Exploring the reactivity of a coordinatively unsaturated Cp*Ru(κ^2-P,O) complex with small molecule substrates: application in E–H bond activation (E = H, B, and Si)†

Matthew A. Rankin,‡[a] Kevin D. Hesp,[a] Gabriele Schatte,[b] Robert McDonald[c] and Mark Stradiotto*[a]

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Treatment of $[Cp^*RuCl]_4$ with 1-diisopropylphosphino-2-indanone (**1**) afforded Cp*Ru(Cl)(κ^2-P,O-**1**) (**2**) in 96% isolated yield. Dehydrohalogenation of **2** under an atmosphere of N_2 provided the dinuclear complex **4** (78% isolated yield), which is comprised of two coordinatively unsaturated Cp*Ru(κ^2-P,O) fragments (**3**) linked by an end-on coordinated μ-N_2 ligand. Although complex **3** has not been observed directly, reactivity studies demonstrated that **4** can serve as a convenient source of **3**. Isolable adducts of **3** were prepared *via* exposure of **4** to an atmosphere of CO (93% yield, **5a**) or two equivalents of PhCN (91% yield, **5b**). Exposure of **4** to an atmosphere of H_2 afforded the adduct **3**·**(σ-H$_2$)** (**6**) quantitatively; the clean conversion of **6** back into **4** occurred upon evacuation and re-introduction of a N_2 atmosphere. Treatment of **4** with two equivalents of $PhSiH_3$ or Ph_2SiH_2 afforded products featuring $(H)_2$Ru–SiPhX–O fragments (**7a** and **7b**, respectively; both 95% isolated yield) corresponding to net double geminal Si–H bond activation of the organosilane in which the extruded silylene fragment has inserted into the Ru–O bond of the putative intermediate **3**. Similar reactivity was observed upon treatment of **4** with two equivalents of mesitylborane to give **8** (82% isolated yield). While minimal Ru–H···Si interactions were identified for **7a**,**b** in solution and the solid state, the hydride ligands in **8** were observed to bridge ruthenium and boron. Crystallographic characterization data were obtained for **2**·$0.5C_6H_6$, **4**, **7b**, and **8**.

Introduction

Coordinatively unsaturated (η^5-C_5R_5)RuL_n (η^5-C_5H_5 = Cp; η^5-C_5Me_5 = Cp*) complexes serve as a rich source of novel stoichiometric and catalytic reactivity.[1] While considerable insights have been gained through the study of both neutral Cp*RuL(X) complexes and $[Cp^*RuL_2]^+X^-$ salts, investigations probing the reactivity of coordinatively unsaturated Cp*Ru(κ^2-L,X) complexes supported by monoanionic, heterobidentate LX-type ligands are rare.[2] Nonetheless, such reactivity surveys are warranted, since studies of alternative classes of Cp*RuL_n complexes supported by new ancillary ligands continue to advance our understanding of how alterations to the ligand steric and/or electronic properties can influence the reactivity behavior of coordinatively unsaturated ruthenium species.

In building on pioneering research by the groups of Tilley,[3] Caulton,[4] and Valerga,[1c] who have established the utility of the Cp*RuPR_3(X) subset of complexes for facile E–H bond activations (E = main group element), and in light of various accounts of cooperative substrate activation across a Ru–X moiety (*e.g.* X = NR_2, OR, PR_2),[5] we identified coordinatively unsaturated Cp*Ru(κ^2-P,O) complexes supported by phosphinoenolate chelating ligands as appealing targets of inquiry. Although heterobidentate species of this type were unknown prior to this work,[6] Caulton and co-workers[4] had demonstrated that π-donation from oxygen in monodentate complexes such as Cp*Ru(P^iPr_2Ph)(OCH_2CF_3) can serve to stabilize such unsaturated species, as well as to promote metal-mediated substrate transformations. Herein we report on the reactivity of the coordinatively unsaturated Cp*Ru(κ^2-P,O) complex **3**,[7] which is apparently generated *in situ* from the isolable dinitrogen complex **3$_2$(μ-N$_2$)** (**4**). In addition to forming adducts with a range of two-electron donor ligands, complex **3** engages in E–H bond activation chemistry with Ph_2SiH_2, $PhSiH_3$, and $MesBH_2$ (Mes = 2,4,6-trimethylphenyl), affording products derived from the net insertion of silicon or boron into the Ru–O bond of **3**.

Results and discussion

In seeking to prepare a synthetic precursor to a coordinatively unsaturated Cp*Ru(κ^2-P,O) phosphinoenolate complex, ketone **1** was treated with 0.25 $[Cp^*RuCl]_4$ (Scheme 1); after 45 min, ^{31}P NMR analysis of the reaction mixture revealed the clean formation of a single phosphorus-containing product (100.5 ppm; **2**), which in turn was obtained in 96% isolated yield. Both NMR spectroscopic and X-ray crystallographic data confirmed the identity of **2** as Cp*Ru(Cl)(κ^2-P,O-1-diisopropylphosphino-2-indanone). An ORTEP[8] diagram for **2**·$0.5C_6H_6$ is provided in

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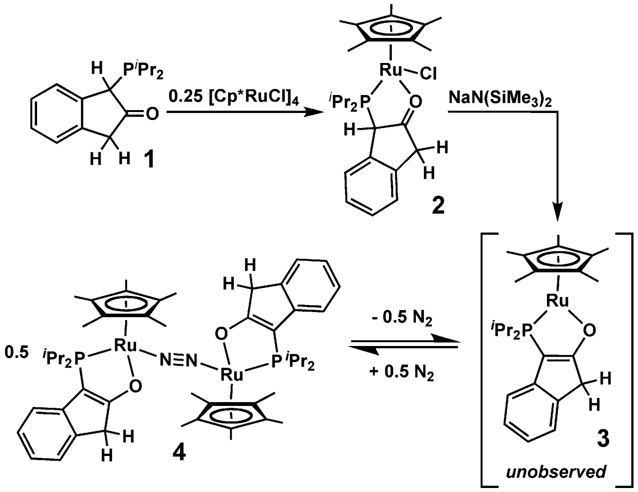
[a] Department of Chemistry, Dalhousie University, Halifax, NS B3H 4J3, Canada. E-mail: mark.stradiotto@dal.ca; Fax: +1 902 494-1310; Tel: +1 902 494-7190

[b] Saskatchewan Structural Sciences Centre, University of Saskatchewan, Saskatoon, SK S7N 5C9, Canada

[c] X-Ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

† CCDC reference numbers 654072–654074 and 719567. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b903420j

‡ Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA 02139.



Scheme 1 Synthesis of **2** and the proposed interconversion of **3** and **4**.

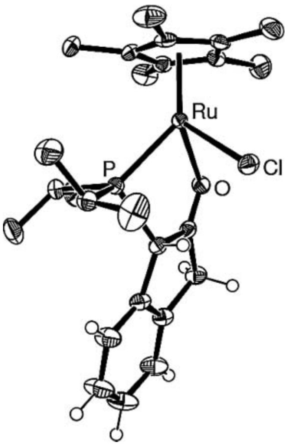


Fig. 1 ORTEP diagram for **2**·0.5C$_6$H$_6$ shown with 50% displacement ellipsoids and with selected H atoms and the benzene solvate omitted for clarity.

Fig. 1, while diffraction data and selected metrical parameters for each of the crystallographically characterized compounds reported herein are provided in Tables 1 and 2, respectively.† The structural features of **2** compare well with those of the only other crystallographically characterized Cp*RuCl(κ^2-*P*,*O*) complex to feature a phosphinoketone ligand;[9] notably, the relatively short O–C distance (1.228(3) Å) supports the description of **2** as a phosphinoketone complex, unlike the phosphinoenolate species featured herein (*vide infra*).

