analogous to that described for the synthesis of **4·CO** was employed, using H_2 in place of CO. Introduction of an atmosphere of H_2 to **3** caused the solution to lighten gradually in color from dark red to bright orange over the course of several minutes. After 10 min, ^{31}P and ^{1}H NMR data collected on this reaction mixture indicated the quantitative conversion of **3** into **1**.

Reaction of 3 with ^{i}PrOH. In a glass vial, a solution of **3** (0.023 g, 0.045 mmol) in C_6D_6 (ca. 1 mL) was treated with ^{i}PrOH (0.10 mL, 1.3 mmol, ca. 29 equiv), which resulted in a lightening of the solution from dark red to red-orange. The solution was then transferred to an NMR tube and reaction progress was observed by use of ^{31}P and ^{1}H NMR methods. After 30 min, quantitative conversion to the previously characterized[6d] Ru hydridocarbene allylic isomer of **1** (i.e., **1b**) was noted. After 1.5 h, partial conversion of **1b** to **1** was observed, with full isomerization to **1** noted after 24 h.

Formation of 5 and Synthesis of 7. To a glass vial containing a magnetically stirred solution of **3** (0.084 g, 0.17 mmol) in C_6H_6 (8 mL), was added solid Ph_3SiH (0.043 g, 0.17 mmol). The vial was sealed with a PTFE-lined cap and the solution was stirred magnetically for three weeks, during which time the progress of the reaction was monitored by use of NMR methods; a slight lightening of the solution was observed over this time period. After a total of 45 min, ^{31}P NMR revealed the presence of ca. 1:1 ratio of **3** and a new species **5** (54.1 ppm). Diagnostic ^{1}H NMR data for **5** (C_6D_6): 10.30 (s, 1H, Ru=CH), 5.72 (d, J = 4.1 Hz, 1H, C1−H), −9.21 (d, $^2J_{PH}$ = 24.3 Hz, 1H, Ru−H). After a total of 24 h, ^{31}P NMR revealed the presence of **3**, **5**, and **7** in ca. 2:2:1 ratio. A total reaction time of three weeks was required in order to achieve quantitative conversion to **7**, at which time the solvent and other volatile materials were removed *in vacuo*, yielding an oily yellow solid. The solid was triturated with pentane (2 × 1.5 mL) and dried *in vacuo* to yield **7** as an analytically pure, yellow powder (0.12 g, 0.15 mmol, 93%). Anal. calcd for $C_{45}H_{54}PNSiRu$: C 70.27; H 7.08; N 1.82. Found: C 70.33; H 7.01; N 1.84. ^{1}H NMR (C_6D_6): δ 12.40 (s, 1H, Ru=CH), 7.59−7.56 (m, 6H, Si-aryl Hs), 7.34−7.12 (m, 11H, 9 Si-aryl Hs and C4−H and C7−H), 7.09 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 6.91 (t, $^3J_{HH}$ = 6.5 Hz, 1H, C6−H or C5−H), 5.83 (d, J = 1.5 Hz, 1H, C3−H), 3.62 (d, $^2J_{PH}$ = 15.5 Hz, 1H, C1−H), 3.37 (s, 3H, NMe), 2.90 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.59−1.56 (m, 16H, C$_5$Me$_5$ and P(C*H*Me$_c$Me$_d$)), 1.31 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.96 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.79 (d of d, $^3J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.37 (d of d, $^3J_{PH}$ = 9.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)); ^{13}C{^{1}H} (C_6D_6): δ 249.7 (d, $^2J_{PC}$ = 20.1 Hz, Ru=C), 153.3 (C2), 142.6 (C3a or C7a), 139.7 (d, J_{PC} = 9.2 Hz, C7a or C3a), 136.2 (Si-aryl CHs), 133.7 (Si-aryl C), 130.0 (Si-aryl CHs), 128.4 (Si-aryl CHs), 126.3 (C4 or C7), 123.9 (C7 or C4), 123.3 (C5 or C6), 120.2 (C6 or C5), 108.6 (C3), 97.5 (*C*$_5$Me$_5$), 50.1 (NMe), 44.8 (d, $^1J_{PC}$ = 8.7 Hz, C1), 28.6 (d, $^1J_{PC}$ = 20.6 Hz, P(*C*HMe$_c$Me$_d$)), 26.7 (d, $^1J_{PC}$ = 22.3 Hz, P(*C*HMe$_a$Me$_b$)), 20.0 (d, $^2J_{PC}$ = 3.6 Hz, P(CH*Me$_a$*Me$_b$)), 19.3−19.2 (m, P(CH*Me$_c$Me$_d$*)), 17.6 (d, $^2J_{PC}$ = 7.9 Hz, P(CHMe$_a$*Me$_b$*)), 10.9 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (C_6D_6): δ 86.5; ^{29}Si{^{1}H} NMR (C_6D_6): δ 30.6 (^{1}H−^{29}Si HMBC).

Formation of 6 and Synthesis of 8. To a glass vial containing a magnetically stirred solution of **3** (0.092 g, 0.18 mmol) in benzene (6 mL), was added Ph_2SiH_2 (0.036 mL, 0.18 mmol) via Eppendorf micropipette. The vial was sealed with a PTFE-lined cap and the solution was stirred magnetically for 24 h, during which time the progress of the reaction was monitored by use of NMR methods. After 5 min, ^{31}P NMR revealed the conversion of **3** to a mixture of **6** (54.8 ppm) and **8** (ca. 10:1). Diagnostic ^{1}H NMR data for **6** (C_6D_6): 9.68 (s, 1H, Ru=CH), 5.96 (d, J = 3.7 Hz, 1H, C1−H), 5.10 (s, 1H, Si−H), −9.90 (d, $^2J_{PH}$ = 25.2 Hz, 1H, Ru−H). A total reaction time of 24 h was required in order to achieve quantitative conversion to **8**, after which time the solvent and other volatile materials were removed *in vacuo*, yielding an oily yellow solid. The solid was triturated with pentane (2 × 1.5 mL) and the product was dried *in vacuo* to afford **8** as an analytically pure, yellow powder (0.11 g, 0.16 mmol, 91%). Anal. calcd for $C_{39}H_{50}PNSiRu$: C 67.59; H 7.28; N 2.02. Found: C 67.30; H 7.30; N 2.04. ^{1}H NMR (C_6D_6): δ 7.80 (d, $^3J_{HH}$ = 7.0 Hz, 2H, Si-aryl Hs), 7.47 (d, $^3J_{HH}$ = 7.0 Hz, 2H, Si-aryl Hs), 7.28−7.04 (m, 8H, 6 Si-aryl Hs and 2 aryl Hs), 6.74 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 6.51 (d,^{3} J_{HH} = 7.5 Hz, 1H, C4−H or C7−H), 5.34 (s, 1H, C3−H), 3.76 (d, J = 6.5 Hz, 1H, Ru−C(H_a)(H$_b$)-N), 3.43 (d, J = 7.0 Hz, 1H, Ru−C(H$_a$)(H_b)-N), 2.64 (s, 3H, NMe), 2.36−2.29 (m, 2H, P(C*H*Me$_a$Me$_b$) and P(C*H*Me$_c$Me$_d$)), 1.72 (s, 15H, C$_5$Me$_5$), 1.17 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.94 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.81−0.77 (m, 6H, P(CHMe$_a$*Me$_b$*) and P(CHMe$_c$*Me$_d$*)), −9.40 (d, $^2J_{PH}$ = 22.5 Hz, 1H, Ru−H); ^{13}C{^{1}H} (C_6D_6): δ 164.2 (d, $^2J_{PC}$ =

2.9 Hz, C2), 147.1 (d, J_{PC} = 2.4 Hz, C3a or C7a), 144.1 (d, $^3J_{PC}$ = 8.2 Hz, Si-aryl C), 142.3 (d, $^3J_{PC}$ = 2.3 Hz, Si-aryl C), 137.2 (Si-aryl CHs), 137.1 (d, J_{PC} = 7.3 Hz, C7a or C3a), 133.9 (Si-aryl CHs), 128.4 (Si-aryl CHs), 127.3 (Si-aryl CH), 127.2 (Si-aryl CH), 127.0 (Si-aryl CH), 126.5 (C5 or C6), 126.2 (C4 or C7), 118.0 (C6 or C5), 116.6 (C7 or C4), 94.5 (C_5Me_5), 92.6 (C3), 63.7 (d, $^1J_{PC}$ = 6.2 Hz, C1), 43.6 (d, $^2J_{PC}$ = 13.0 Hz, Ru-CH_2−N), 42.5 (NMe), 29.5 (d, $^1J_{PC}$ = 6.0 Hz, P(*C*HMe$_c$Me$_d$)), 28.8 (d, $^1J_{PC}$ = 22.6 Hz, P(*C*HMe$_a$Me$_b$)), 22.9 (d, $^2J_{PC}$ = 5.5 Hz, P(CHMe$_c$*Me$_d$*)), 19.8 (P(CHMe$_a$*Me$_b$*)), 19.4 (m, P(CH*Me$_c$*Me$_d$)), 18.9 (m, P(CH-*Me$_a$*Me$_b$)), 10.7 (C_5*Me$_5$*); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.1; $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 9.8 ($^1H-^{29}Si$ HMBC, $^2J_{SiH}$ = 21.0 Hz (^1H-coupled $^1H-^{29}Si$ HMQC). A crystal of **8** suitable for X-ray diffraction analysis was grown from a concentrated pentane solution at −35 °C.