In an effort to effect the dehydrohalogenation of **2** as a route to the target complex **3**, a deep red solution of the former in benzene was treated with NaN(SiMe$_3$)$_2$ (Scheme 1); ^{31}P{^{1}H} NMR analysis of the resulting dark green solution revealed the quantitative conversion to a product (**4**) that exhibited a single broad resonance (50.1 ppm, $\Delta\nu_{1/2}$ = 213 Hz, 300 K). Upon work-up, **4** was isolated in 78% yield. Combustion analysis data provided preliminary evidence for the presence of a coordinated N$_2$ ligand in **4**. Such a proposal also appeared to be consistent with the observation of a distinctly different ^{31}P{^{1}H} NMR resonance (44.9 ppm, $\Delta\nu_{1/2}$ = 240 Hz, 300 K; possibly corresponding to **3** for degassed solutions of **4**, which in turn afforded the originally observed spectrum (*vide supra*) upon re-introduction of dinitrogen. The more definitive identification of **4** as a dinuclear phosphinoenolate species (*i.e.*

Table 1 Crystallographic data for **2**, **4**, **7b**, and **8**

	2	**4**	**7b**	**8**
Empirical formula	$C_{28}H_{39}ClOPRu$	$C_{50}H_{70}N_2O_2P_2Ru_2$	$C_{37}H_{47}OPRuSi$	$C_{34}H_{48}BOPRu$
Formula weight	559.08	995.16	667.88	615.57
Crystal dimensions	0.20 × 0.18 × 0.10	0.08 × 0.05 × 0.05	0.48 × 0.45 × 0.22	0.64 × 0.28 × 0.26
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/m$
a/Å	20.2188(2)	17.4049(11)	13.0305(12)	9.6050(6)
b/Å	8.5282(3)	13.5276(8)	14.5399(13)	12.3491(8)
c/Å	16.0143(3)	23.1490(19)	17.6901(16)	13.2765(9)
α/°	90	90	90	90
β/°	105.8122(10)	118.873(3)	90	96.8204(8)
γ/°	90	90	90	90
V/Å^3	2656.77(11)	4772.8(6)	3351.6(5)	1563.62(18)
Z	4	4	4	2
ρ_{calcd}/g cm^{-3}	1.398	1.385	1.324	1.307
μ/mm^{-1}	0.769	0.739	0.579	0.577
Range of transmission	0.9271–0.8614	0.9640–0.9432	0.8833–0.7687	0.8645–0.7091
2θ limit/°	55.88	43.94	55.02	54.96
	$-26 \le h \le 26$	$-17 \le h \le 18$	$-16 \le h \le 16$	$-12 \le h \le 12$
	$-10 \le k \le 11$	$-14 \le k \le 14$	$-18 \le k \le 18$	$-16 \le k \le 16$
	$-21 \le l \le 21$	$-24 \le l \le 24$	$-22 \le l \le 22$	$-17 \le l \le 17$
Total data collected	21126	16933	29235	13179
Independent reflections	6346	5742	7686	3751
R_{int}	0.0417	0.1289	0.0224	0.0151
Observed reflections	5293	3537	7361	3556
Data/restraints/parameters	6346/0/303	5742/0/541	7686/2/382	3751/0/239
Goodness-of-fit	1.076	1.023	1.098	1.140
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0324	0.0557	0.0270	0.0263
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0783	0.1136	0.0712	0.0733
Largest peak, hole/e Å^{-3}	0.809, −0.718	0.466, −0.455	0.889, −0.287	0.453, −0.585

Table 2 Selected interatomic distances (Å) for **2**, **4**, **7b**, and **8**[a]

	2	**4**[b]	**7b**[c]	**8**[d]
Ru–O	2.2204(15)	2.147(6), 2.151(6)	N/A	N/A
Ru–P	2.3421(6)	2.360(2), 2.370(3)	2.3081(5)	2.3090(7)
Ru–X	2.4508(6)	1.996(7), 1.994(7)	2.3102(6)	2.103(2)
^{i}Pr$_2$P–C	1.873(2)	1.763(8), 1.797(9)	1.820(2)	1.826(2)
O–C	1.228(3)	1.307(10), 1.291(10)	1.333(3)	1.337(2)

[a] X = Cl (**2**), N (**4**), Si (**7b**), and B (**8**); N/A = not applicable. [b] N–N = 1.131(8) Å; C1–C2 = 1.515(12) Å and 1.519(12) Å; C2–C3 = 1.385(12) Å and 1.377(13) Å; Ru–N–N = 165.5(7)° and 163.5(6)°. [c] Ru–H distances fixed at 1.55 Å during refinement; Ru–H · · · Si 2.12 Å and 2.14 Å (measured in final refined structure); Si–O = 1.7053(16) Å; C1–C2 = 1.507(3) Å; C2–C3 = 1.360(3) Å. [d] Ru–H = 1.58(2) Å; B–H = 1.51(2) Å; B–O = 1.437(3) Å; C1–C2 = 1.506(3) Å; C2–C3 = 1.363(3) Å.

3_2(μ-N$_2$)) was ultimately achieved by use of single-crystal X-ray diffraction techniques (Fig. 2). Given the stereogenic nature of the ruthenium centers in **4**, this dinuclear complex can exist in C_s- and C_2-symmetric forms. While the crystalline sample that was subjected to X-ray diffraction analysis corresponds to the C_2-symmetric isomer, the broadness observed in the NMR spectra of **4** at 300 K may be attributable in part to rapid exchange between isomeric forms of **4**. Compound **4** represents a rare example of a crystallographically characterized (η^5-C$_5$R$_5$)RuL$_n$ complex featuring a bridging dinitrogen ligand.[1c,10] The Ru–N (1.996(7) Å and 1.994(7) Å) and N–N (1.131(8) Å; *cf.* 1.0977 Å in free N$_2$[10b]) distances in **4** compare well with those of [(CpRuP$_2$)$_2$(μ-N$_2$)]$^{2+}$ dications reported by Valerga and co-workers,[11] and suggest that π-back donation from ruthenium to the coordinated dinitrogen unit is modest in **4**. By comparison, the isolable monodentate complex Cp*Ru(PCy$_3$)(OCH$_2$CF$_3$) reported by Caulton *et al.* apparently does not exhibit a propensity to coordinate dinitrogen. In contrast to the rather short Ru–O distance observed in Cp*Ru(PCy$_3$)(OCH$_2$CF$_3$) (1.992(10) Å)[4a] the longer Ru–O distances in **4** (2.147(6) Å and 2.151(6) Å) suggest that π-donation from oxygen to ruthenium is negligible in this dinuclear complex, in keeping with the adduct Cp*Ru(PCy$_3$)(OCH$_2$CF$_3$)(CO) (Ru–O 2.090(3) Å).[4a]

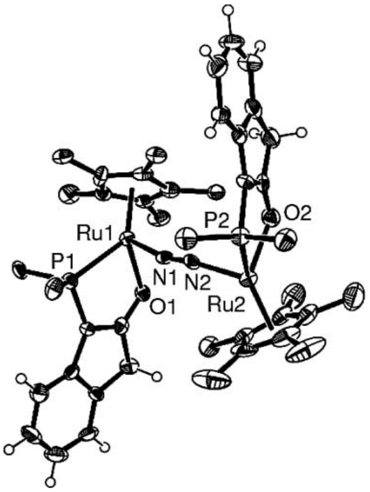
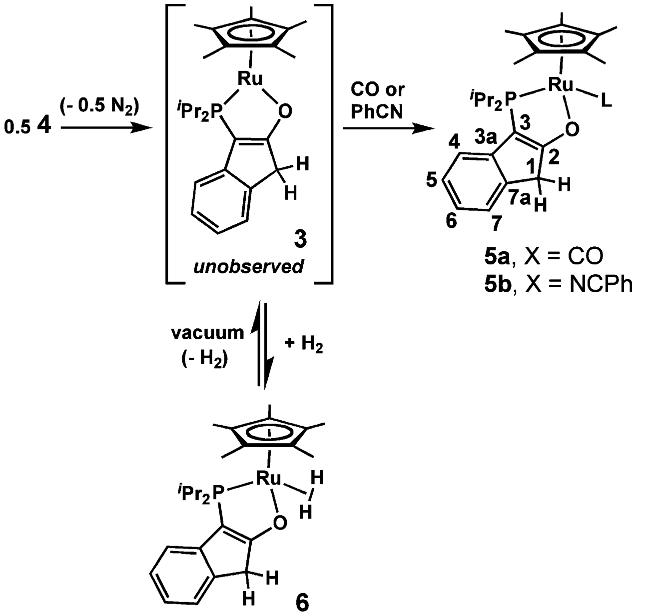


Fig. 2 ORTEP diagram for **4** shown with 50% displacement ellipsoids and with selected H atoms and the isopropyl methyl groups omitted for clarity.

For samples of **4** dissolved in toluene-d_8 that were sealed under an atmosphere of dinitrogen, the initially deep green solutions (300 K) turned to red-brown (reversibly) upon cooling below 250 K; conversely, only deep green solutions were observed over this temperature range for samples that had been thoroughly degassed. In tracking the ^{31}P{^{1}H} NMR behavior of **4** under similar conditions (223 K), a single sharp resonance (52.1 ppm, $\Delta\nu_{1/2} = 9$ Hz) was observed for samples prepared under dinitrogen (*cf.* 50.1 ppm, $\Delta\nu_{1/2} = 213$ Hz, 300 K); conversely, two equal-intensity ^{31}P{^{1}H} NMR resonances (52.0 ppm, $\Delta\nu_{1/2} = 10$ Hz; 39.1 ppm, $\Delta\nu_{1/2} = 65$ Hz) were observed for degassed samples of **4** under similar conditions. We are hesitant to provide a definitive interpretation of these temperature-dependent features. However, it is plausible that such behavior may be attributable in part to a dynamic equilibrium involving isomers of **4** and the mononuclear complexes **3** and/or **3·N$_2$**, whereby the position of this equilibrium is dependent both on temperature and on the availability of dissolved dinitrogen.[12] Additional contributions to the observed temperature-dependent NMR spectral features arising from restricted rotation about the Ru–N–N–Ru axis in **4** cannot be discounted.

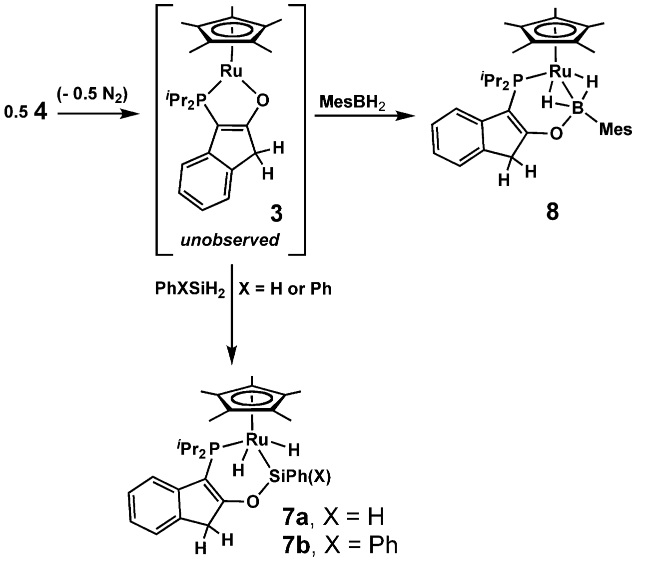
Although the target complex **3** has not been observed directly, the ability of **4** to serve as a reactive source of **3** was demonstrated upon exposure to an atmosphere of CO, or two equivalents of PhCN (Scheme 2). In both cases, the corresponding **3·L** adduct (**5a**, **L** = CO, 93%; **5b**, **L** = PhCN, 91%) was obtained and structurally characterized. The observation of nearly identical C–O stretching frequencies in the IR spectra of **5a** (*i.e.* **3·CO**; 1903 cm^{-1}) and Cp*Ru(P^{i}Pr$_2$Ph)(OCH$_2$CF$_3$)(CO) (1906 cm^{-1})[4d] suggests that the *P*,*O* ligand sets in these complexes have comparable electron-donating abilities.



Scheme 2 Reactions of putative **3** leading to the **3·L** adducts **5a**,**b** and **6** (the indenyl numbering convention is provided for **5**).

Having demonstrated that **4** can be exploited as a masked source of **3**, we sought to examine the reactivity of *in situ* generated **3** with E–H σ-bonds, beginning with H$_2$. The reactivity of coordinatively unsaturated (η^5-C$_5$R$_5$)RuL$_n$ complexes with

H_2 has been found to be highly dependent on the nature of the ancillary ligands.[13] For example, while $Cp^*RuP^iPr_3(Cl)$ and $[Cp^*Ru(\kappa^2\text{-}NMe_2CH_2CH_2NMe_2)]^+X^-$ are apparently unreactive towards H_2,[3c,14] related $[Cp^*RuP_2]^+X^-$ complexes react to give $[Cp^*RuP_2(H)_2]^+X^-$; in some cases, non-classical $[Cp^*RuP_2(\sigma\text{-}H_2)]^+X^-$ species exist in equilibrium with the dihydride product, or are detected spectroscopically at low temperatures as reactive intermediates.[1c,13] Motivated by the divergent reactivity exhibited by (η^5-C_5R_5)RuL_n species featuring either homobidentate N- or P-based ligands, we sought to probe the behavior of the hybrid “hard–soft” chelate complex **3** with H_2. Upon exposure of a degassed C_6D_6 solution of **4** to an atmosphere of H_2 at ambient temperature, the quantitative formation of a single phosphorus-containing product (**6**; δ $^{31}P = 65.2$, $\Delta\nu_{1/2} = 180$ Hz, toluene-d_8, 300 K) was observed, which also exhibited a somewhat broad ^1H NMR resonance centered at −5.73 ppm ($\Delta\nu_{1/2} = 23$ Hz, toluene-d_8, 300 K). Our assignment of **6** as a non-classical σ-H_2 adduct, rather than a dihydride complex, was made on the basis of the rather short measured $T_{1(\text{min})}$ relaxation value (17 ms, 218 K, 250 MHz) for the dihydrogen ligand in this complex.[13] While ^1H and ^{13}C NMR data collected at 300 K pointed to a C_s-symmetric structure for **6**, the ^1H NMR spectrum of **6** collected at 223 K is in keeping with a σ-H_2 adduct of **3** possessing C_1-symmetry; as was observed for solutions of **4** (*vide supra*), over this temperature range initial green solutions of **6** (300 K) are transformed reversibly into brown solutions upon cooling below 253 K. Although we are hesitant to comment definitively regarding the origins of these spectroscopic and coloration changes, such phenomena may be attributable in part to the exchange of free and bound H_2 in **6**; a process that is slowed on the ^1H NMR time scale at 223 K. By comparison, Caulton and co-workers[4c] have noted that treatment of $Cp^*Ru(P^iPr_2Ph)(OCH_2CF_3)$ with less than 2 equivalents of H_2 under similar conditions afforded the dihydride complex $Cp^*Ru(P^iPr_2Ph)(OCH_2CF_3)(H)_2$, while the addition of excess H_2 produced $HOCH_2CF_3$ and the trihydride $Cp^*Ru(P^iPr_2Ph)(H)_3$. As was observed for $Cp^*Ru(P^iPr_2Ph)(OCH_2CF_3)(H)_2$,[4c] compound **6** liberates H_2 upon exposure to vacuum; as a result, we have thus far not been successful in isolating **6** in an analytically pure form.



Scheme 3 Reactions of putative **3** with $PhXSiH_2$ and $MesBH_2$ (X = H or Ph; Mes = 2,4,6-trimethylphenyl).