Isomerization of 8 to 9. After extended time periods in solution (0.016 g, 0.8 mL C_6D_6), **8** was observed by use of ^{31}P NMR to convert partially to a new phosphorus-containing species, **9** (the $SiPh_2H$ analogue of **7**). After one week, the **8**:**9** ratio was ca. 10:1. Periodic monitoring of the solution by ^{31}P NMR revealed a ratio of **8**:**9** of 1:8 after 5 months. Continued observation found little change in this ratio up to 8 months. In an effort to accelerate the transformation of **8** to **9**, a solution of **8** (0.018 g, 0.8 mL C_6D_6) was heated at 60 °C. However, **9** was observed to decompose to a variety of phosphorus-containing species under these conditions within 48 h. Data for **9**: ^1H NMR (C_6D_6): δ 11.66 (s, 1H, Ru=CH), 7.89−7.86 (m, 2H, Si-aryl Hs), 7.50−7.47 (m, 2H, Si-aryl Hs), 7.40 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4−H or C7−H), 7.32−7.08 (m, 9H, 3 aryl Hs and 6 Si-aryl Hs), 5.91 (d, J = 1.0 Hz, 1H, C3−H), 5.75 (d, J = 4.5 Hz, 1H, Si−H), 5.49 (d, $^2J_{PH}$ = 14.5 Hz, 1H, C1−H), 3.08−3.01 (m, 4H, NMe and P(*C*HMe$_a$Me$_b$)), 1.69 (s, 15H, C_5Me_5), 1.51 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.36 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.91 (d of d, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.81 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.48 (d of d, $^3J_{PH}$ = 10.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)); $^{13}C\{^1H\}$ (C_6D_6): δ 250.8 (d, J_{PC} = 17.2 Hz, Ru=C), 153.0 (C2), 149.8 (Si-aryl C), 145.7 (Si-aryl C), 143.2 (C3a or C7a), 140.2 (d, J_{PC} = 8.4 Hz, C7a or C3a), 137.6 (Si-aryl CHs), 135.7 (Si-aryl CHs), 127.1 (Si-aryl CH or aryl CH), 126.9 (Si-aryl CH or aryl CH), 126.8 (Si-aryl CH or aryl CH), 126.7 (Si-aryl CH or aryl CH), 126.5 (Si-aryl CH or aryl CH), 124.7 (C4 or C7), 123.3 (Si-aryl CH or aryl CH), 120.4 (Si-aryl CH or aryl CH), 109.0 (C3), 96.7 (C_5Me_5), 49.8 (NMe), 44.3 (d, $^1J_{PC}$ = 9.7 Hz, C1), 29.2 (d, $^1J_{PC}$ = 18.9 Hz, P(*C*HMe$_c$Me$_d$)), 27.0 (d, $^1J_{PC}$ = 23.5 Hz, P(*C*HMe$_a$Me$_b$)), 19.4 (m, P(CH*Me$_a$*Me$_b$)), 19.2 (d, $^2J_{PC}$ = 3.3 Hz, P(CHMe$_a$*Me$_b$*)), 19.0 (d, $^2J_{PC}$ = 6.9 Hz, P(CHMe$_c$*Me$_d$*)), 17.7 (d, $^2J_{PC}$ = 7.3 Hz, P(CH*Me$_c$*Me$_d$)), 10.9 (C_5*Me$_5$*); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 91.2; $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 26.6, $^1J_{SiH}$ = 157.8 Hz (^1H-coupled $^1H-^{29}Si$ HMQC).