The rich and diverse reactivity of coordinatively unsaturated ruthenium complexes with organosilanes is well-documented,[15] including reactions leading to isolable η^2-Si–H adducts as well as to unusual $[Cp^*(PR_3)(H)_2Ru{=}SiHR]^+X^-$ species that are generated *via* double geminal Si–H bond activation of $RSiH_3$.[3a,b] In this context, we became interested in exploring the reactivity of **3** with silanes (Scheme 3). Treatment of **4** with 2 equivalents of $PhSiH_3$ in benzene resulted in the consumption of the starting complex after 15 min, along with the formation of three phosphorus-containing products (^{31}P NMR; including **7a**). Subsequent NMR analysis of the reaction mixture after a total of 3 h revealed the quantitative formation of **7a**, which in turn was obtained in 95% isolated yield. While under similar conditions employing 2 equivalents of Ph_2SiH_2 the product **7b** was formed quantitatively after only 15 min and isolated in 95% yield, an intractable product mixture was generated under similar conditions employing Ph_3SiH. The NMR spectral data obtained for each of **7a** and **7b** was found to be consistent with the formulation of these products as arising from overall double geminal Si–H bond activation and net insertion of a silylene fragment into the Ru–O bond of putative **3**. Particularly diagnostic was the observation of two unique Ru–H signals (−11.14 and −11.92 ppm) and a Si–H resonance in the ^1H NMR spectrum of the C_1-symmetric **7a**, whereas a single resonance (−11.02 ppm) attributable to a $Ru(H)_2$ group was observed in the ^1H NMR spectrum obtained for the C_s-symmetric **7b**. In the case of **7b**, this structural proposal was confirmed by use of single-crystal X-ray diffraction techniques (Fig. 3). The crystallographically determined structure of **7b** exhibits Ru–Si (2.3102(6) Å) and Si–O (1.7053(16) Å) distances that are in keeping with those found in related complexes featuring bidentate $Ru(\kappa^2\text{-}SiPh_2OC_5H_4N)$ and $Ru(\kappa^2\text{-}SiPh_2OC(Me){=}O)$ ligands.[16] In contrast to **8** (*vide infra*), the somewhat long Ru–H···Si contacts observed in the solid state structure of **7b** (*ca.* 2.12 Å and 2.14 Å), along with the relatively low measured $^2J_{\text{SiH}}$ values (**7a**: 9.4 Hz; **7b**: 9.8 Hz),[17] appear to support the description of **7a** and **7b** as being dihydridosilyl complexes. One plausible mechanism that accounts for the formation of **7a**,**b** involves initial intermolecular Si–H oxidative addition to **3**, followed by Si–O reductive elimination[18] and finally intramolecular Si–H oxidative addition involving a tethered silyl ether fragment. However, alternative reaction

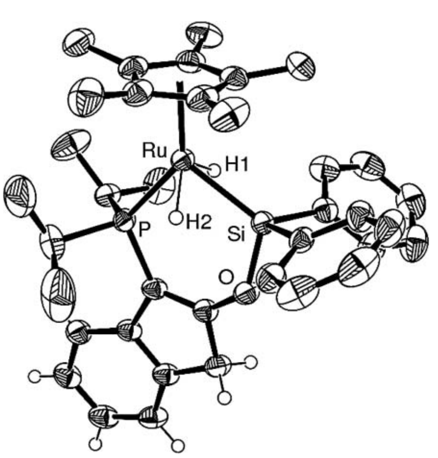


Fig. 3 ORTEP diagram for **7b** shown with 50% displacement ellipsoids and with selected H atoms omitted for clarity.

sequences including those involving Ru=SiRX (X = H, Ph) intermediates[19] cannot be ruled out. The possibility of chemical exchange involving the Ru–H and Si–H groups of **7a** was probed by use of 1D and 2D ^{1}H EXSY NMR techniques. Notably, the absence of detectable chemical exchange in this system indicates that any Si–H elimination/addition processes in **7a** must occur at rates that are slow relative to the dynamic exchange NMR time scale.

Having documented the facile net extrusion of silylene fragments leading to silicon insertion into the Ru–O bond of **3** (*vide supra*), and given the current interest in the metal-mediated activation of monoboranes,[20] we sought to extend our reactivity survey of **3** to include transformations involving mesitylborane ($MesBH_2$).[21] Treatment of a dark green solution of **4** with a stoichiometric equivalent of $MesBH_2$ resulted in an immediate color change to orange-yellow; ^{31}P NMR analysis of the reaction mixture after 30 min revealed the clean formation of **8** (Scheme 3), which in turn was isolated in 82% yield. The assignment of **8** as a C_s-symmetric dihydroborate complex arising from the net insertion of $MesBH_2$ into the Ru–O bond of putative **3** is supported by NMR spectroscopic data (*e.g.* $\delta\,^1\mathrm{H} = -13.12$, $Ru(H)_2B$; $\delta\,^{31}\mathrm{P} = 56.4$; $\delta\,^{11}\mathrm{B} = 59.0$), as well as single-crystal X-ray diffraction data (Fig. 4). Compound **8** is crystallographically mirror symmetric in the crystal. While the overall addition of $MesBH_2$ to **3** furnishes a $Ru(H)_2B$–O core in **8** that is conceptually related to the $Ru(H)_2Si$–O core in **7a**,**b**, some important structural differences were noted between **7a**,**b** and **8**. Whereas significant Ru–H···Si interactions were not detected in **7a**,**b** (*vide supra*), the notable sharpening of the hydride ^{1}H NMR resonance in **8** upon ^{11}B-decoupling suggested the presence of some form of B···H interaction in solution. Furthermore, a symmetrical Ru–H–B bridging motif is apparent in the solid state structure of **8** (Ru–H = 1.58(2) Å; B–H = 1.51(2) Å).[22]

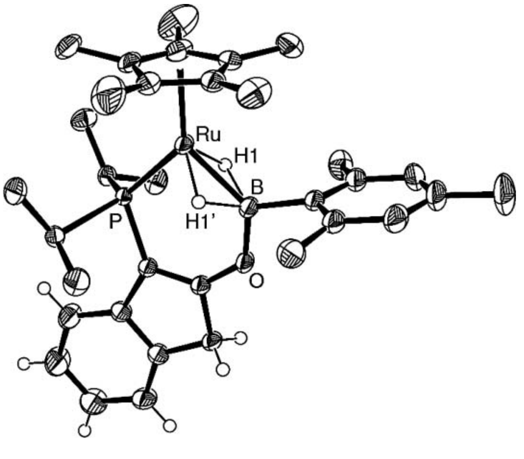


Fig. 4 ORTEP diagram for **8** (featuring one of the two disordered components of the isopropyl fragments) shown with 50% displacement ellipsoids and with selected H atoms omitted for clarity.

Summary and conclusions

In summary, we have reported herein on the reactivity of the coordinatively unsaturated Cp*Ru(κ^2-*P*,*O*) species **3**, which is conveniently generated *in situ* upon loss of N_2 from the dinuclear adduct **4**. In addition to forming adducts with a range of other two-electron donor ligands (CO, PhCN and σ-H_2), compound **3** has been observed to engage in Si–H and B–H bond activation chemistry. For reactions involving Ph_2SiH_2 and $PhSiH_3$, dihydridosilyl products (**7a**,**b**) arising from overall double geminal Si–H bond activation and net insertion of a silylene fragment into the Ru–O bond of putative **3** were obtained. While the net insertion of boron into the Ru–O bond of **3** was also observed in reactions involving $MesBH_2$, the corresponding product (**8**) is perhaps best described as featuring a tethered dihydridoborate fragment which features two symmetrical Ru–H–B bridges. Given the relative rarity of coordinatively unsaturated Cp*RuL$_n$ complexes supported by monoanionic, heterobidentate ligands, we are currently exploring further the synthesis and reactivity of structural variants of **3** and related derivatives, and will report on the results of these studies in due course.

Experimental

General considerations

Unless stated otherwise, 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 a 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 non-deuterated solvents dichloromethane, 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 was 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. Benzene-d_6 and toluene-d_8 (Cambridge Isotopes) were degassed by using three repeated freeze–pump–thaw cycles and then dried over 4 Å molecular sieves for 24 h prior to use. All solvents used within the glovebox were stored over activated 4 Å molecular sieves. Each of $[Cp^*RuCl]_4$,[23] 1-diisopropylphosphino-2-indanone **1**,[24] and mesitylborane[25] were prepared using literature procedures, and were dried *in vacuo* for 24 h prior to use. $NaN(SiMe_3)_2$ (Aldrich) was dried *in vacuo* for 24 h prior to use. Hydrogen (99.999%, UHP Grade) and carbon monoxide gases (99.5%, chemically pure grade) were obtained from Air Liquide and were used as received. Whereas PhCN (Aldrich) was degassed by sparging with dinitrogen gas, $PhSiH_3$ (Strem) was degassed by using three repeated freeze–pump–thaw cycles, and Ph_2SiH_2 (Gelest, shipped under argon) was not degassed; each of these reagents was dried over 4 Å molecular sieves for 24 h prior to use. Variable-temperature NMR experiments were conducted on a Bruker AC-250 spectrometer. Unless otherwise stated, ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, 99.4 and 202.5 MHz (respectively) 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. ^{29}Si NMR chemical shift assignments are given on the basis of data obtained from ^1H–^{29}Si HMQC (^1H-coupled experiments were employed in the determination of $^1J_{SiH}$ values) as well as ^1H–Si HMBC (*J*-HMBC experiments were employed in the determination of $^nJ_{SiH}$ values for $n > 1$) experiments. IR data were collected on a Bruker VECTOR 22 FT-IR instrument. Raman data were collected on powdered samples (sealed in glass capillaries under dry dinitrogen) using a Bruker RFS 100 FT-Raman spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada.

Synthesis of 2

To a glass vial containing a magnetically stirred suspension of $[Cp^*RuCl]_4$ (0.72 g, 0.66 mmol) in CH_2Cl_2 (4 mL) was added a solution of **1** (0.66 g, 2.66 mmol) in CH_2Cl_2 (4 mL) all at once *via* a Pasteur pipette. The addition caused an immediate color change of the suspension from dark brown to dark red. The vial was then sealed with a PTFE-lined cap and the solution was stirred magnetically for 45 min. ^{31}P NMR data collected on an aliquot of this solution indicated the quantitative formation of the target complex. The CH_2Cl_2 solvent was then removed *in vacuo*, yielding an oily dark red solid. The solid was then triturated with pentane (1.5 mL) and the pentane was removed *in vacuo.* The residue was then washed with pentane (2 × 3 mL) and dried *in vacuo* to yield **2** as an analytically pure orange-pink powder (1.32 g, 2.55 mmol, 96%). Anal. Calcd. for $C_{25}H_{36}POClRu$: C 57.74; H 6.98; N 0.00. Found: C 57.93; H 6.68; N < 0.3. ^1H NMR (C_6D_6): δ 7.03–6.91 (m, 3H, aryl-Hs), 6.62 (d, $^3J_{HH} = 7.0$ Hz, 1H, C4–H or C7–H), 5.27 (d, $^2J_{PH} = 12.0$ Hz, 1H, $^iPr_2PC$–H), 2.85 (m, 1H, $C(H_a)(H_b)$), 2.64 (m, 1H, $C(H_a)(H_b)$), 2.57 (m, 1H, $P(CHMe_aMe_b)$), 1.96 (m, 1H, $P(CHMe_cMe_d)$), 1.77 (d, $J = 1.5$ Hz, 15H, C_5Me_5), 1.69 (dd, $^3J_{PH} = 13.0$ Hz, $^3J_{HH} = 7.5$ Hz, 3H, $P(CHMe_aMe_b)$), 1.32 (dd, $^3J_{PH} = 17.5$ Hz, $^3J_{HH} = 7.0$ Hz, 3H, $P(CHMe_aMe_b)$), 0.86 (dd, $^3J_{PH} = 14.0$ Hz, $^3J_{HH} = 7.0$ Hz, 3H, $P(CHMe_cMe_d)$), 0.58 (dd, $^3J_{PH} = 12.0$ Hz, $^3J_{HH} = 7.0$ Hz, 3H $P(CHMe_cMe_d)$); $^{13}C\{^1H\}$ (C_6D_6): δ 226.2 (m, C2), 138.5 (d, $J = 8.1$ Hz, C3a or C7a), 137.8 (d, $J = 3.3$ Hz, C7a or C3a), 127.3 (C5 or C6), 127.0 (aryl-CH), 125.4 (C4 or C7), 124.8 (aryl-CH), 79.8 (C_5Me_5), 60.8 ($^iPr_2PC$–H), 41.6 (CH_2), 27.5 (d, $^1J_{PC} = 11.2$ Hz, $P(CHMe_cMe_d)$), 26.4 (d, $^1J_{PC} = 16.3$ Hz, $P(CHMe_aMe_b)$), 21.6 ($P(CHMe_aMe_b)$), 20.9 (d, $^2J_{PC} = 9.7$ Hz, $P(CHMe_aMe_b)$), 18.2 (d, $^2J_{PC} = 4.8$ Hz, $P(CHMe_cMe_d)$), 17.6 ($P(CHMe_cMe_d)$), 11.3 (C_5Me_5); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 100.5. Slow evaporation of a concentrated benzene solution of the target complex produced a crystal of $\mathbf{2}\cdot0.5C_6H_6$ suitable for X-ray diffraction analysis.

Synthesis of 4

To a glass vial containing a magnetically stirred deep red suspension of **2** (0.10 g, 0.19 mmol) in benzene (8 mL), was added solid $NaN(SiMe_3)_2$ (0.037 g, 0.20 mmol) all at once. The vial was sealed with a PTFE-lined cap and magnetic stirring was initiated. Over the course of several seconds, the reaction mixture became dark green. After 45 min, ^{31}P NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of **4**. The solution was filtered through Celite® and the benzene solvent and other volatile materials were removed *in vacuo*, yielding an oily dark green solid. The residue was triturated with pentane (2 × 1 mL), after which the pentane was removed *in vacuo*. Pentane (2 × 3 mL) was then added to wash the solid, and the dark green supernatant solution was removed carefully *via* a Pasteur pipette, leaving a greenish-brown solid. Analysis of ^{31}P NMR data collected on the pentane washings indicated relatively minor amounts of **4** and as such these washings were discarded. The residue was dried *in vacuo*, yielding **4** as a greenish-beige powder (0.074 g, 0.074 mmol, 78%). Anal. Calcd. for $C_{50}H_{70}P_2O_2N_2Ru_2$: C 60.32; H 7.09; N 2.82. Found: C 60.34; H 7.10; N 2.10. The somewhat low N% value determined for **4** is in keeping with some other ruthenium dinitrogen complexes.[11] ^1H NMR (500.1 MHz, 300 K, C_6D_6, under dinitrogen): δ 7.38–6.80 (broad m, 4H, aryl-Hs), 3.35–3.17 (broad m, 2H, CH_2), 2.62–2.38 (broad m, 2H, $P(CHMe_2)_2$), 1.71–0.93 (broad m, 27H, C_5Me_5 and $P(CHMe_2)_2$). $^{31}P\{^1H\}$ NMR (202.5 MHz, 300 K, C_6D_6, under dinitrogen): δ 50.1 ($\Delta\nu_{1/2} = 213$ Hz). ^1H NMR (250.1 MHz, 300 K, toluene-d_8, degassed sample): δ 7.43–6.80 (broad m, 4H, aryl-Hs), 3.28–3.05 (broad m, 2H, CH_2), 2.77–0.53 (broad m, 29H, $P(CHMe_2)_2$ and C_5Me_5 and $P(CHMe_2)_2$); $^{31}P\{^1H\}$ NMR (101.3 MHz, 300 K, toluene-d_8, degassed sample): δ 44.9 ($\Delta\nu_{1/2} = 240$ Hz). No useful information could be derived from the ^{13}C NMR spectrum of **4** (125.8 MHz, 300 K, C_6D_6, under dinitrogen). While no N–N stretch was observed in the IR spectrum of a bulk sample of **4**, the corresponding Raman spectrum exhibited a band at 2042 cm^{-1}, thereby suggesting the presence of a symmetrical species in this bulk sample featuring a μ-N_2 ligand. Layering of a C_6D_6 solution of **4** with pentane and slow evaporation of the resultant mixture over the course of approximately two weeks produced a crystal suitable for X-ray diffraction analysis. Low-temperature NMR data for **4**: ^1H NMR (250.1 MHz, 223 K, toluene-d_8, under dinitrogen): δ 7.19–6.96 (m, 4H, aryl-Hs), 3.60–3.15 (AB multiplet, 2H, $C(H_a)(H_b)$), 2.86 (m, 1H, $P(CHMe_aMe_b)$), 2.04 (m, 1H, $P(CHMe_cMe_d)$), 1.78–0.97 (m, 27H, C_5Me_5 and $P(CHMe_aMe_b)$ and $P(CHMe_cMe_d)$); $^{31}P\{^1H\}$ NMR (101.3 MHz, 223 K, toluene-d_8, under dinitrogen): δ 52.1 ($\Delta\nu_{1/2} = 9$ Hz); $^{31}P\{^1H\}$ NMR (101.3 MHz, 223 K, toluene-d_8, degassed sample): δ 52.0 ($\Delta\nu_{1/2} = 10$ Hz), 39.1 ($\Delta\nu_{1/2} = 65$ Hz) (1 : 1 ratio).