Formation of 10. To a glass vial containing a solution of **3** (0.10 g, 0.20 mmol) in benzene (7 mL) was added $PhNH_2$ (0.019 mL, 0.20 mmol) via Eppendorf micropipette. The addition caused an immediate color change from dark red to dark orange. After 10 min, ^{31}P NMR data collected on an aliquot of this solution indicated the clean conversion to two phosphorus-containing products exhibiting resonances at 64.0 ppm (tentatively assigned as **4·NH$_2$Ph** by comparison of ^1H NMR data to that of **4·NH$_3$** and **4·NC$_5$H$_{11}$**) and 76.2 ppm (**10**) (ca. 4:1 ratio); after 2 h, the ratio of **4·NH$_2$Ph**:**10** was ca. 2:1. After 72 h, ^{31}P NMR analysis revealed the presence of **10** and an as-yet-unidentified species (br. m, 62.1 ppm) in a ratio of ca. 10:1. Efforts to obtain **10** in analytically pure form have thus far proven unsuccessful. Data for **10**: ^1H NMR (C_6D_6): δ 12.88 (d of d, $^4J_{HH}$ = 15.5 Hz, $^3J_{PH}$ = 2.0 Hz, 1H, Ru=CH), 9.71 (d, $^4J_{HH}$ = 15.5 Hz, 1H, N−H), 7.27 (m, 1H, N-aryl H), 7.19 (m, 1H, N-aryl H), 7.07 (m, 1H, aryl H), 6.88−6.83 (m, 3H, aryl Hs), 6.82−6.78 (m, 2H, N-aryl Hs), 6.73 (m, 1H, N-aryl H), 3.39−3.25 (AB m, 2H, C(*H$_a$*)(*H$_b$*)), 2.90 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.69 (s, 3H, NMe), 1.96 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.71 (s, 15H, C_5Me_5), 1.34 (d of d, $^3J_{PH}$ = 10.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.18 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)), 0.94 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.81 (d of d, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)); $^{13}C\{^1H\}$ (C_6D_6): δ 235.3 (d, $^2J_{PC}$ = 13.3 Hz, Ru=C), 184.3 (d, $^2J_{PC}$ = 26.2 Hz, C2), 149.7 (N-aryl C), 142.1 (C3a or C7a), 139.4 (d, J = 8.2 Hz, C7a or C3a), 130.0 (2 aryl CHs), 127.5 (N-aryl CH), 123.8 (N-aryl CH), 123.3 (N-aryl CH), 117.0 (aryl CH), 115.8 (2 N-aryl CHs), 115.0 (aryl CH), 94.6 (C_5Me_5), 88.4 (d, $^1J_{PC}$ = 43.8 Hz, C3), 45.3 (NMe), 35.2 (d, $^3J_{PC}$ = 10.8 Hz, C1), 29.4 (d, $^1J_{PC}$ = 17.2 Hz, P(*C*HMe$_c$Me$_d$)), 24.3 (d, $^1J_{PC}$ = 34.3 Hz, P(*C*HMe$_a$Me$_b$)), 20.2 (P(CH*Me$_a$*Me$_b$)), 19.7 (d, $^2J_{PC}$ = 7.2 Hz, P(CH*Me$_c$*Me$_d$)), 19.4−19.2 (m, P(CHMe$_a$*Me$_b$*) and P(CHMe$_c$*Me$_d$*)), 11.1 (C_5*Me$_5$*); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 76.2.