Synthesis of 5a

Within a glovebox, a J. Young NMR tube was charged with **4** (0.045 g, 0.045 mmol) and 0.8 mL of C_6D_6. The tube was sealed and the solution was mixed by inversion of the tube several times. The tube containing the resulting deep green 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 change gradually in color to brown over the course of several min. After 30 min, ^{31}P and ^1H NMR data collected on this reaction mixture indicated quantitative conversion to **5a**. Upon removal of solvent and other volatile materials *in vacuo*, followed by trituration with pentane (2 × 1.5 mL), **5a** was isolated as an analytically pure, tan powder (0.043 g, 0.084 mmol, 93%). Anal. Calcd. for $C_{26}H_{35}PO_2Ru$: C 61.02; H 6.90; N 0.00. Found: C 61.01; H 6.97; N < 0.3. ^1H NMR (C_6D_6): δ 7.22 (m, 1H, C5–H or C6–H), 7.01 (d, $^3J_{HH} = 7.5$ Hz, 1H, C4–H or C7–H), 6.93–6.87 (m, 2H, aryl-Hs), 3.28–3.17 (m, 2H, $C(H_a)(H_b)$), 2.84 (m, 1H, $P(CHMe_aMe_b)$), 2.01 (m, 1H, $P(CHMe_cMe_d)$), 1.59 (d, $J = 1.0$ Hz, 15H, C_5Me_5), 1.38 (dd, $^3J_{PH} = 16.0$ Hz, $^3J_{HH} = 7.0$ Hz, 3H, $P(CHMe_aMe_b)$), 1.23 (dd,

$^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe_cMe$_d$)), 1.02–0.94 (m, 6H, P(CHMe$_a$$Me_b$) and P(CHMe$_c$$Me_d$)); ^{13}C{^{1}H} (C$_6D_6$): δ 208.6 (d, $^2J_{PC}$ = 19.1 Hz, CO), 200.8 (d, $^2J_{PC}$ = 21.3 Hz, C2), 146.7 (C3a or C7a), 139.7 (d, J = 8.6 Hz, C7a or C3a), 127.2 (C5 or C6), 124.4 (aryl-CH), 120.0 (aryl-CH), 116.4 (C4 or C7), 99.9 (d, $^1J_{PC}$ = 48.8 Hz, C3), 94.1 (C_5Me$_5$), 38.6 (d, $^3J_{PC}$ = 8.8 Hz, C1), 27.0 (d, $^1J_{PC}$ = 18.6 Hz, P(CHMe$_c$Me$_d$)), 24.2 (d, $^1J_{PC}$ = 35.6 Hz, P(CHMe$_a$Me$_b$)), 19.8 (d, $^2J_{PC}$ = 6.3 Hz, P(CHMe_cMe$_d$)), 19.8 (d, $^2J_{PC}$ = 6.3 Hz, P(CHMe$_a$$Me_b$) or P(CHMe$_c$$Me_d$)), 18.9–18.8 (m, P(CH$Me_aMe_b$) and either P(CHMe$_c$$Me_d$) or P(CHMe$_a$$Me_b$)), 10.3 (C$_5$$Me_5$); ^{31}P{^{1}H} NMR (C$_6D_6$): δ 63.0. FTIR (CsI; cm^{-1}) ν(CO): 1903.

Synthesis of 5b

To a glass vial containing a magnetically stirred solution of **4** (0.11 g, 0.11 mmol) in benzene was added PhCN (0.025 mL, 0.24 mmol) all at once *via* an Eppendorf pipette. A change in the color of the solution from dark green to orange-red was observed upon the addition of PhCN. The vial was sealed with a PTFE-lined cap, and the solution was stirred for 30 min. ^{31}P NMR data collected on an aliquot of this solution indicated quantitative conversion to **5b**. The solvent and other volatile materials were removed *in vacuo*, yielding an oily dark red-brown solid. The residue was triturated with pentane (2 × 1.5 mL), and the pentane was removed *in vacuo* to yield **5b** as an analytically pure, orange-brown powder (0.12 g, 0.20 mmol, 91%). Anal. Calcd. for C$_{32}$H$_{40}$PONRu: C 65.49; H 6.88; N 2.39. Found: C 65.49; H 6.64; N 2.31. ^{1}H NMR (C$_6$D$_6$): δ 7.25 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5–H or C6–H), 7.16 (m, 1H, C4–H or C7–H), 7.02–6.97 (m, 3H, 2 NC–aryl-Hs and either C7–H or C4–H), 6.85 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C6–H or C5–H), 6.81 (t, $^3J_{HH}$ = 7.0 Hz, 1H, NC–aryl-H), 6.64 (apparent t, $^3J_{HH}$ = 7.5 Hz, 2H, NC–aryl-Hs), 3.44–3.35 (broad s, 2H, C(H_a)(H_b)), 1.74 (s, 15H, C$_5$Me$_5$), 1.43–1.25 (m, 14H, P(CHMe$_a$Me$_b$) and P(CHMe$_c$Me$_d$) and P(CHMe_aMe$_b$) and P(CHMe_cMe$_d$)); ^{13}C{^{1}H} (C$_6$D$_6$): δ 199.8 (d, $^2J_{PC}$ = 23.7 Hz, C2), 149.0 (C3a or C7a), 139.0 (d, J = 7.8 Hz, C7a or C3a), 131.6–131.4 (m, NC–aryl-CHs), 129.0 (NC–aryl-CHs), 126.7 (C5 or C6), 123.9 (C4 or C7), 118.7 (C6 or C5), 115.9 (C7 or C4), 113.7 (NC–aryl-C), 98.5 (d, $^1J_{PC}$ = 41.6 Hz, C3), 82.8 (C_5Me$_5$), 39.3 (d, $^3J_{PC}$ = 8.1 Hz, C1), 20.9–19.2 (broad m, P(CHMe$_a$Me$_b$) and P(CHMe$_c$Me$_d$) and P(CHMe_aMe$_b$) and P(CHMe_cMe$_d$)), 10.8 (C$_5$$Me_5$); ^{31}P{^{1}H} NMR (C$_6D_6$): δ 53.9.