Synthesis of 11. To a glass vial containing a solution of **3** (0.10 g, 0.20 mmol) in benzene (7 mL) was added pyrrole (0.016 mL, 0.23 mmol) via Eppendorf micropipette. The addition caused an immediate color change from dark red to a lighter red-orange. After 10 min, analysis of ^{31}P NMR data collected on an aliquot of this solution indicated quantitative conversion to **11**. The mixture was then dried *in vacuo*, followed by trituration with pentane (1.5 mL). After removal of volatile materials *in vacuo*, **11** was isolated as an analytically pure, reddish-brown powder (0.11 g, 0.19 mmol, 95%). Anal. calcd for $C_{31}H_{43}PN_2Ru$: C 64.65; H 7.53; N 4.87. Found: C 64.51; H 7.35; N 4.72. ^1H NMR (C_6D_6): δ 12.49 (s, 1H, Ru=CH), 7.28 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4−H or C7−H), 7.23 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C7−H or C4−H), 7.17 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 7.01 (apparent d of t, J = 7.5 Hz, J = 1.0 Hz, 1H, C6−H or C5−H), 6.85 (br. m, 1H, pyrrole-H), 6.68−6.53 (br. m, 2H, pyrrole-Hs), 6.11 (br. m, 1H, pyrrole-H), 5.94 (d, J = 1.5 Hz, 1H, C3−H), 5.09 (d, $^2J_{PH}$ = 14.5 Hz, 1H, C1−H), 3.09 (s, 3H, NMe), 2.97 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.64 (d, J = 1.0 Hz, 15H, C_5Me_5), 1.48 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.17 (m, 1H, P(C*H*Me$_c$Me$_d$)), 0.94 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.50 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.31 (d of d, $^3J_{PH}$ = 10.5 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHMe$_c$*Me$_d$*)); $^{13}C\{^1H\}$ (C_6D_6): δ 247.4 (d, $^2J_{PC}$ = 20.1 Hz, Ru=C), 151.7 (C2), 143.5 (C3a or C7a), 140.5 (d, J_{PC} = 8.8 Hz, C7a or C3a), 126.7 (C5 or C6), 124.6 (C4 or C7), 123.5 (C6 or C5), 120.7 (C7 or C4), 109.6 (C3), 108.3−108.0 (br. m, pyrrole-CHs), 97.2 (C_5Me_5), 49.7 (NMe), 45.0 (d, $^1J_{PC}$ = 7.3 Hz, C1), 27.5 (d, $^1J_{PC}$ = 23.3 Hz, P(*C*HMe$_c$Me$_d$)), 26.2 (d, $^1J_{PC}$ = 17.2 Hz, P(*C*HMe$_a$Me$_b$)), 21.6 (d, $^2J_{PC}$ = 4.4 Hz, P(CH*Me$_a$*Me$_b$)), 19.1 (P(CH*Me$_c$*Me$_d$)), 18.2 (d, $^2J_{PC}$ = 4.9 Hz, P(CHMe$_a$*Me$_b$*)), 17.1 (d, $^2J_{PC}$ = 5.5 Hz, P(CHMe$_c$*Me$_d$*)), 10.5 (C_5*Me$_5$*); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 89.0. Upon dissolution of **11** (0.022 g) in C_6D_6 (0.8 mL), partial isomerization to the corresponding vinylic isomer **11b** (analogous to **10**), as well as dissociation to give **3**, was noticed over the course of 24 h (ratio of **11**:**11b**:**3**, ca. 21:11:1 ^{31}P NMR). Selected NMR data for **11b**: ^1H NMR (C_6D_6): δ 12.80 (d, J = 2.0 Hz, 1H, Ru=CH), 6.54 (apparent t, J = 2.0 Hz, 2H, pyrrole-Hs), 6.36 (apparent t, J = 2.0 Hz, 2H, pyrrole-Hs), 3.02 (s, 3H, NMe), 2.96−2.92 (m, 2H, C(*H$_a$*)(*H$_b$*)), 1.61 (d, J = 1.0 Hz, 15H, C_5Me_5), 1.19 (d of d, $^3J_{PH}$ = 19.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*Me)), 1.05 (d of d, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*Me)), 0.85 (d of d, $^3J_{PH}$ = 13.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*Me)), 0.65 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*Me)); $^{13}C\{^1H\}$ (C_6D_6): δ 249.1 (d, $^2J_{PC}$ = 20.8 Hz, Ru=C), 133.2 (2 pyrrole-CHs), 107.3 (2 pyrrole-CHs), 99.2 (C_5Me_5), 49.9 (NMe), 40.7 (C1), 31.6 (d, $^1J_{PC}$ = 24.9 Hz, P(*C*HMeMe)), 24.0 (d, $^1J_{PC}$ = 25.2 Hz, P(*C*HMeMe)), 19.3 (d, $^2J_{PC}$ = 6.2 Hz, P(CH*Me*Me)), 18.5 (d, $^2J_{PC}$ = 10.7 Hz, P(CH*Me*Me)), 10.6 (C_5*Me$_5$*); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.6.

Synthesis of 12. Within a glovebox, a Schlenk flask was charged with **4·PHPh$_2$** (0.10 g, 0.14 mmol), a magnetic stirbar, and benzene (6 mL). After sealing the reaction flask, it was

removed from the glovebox, connected to a Schlenk line, and heated at 50 °C under the influence of magnetic stirring for 7 days. Analysis of ^{31}P NMR data collected on an aliquot of this solution indicated quantitative conversion to **12**. The solvent and other volatile materials were removed *in vacuo*, affording an oily yellow solid. The residue was triturated with pentane (2 × 3 mL), and the pentane was removed *in vacuo* to yield **12** as an analytically pure, beige powder (0.091 g, 0.13 mmol, 91%). Anal. calcd for $C_{39}H_{49}P_2NRu$: C 67.40; H 7.11; N 2.02. Found: C 67.43; H 7.23; N 1.65. ^{1}H NMR (C_6D_6): δ 10.85 (d, J = 16.0 Hz, 1H, Ru=CH), 8.09 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4−H or C7−H), 8.04 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C7−H or C4−H), 7.56−7.45 (m, 2H, P-aryl Hs), 7.38−7.28 (m, 4H, 2 P-aryl Hs and C5−H and C6−H), 7.11−7.07 (m, 4H, 3 P-aryl Hs and C1−H), 6.98−6.95 (m, 3H, P-aryl CHs), 6.69 (br. d, $^3J_{HH}$ = 15.5 Hz, 1H, N−H), 3.51 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.03 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.64 (s, 15H, C_5Me_5), 1.58−1.52 (m, 6H, NMe and P(CH*Me$_c$*Me$_d$)), 1.02 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.69 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHMe$_c$*Me$_d$*)), 0.56 (d of d, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)); ^{13}C{^{1}H} (C_6D_6): δ 240.5 (apparent t, J = 14.3 Hz, Ru=C), 142.1 (d, $^1J_{PC}$ = 43.7 Hz, P-aryl C), 141.7 (m, C3a or C7a), 135.9 (d, J_{PC} = 11.1 Hz, P-aryl CHs), 134.6 (m, C7a or C3a), 133.4 (d, J_{PC} = 10.2 Hz, P-aryl CHs), 129.1 (P-aryl CH), 128.5 (P-aryl CH), 127.5 (m, P-aryl CHs), 127.0 (d, J_{PC} = 9.3 Hz, P-aryl CHs), 122.3 (C4 or C7), 120.5 (C7 or C4), 117.9 (C5 or C6), 117.4 (C6 or C5), 106.1 (d, J_{PC} = 14.2 Hz, C1), 95.2 (C_5Me_5), 41.7 (NMe), 28.9 (d, $^1J_{PC}$ = 26.0 Hz, P(*C*HMe$_c$Me$_d$)), 25.8 (d, $^1J_{PC}$ = 33.0 Hz, P(*C*HMe$_a$Me$_b$)), 21.8 (P(CHMe$_a$*Me$_b$*)), 21.7 (d, $^2J_{PC}$ = 6.2 Hz, P(CHMe$_c$*Me$_d$*)), 19.4 (d, $^2J_{PC}$ = 6.7 Hz, P(CH*Me$_c$*-Me$_d$)), 19.1 (d, $^2J_{PC}$ = 3.8 Hz P(CH*Me$_a$*Me$_b$)), 10.0 (C_5Me_5); ^{31}P{^{1}H} NMR (C_6D_6): δ 72.6 (d, $^2J_{PP}$ = 26.3 Hz), 64.0 (d, $^2J_{PP}$ = 26.3 Hz). Slow evaporation of a C_6H_6 solution of **12** produced a crystal of **12**$(C_6H_6)_{2.5}$ suitable for single-crystal X-ray diffraction analysis.