Synthesis of 6

Within a glovebox, a J. Young NMR tube was charged with **4** (0.020 g, 0.020 mmol) and 0.8 mL of toluene-d_8. The tube was sealed and the solution was mixed by inversion of the tube several times. The tube containing the resulting deep green solution was removed from the glovebox, connected to a Schlenk line, and degassed *via* three repeated freeze–pump–thaw cycles. Introduction of an atmosphere of H$_2$ to a degassed solution of **4** caused the solution to lighten gradually in color from deep green to lime green over the course of several min. After 20 min, ^{31}P and ^{1}H NMR data collected on this reaction mixture indicated the quantitative conversion of **4** into **6**. Whereas solutions of **6** prepared in this manner were found to be stable for a minimum of 8 h, some decomposition (^{31}P NMR) was detected upon standing for 18 h. For freshly prepared solutions of **6**, removal of volatiles *in vacuo* led to the quantitative conversion of **6** back to **4** (as determined by ^{31}P NMR analysis of a C$_6$D$_6$ solution of the dried solid that had been prepared under an atmosphere of dinitrogen). ^{1}H NMR (500.1 MHz, 300 K, toluene-d_8): δ 7.20 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5–H or C6–H), 7.01 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4–H or C7–H), 6.93 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C7–H or C4–H), 6.86 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C6–H or C5–H), 3.25 (s, 2H, CH$_2$), 2.45 (m, 2H, P(CHMe$_a$Me$_b$), 1.64 (s, 15H, C$_5$Me$_5$), 1.19 (dd, $^3J_{PH}$ = 13.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe_aMe$_b$)), 1.11 (dd, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 6.5 Hz, 6H, P(CHMe$_a$$Me_b$)), –5.73 (broad s, $\Delta\nu_{1/2}$ = 23 Hz, 2H, Ru(H$_2$)); ^{13}C{^{1}H} (125.8 MHz, 300 K, toluene-d_8): δ 199.9 (m, C2), 146.8 (m, C3a or C7a), 139.9 (m, C7a or C3a), 126.8 (C5 or C6), 124.2 (C4 or C7), 119.7 (C6 or C5), 116.3 (C7 or C4), 81.1 (C_5Me$_5$), 38.6 (d, $^3J_{PC}$ = 8.4 Hz, C1), 24.5 (broad m, P(CHMe$_a$Me$_b$)), 19.6–19.3 (broad m, P(CHMe_aMe$_b$)), 11.1 (C$_5$$Me_5$); ^{31}P{^{1}H} NMR (202.5 MHz, 300 K, toluene-d_8): δ 65.2 (broad m, $\Delta\nu_{1/2}$ = 180 Hz). The $T_{1(\min)}$ relaxation time value (218 K, 17 ms, 250 MHz) associated with the σ-H$_2$ unit in **6** was obtained by using the inversion-recovery technique.[13] Variable-temperature behavior of **6**. The initially green toluene solution of **6** observed at 300 K becomes brown in appearance (reversibly) upon cooling below 253 K. ^{1}H NMR (250.1 MHz, 223 K, toluene-d_8): δ 7.34–6.94 (m, 4H, aryl-Hs), 3.40–3.15 (AB multiplet, 2H, C(H_a)(H_b)), 2.53 (m, 1H, P(CHMe$_a$Me$_b$)), 1.98 (m, 1H, P(CHMe$_c$Me$_d$)), 1.63 (s, 15H, C$_5$Me$_5$), 1.42–0.83 (m, 12H, P(CHMe_aMe$_b$) and P(CHMe_cMe$_d$)), –6.40 (broad s, $\Delta\nu_{1/2}$ = 51 Hz, 2H, Ru(H$_2$)); ^{31}P{^{1}H} NMR (101.3 MHz, 223 K, toluene-d_8): δ 72.2 ($\Delta\nu_{1/2}$ = 20 Hz).

Synthesis of 7a

To a glass vial containing a magnetically stirred deep green suspension of **4** (0.020 g, 0.020 mmol) in C$_6$D$_6$ (2 mL), was added PhSiH$_3$ (0.0051 mL, 0.041 mmol) *via* a microsyringe. The vial was sealed with a PTFE-lined cap and magnetic stirring was initiated. Over the course of several seconds, the reaction mixture became an orange-yellow homogeneous mixture. After 3 h, ^{31}P NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of **7a**. The benzene solvent and other volatile materials were removed *in vacuo*, yielding an oily orange solid. The residue was triturated with pentane (2 × 1 mL), after which the pentane was removed *in vacuo* to yield **7a** as an orange powder (0.023 g, 0.038 mmol, 95%). Anal. Calcd. for C$_{31}$H$_{43}$POSiRu: C 62.91; H 7.32; N 0.00. Found: C 62.95; H 7.04; N < 0.3. ^{1}H NMR (C$_6$D$_6$): δ 8.18–8.15 (m, 2H, Si–aryl-Hs), 7.42–7.36 (m, 3H, 2 Si–aryl-Hs and aryl-H), 7.26 (m, 1H, Si–aryl-H), 7.16 (m, 1H, aryl-H), 6.96–6.89 (m, 2H, aryl-Hs), 6.61 (m, 1H, Si–H), 3.26–2.98 (m, 2H, C(H_a)(H_b)), 2.74–2.61 (m, 2H, P(CHMe$_a$Me$_b$) and P(CHMe$_c$Me$_d$)), 1.73 (s, 15H, C$_5$Me$_5$), 1.09–1.00 (m, 9H, P(CHMe_aMe$_b$) and P(CHMe_cMe$_d$)), 0.94 (dd, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$$Me_d$)), –11.14 (d, 1H, J = 34.0 Hz, Ru–H$_a$), –11.92 (apparent dd, 1H, J = 32.5 Hz, J = 5.0 Hz, Ru–H$_b$); ^{13}C{^{1}H} (C$_6$D$_6$): δ 177.0 (d, $^2J_{PC}$ = 8.6 Hz, C2), 146.5 (C3a or C7a), 145.5 (Si–aryl-C), 135.2–135.1 (m, Si–aryl-CHs and either C7a or C3a), 128.9 (Si–aryl-CH), 128.2–128.1 (Si–aryl-CHs), 126.2 (aryl-CH), 123.5 (aryl-CH), 122.5 (aryl-CH), 120.2 (aryl-CH), 103.1 (d, $^1J_{PC}$ = 54.1 Hz, C3), 95.6 (C_5Me$_5$), 42.7 (d, $^3J_{PC}$ = 7.7 Hz, C1), 29.1 (d, $^1J_{PC}$ = 25.9 Hz, P(CHMe$_c$Me$_d$)), 27.9 (d, $^{1}J_{PC}$ = 27.2 Hz, P(*C*HMe$_a$Me$_b$)), 20.7 (P(CHMe$_c$*Me*$_d$)), 20.4 (d, $^{2}J_{PC}$ = 7.9 Hz, P(CH*Me*$_a$Me$_b$) or P(CHMe$_a$*Me*$_b$) or P(CH*Me*$_c$Me$_d$)), 20.3 (P(CHMe$_a$*Me*$_b$) or P(CH*Me*$_c$Me$_d$) or P(CH*Me*$_a$Me$_b$)), 19.0 (d, $^{2}J_{PC}$ = 5.9 Hz, P(CH*Me*$_c$Me$_d$) or P(CH*Me*$_a$Me$_b$) or P(CHMe$_a$*Me*$_b$)), 11.6 (C_5*Me*$_5$); ^{31}P{^{1}H} NMR (C_6D_6): δ 67.4;^{29}Si{^{1}H} NMR (C_6D_6): δ 60.4 (^{1}H–^{29}Si HMBC/HMQC), $^{1}J_{SiH}$ = 199.7 Hz (^{1}H-coupled ^{1}H–^{29}Si HMQC), $^{2}J_{SiH}$ = 9.4 Hz (*J*-HMBC).