Synthesis of 13. To a glass vial containing a magnetically stirred solution of **3** (0.10 g, 0.20 mmol) in benzene (6 mL) was added PH_2Ph (0.023 mL, 0.20 mmol) via Eppendorf micropipette. An immediate lightening of the solution from dark red to a lighter red was observed upon the addition of PH_2Ph. The vial was sealed with a PTFE-lined cap, and the solution was stirred for 15 min, after which time the solution was red-orange in color. At this stage, analysis of ^{31}P NMR data collected on an aliquot of this solution indicated the complete consumption of **3** and conversion to multiple phosphorus-containing species. After a total reaction time of 72 h, the solution was observed to be orange-yellow in color, and analysis of ^{31}P NMR data collected on an aliquot of this solution indicated quantitative conversion to **13**. The solvent and other volatile materials were removed *in vacuo*, affording an oily pale yellow solid. The residue was triturated with pentane (2 × 3 mL), and the pentane was removed *in vacuo* to yield **13** as an analytically pure, beige powder (0.11 g, 0.18 mmol, 88%). Anal. calcd for $C_{33}H_{45}P_2NRu$: C 64.04; H 7.33; N 2.26. Found: C 63.65; H 7.14; N 2.28. ^{1}H NMR (C_6D_6): δ 10.76 (d, J = 17.0 Hz, 1H, Ru=CH), 8.02 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4−H or C7−H), 7.94 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C7−H or C4−H), 7.48−7.43 (m, 2H, P-aryl Hs), 7.32 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 7.26 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C6−H or C5−H), 7.18−7.16 (m, 3H, P-aryl Hs), 6.89−6.73 (m, 3H, N−H and P−H and C1−H), 3.38 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.97 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.68 (d, 3H, J = 5.0 Hz, NMe), 1.56 (s, 15H, C_5Me_5), 1.34 (d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.98 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.82 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)), 0.76 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H P(CHMe$_a$*Me$_b$*)); ^{13}C{^{1}H} (C_6D_6): δ 241.6 (apparent t, J = 14.1 Hz, Ru=C), 141.4 (m, C3a or C7a), 135.3 (d, J = 17.6 Hz, C7a or C3a), 133.6 (d, J_{PC} = 9.4 Hz, P-aryl CHs), 132.4 (m, P-aryl C), 129.4 (P-aryl CHs), 121.9 (C4 or C7), 119.6 (C7 or C4), 117.6 (C5 or C6), 116.9 (C6 or C5), 106.4 (d, J = 13.5 Hz, C1), 94.4 (C_5Me_5), 41.0 (NMe), 30.7 (d, $^1J_{PC}$ = 25.7 Hz, P(*C*HMe$_c$Me$_d$)), 24.8 (d, $^1J_{PC}$ = 30.8 Hz, P(*C*HMe$_a$Me$_b$)), 21.1 (P(CHMe$_a$*Me$_b$*)), 18.8 (d, $^2J_{PC}$ = 6.4 Hz, P(CH*Me$_c$*Me$_d$)), 18.7−18.5 (m, P(CH*Me$_a$*Me$_b$) and P(CHMe$_c$*Me$_d$*)), 10.0 (C_5Me_5); ^{31}P{^{1}H} NMR (C_6D_6): δ 73.4 (d, $^2J_{PP}$ = 31.4 Hz), 42.9 (d, $^2J_{PP}$ = 31.4 Hz). A crystal of **13** suitable for X-ray diffraction analysis was grown from a concentrated pentane solution at −35 °C.

Crystallographic Solution and Refinement Details. Crystallographic Characterization of 3 and 4·NC$_8$H$_{11}$(2.5NC$_8$H$_{11}$). Crystallographic data were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, and data reduction (including SAINT) were supplied by Bruker. Gaussian integration was employed as the absorption correction method, and the structure was solved by use of a Patterson search/structure expansion for **3** and direct methods for **4**·NC$_8$H$_{11}$(2.5NC$_8$H$_{11}$). Refinements were carried out by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Two crystallographically independent molecules of **3** were identified in the asymmetric unit, and were refined in a satisfactory manner; only one of the two independent molecules of **3** is depicted in the text. One of the noncoordinated 2,6-dimethylaniline solvates in **4**·NC$_8$H$_{11}$(2.5NC$_8$H$_{11}$) was refined on the basis of an inversion-disorder model, employing an occupancy factor of 0.5 for the non-hydrogen atoms and a common isotropic displacement parameter for C and N; the ring carbons of this solvate were refined as an idealized hexagon with a C−C bond distance of 1.39 Å. Otherwise, anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, and all hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom.

Crystallographic Characterization of 4·DMAP, 4·PPh$_3$(C$_6$H$_6$), 8, 12(C$_6$H$_6$)$_{2.5}$, and 13. Crystallographic data were obtained at 173(±2) K on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Cell parameters were initially retrieved using the COLLECT software (Nonius), and refined with the HKL DENZO and SCALEPACK software.[27] Data reduction and absorption correction (multiscan) were also performed with the HKL DENZO and SCALEPACK software. The structures were solved by using the direct methods package in SIR-97,[28] and refined by use of the SHELXL97−2 program,[29] employing full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. For **8**, the restraints DELU, SIMU, and ISOR were used to restrain the anisotropic displacement parameters for the carbon atoms of the C_5Me_5 ligand. With the exception of the Ru−*H* in **8**, the N−*H* in **12**$(C_6H_6)_{2.5}$, and the P−*H* in **13** (the positions of which were located in the difference map and refined) all H-atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement

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parameters based on the isotropic displacement parameter of the attached atom.

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Supporting Information Available: Crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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