Synthesis of 7b

To a glass vial containing a magnetically stirred deep green suspension of **4** (0.060 g, 0.060 mmol) in benzene (8 mL), was added Ph_2SiH_2 (0.025 mL, 0.13 mmol) *via* an Eppendorf pipette. The vial was sealed with a PTFE-lined cap and magnetic stirring was initiated. Over the course of several seconds, the reaction mixture became an orange-yellow homogeneous mixture. After 15 min, ^{31}P NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of **7b**. The benzene solvent and other volatile materials were removed *in vacuo*, yielding an oily orange solid. The residue was triturated with pentane (2 × 1 mL), after which the pentane was removed *in vacuo* to yield **7b** as a peach powder (0.079 g, 0.12 mmol, 95%). Anal. Calcd. for $C_{37}H_{47}POSiRu$: C 66.53; H 7.09; N 0.00. Found: C 66.13; H 6.89; N < 0.3. ^{1}H NMR (C_6D_6): δ 8.03–8.01 (m, 4H, Si–aryl-Hs), 7.41 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, C4–H or C7–H), 7.36 (apparent t, $^{3}J_{HH}$ = 7.0 Hz, 4H, Si–aryl-Hs), 7.27–7.23 (m, 2H, Si–aryl-Hs), 7.13 (m, 1H, aryl-H), 6.96–6.92 (m, 2H, aryl-Hs), 3.17 (s, 2H, CH_2), 2.63 (m, 2H, P(C*H*Me$_a$Me$_b$)), 1.67 (s, 15H, C_5Me_5), 1.09 (dd, $^{3}J_{PH}$ = 17.0 Hz, $^{3}J_{HH}$ = 7.0 Hz, 6H, P(CH*Me*$_a$Me$_b$)), 0.94 (dd, $^{3}J_{PH}$ = 15.5 Hz, $^{3}J_{HH}$ = 7.0 Hz, 6H, P(CHMe$_a$*Me*$_b$)), –11.02 (d, 2H, $^{2}J_{PH}$ = 32.5 Hz, Ru–Hs); ^{13}C{^{1}H} (C_6D_6): δ 177.1 (d, $^{2}J_{PC}$ = 9.1 Hz, C2), 146.5 (C3a or C7a), 146.2 (Si–aryl-C), 135.9 (Si–aryl-CHs), 135.1 (d, *J* = 6.9 Hz, C7a or C3a), 128.4 (Si–aryl-CHs), 127.4 (Si–aryl-CHs), 126.4 (aryl-CH), 123.5 (aryl-CH), 122.4 (C5 or C6), 120.3 (C4 or C7), 103.1 (d, $^{1}J_{PC}$ = 52.3 Hz, C3), 96.1 (*C*$_5$Me$_5$), 42.8 (d, $^{3}J_{PC}$ = 7.4 Hz, C1), 28.6 (d, $^{1}J_{PC}$ = 26.9 Hz, P(*C*HMe$_a$Me$_b$)), 20.3 (P(CHMe$_a$*Me*$_b$)), 19.5 (d, $^{2}J_{PC}$ = 5.8 Hz, P(CH*Me*$_a$Me$_b$)), 11.6 (C_5*Me*$_5$); ^{31}P{^{1}H} NMR (C_6D_6): δ 65.1; ^{29}Si{^{1}H} NMR (C_6D_6): δ 57.4 (^{1}H–^{29}Si HMBC), $^{2}J_{SiH}$ = 9.8 Hz (*J*-HMBC). A crystal of **7b** suitable for X-ray diffraction analysis was grown from a concentrated pentane solution at –35 °C.

Synthesis of 8

To a glass vial containing a magnetically stirred deep green suspension of **4** (0.035 g, 0.035 mmol) in benzene (2 mL), was added solid $MesBH_2$ (0.0093 g, 0.071 mmol) all at once. The vial was sealed with a PTFE-lined cap and magnetic stirring was initiated. Over the course of several seconds, the reaction mixture became orange-yellow in color. After 30 min, ^{31}P NMR data collected on an aliquot of the crude reaction mixture indicated the quantitative formation of **8**. The benzene solvent and other volatile materials were removed *in vacuo*, yielding an oily orange-yellow solid. The residue was triturated with pentane (2 × 1 mL), after which the pentane was removed *in vacuo* to yield **8** as an analytically pure orange-yellow powder (0.036 g, 0.058 mmol, 82%). Anal. Calcd. for $C_{34}H_{48}POBRu$: C 66.30; H 7.86; N 0.00. Found: C 66.30; H 7.56; N < 0.3. ^{1}H NMR (C_6D_6): δ 7.70 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, C4–H or C7–H), 7.22 (m, 1H, aryl-H), 7.02–7.00 (m, 2H, aryl-Hs), 6.93 (s, 2H, B–aryl-H), 3.31 (s, 2H, CH_2), 2.65 (m, 2H, P(C*H*Me$_a$Me$_b$)), 2.62 (s, 6H, B–aryl *o*-Me), 2.33 (s, 3H, B–aryl *p*-Me), 1.60 (d, *J* = 1.5 Hz, 15H, C_5Me_5), 1.22–1.15 (m, 12H, P(CH*Me*$_a$Me$_b$)), –13.12 (broad d, $^{2}J_{PH}$ = 13.5 Hz, 2H, Ru–H–B); ^{13}C{^{1}H} NMR (C_6D_6): δ 176.3 (d, $^{2}J_{PC}$ = 10.8 Hz, C2), 146.3 (C3a or C7a), 136.8 (*o*-B–aryl-C), 135.7 (d, *J* = 6.0 Hz, C7a or C3a), 135.3 (*p*-B–aryl-C), 128.1 (B–aryl-CH), 126.2 (aryl-CH), 123.6 (aryl-CH), 123.1 (aryl-CH), 122.1 (C4 or C7), 101.9 (d, $^{1}J_{PC}$ = 33.7 Hz, C3), 92.4 (*C*$_5$Me$_5$), 42.1 (d, $^{3}J_{PC}$ = 6.4 Hz, C1), 27.9 (d, $^{1}J_{PC}$ = 25.9 Hz, P(*C*HMe$_a$Me$_b$)), 22.9 (B–aryl *o*-Me), 21.3 (B–aryl *p*-Me), 21.2 (P(CHMe$_a$*Me*$_b$)), 19.5 (d, $^{2}J_{PC}$ = 5.0 Hz, P(CH*Me*$_a$Me$_b$)), 11.2 (C_5*Me*$_5$); ^{31}P{^{1}H} NMR (C_6D_6): δ 56.4; ^{11}B{^{1}H} NMR (C_6D_6): δ 59.0 (broad). Storage of a concentrated pentane solution of **8** at –37 °C provided a suitable crystal for single-crystal X-ray diffraction studies.

Crystallographic characterization of 2·0.5C_6H_6 and 4

Crystallographic data for these complexes 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 by using the COLLECT software (Nonius), and refined with the HKL DENZO and SCALEPACK software.[26] Data reduction and absorption correction (multi-scan) were also performed with the HKL DENZO and SCALEPACK software. The structures were solved by using the direct methods package in SIR-97,[27] and refined by use of the SHELXL97-2 program,[28] 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-H atoms. For **2**·0.5C_6H_6, the ^{i}Pr$_2$PC–H position was located in the Fourier difference map and refined freely. Otherwise, all H-atoms were added at calculated positions and refined by using a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Additional crystallographic information is provided in the deposited CIFs: **2**·0.5C_6H_6 (CCDC 654073) and **4** (CCDC 654074).† ORTEP diagrams featured in the manuscript were prepared by use of ORTEP-3 for Windows version 1.074.[8]

Crystallographic characterization of 7b and 8

Crystallographic data for these complexes 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 a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, data reduction, and absorption correction (including SAINT and SADABS) were supplied by Bruker. For **7b** the structure was solved by use of direct methods, while for **8** a Patterson search/structure expansion was employed. Refinement was carried by use of the SHELXL97-2 program,[28] 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 $F_o^2 \geq -3\sigma(F_o^2)$. Compound **8** features crystallographically imposed C_s-symmetry, such that the asymmetric unit contains half of a molecular formula unit. The solution and refinement of **8** was successfully carried out by employing a disorder model involving the isopropyl fragments. Anisotropic displacement parameters were employed throughout for the non-H atoms. All Ru–H positions were located in the Fourier difference map and refined; for **7b** the Ru–H distances fixed at 1.55 Å, while for **8** no such restraints were applied. All other H-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. The final refined value of the absolute structure parameter (–0.024(19)) supported that the absolute structure for **7b** had been chosen correctly.[29] Additional crystallographic information is provided in the deposited CIFs (**7b**, CCDC 654072; **8**, CCDC 719567).† The ORTEP diagrams featured in the manuscript was prepared by use of ORTEP-3 for Windows version 1.074.[8]

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