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Hydrogenation and Silylation of a Double-Cyclometalated Ruthenium Complex: Structures and Dynamic Behavior of Hydrido and Hydridosilicate Ruthenium Complexes

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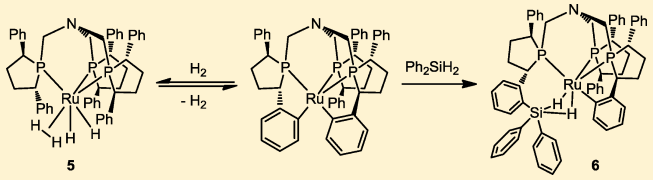
Supporting Information

ABSTRACT: A double-cyclometalated ruthenium complex containing a chiral tripodal phospholane has been prepared by reaction with [Ru(η^4-COD)(η^3-methylallyl)$_2$] via elimination of isobutene. The ruthenium−carbon bonds of this compound were reversibly cleaved by H_2, resulting in an equilibrium between a tri- and a tetrahydride (**4** and **5**). T_1 relaxation time measurements revealed the nonclassical nature of the fluctuating hydrides. Release of the gas led to complete re-formation of the cyclometalated compound. Reaction of **3** with D_2 afforded $\mathbf{D_{10}}$**-5**, in which six *ortho*-phenyl protons and four hydrides were replaced by deuterium. Furthermore, diphenylsilane was found to readily insert into one Ru−C bond to form **6**, containing a κ^3-dihydridosilicate fragment. On the basis of deuterium labeling experiments, the fast exchange between the two hydrides was shown to include a reductive elimination/oxidative addition step involving the remaining metalated phenyl group. Again, pressurization of **6** with H_2 resulted in reversible cleavage of the remaining Ru−C bond, yielding the corresponding trihydride **7**.



INTRODUCTION

Intermediates containing ruthenium−carbon bonds play a vital role in a variety of catalytic transformations.[1] Of particular interest in this context is the activation and functionalization of C−H bonds,[2] and cyclometalations, in particular, are among the most convenient methods to establish Ru−C sigma-bonds.[3] Most often, coordination of the heteroatom of a potentially multidentate ligand facilitates the metalation of an attached alkyl or aryl group to form a ruthenacycle.[4] A large number of monocyclometalated ruthenium complexes are known, whereas there are far fewer examples of mononuclear bis-cyclo-ruthenated structures.[5]

Such compounds show a rich chemistry, as the ruthenium−carbon bond can be transformed in reactions with various substrates such as acetylenes, olefins, carbon monoxide, or hydrogen.[3b]

We recently developed the synthesis of tridentate phospholanomethylamine ligands and investigated their coordination chemistry and catalytic activity for rhodium and gold.[6] Moreover, two tripodal ligands were subsequently reported to form ruthenium η^4-trimethylenemethane complexes.[7] However, as will be shown in this work, the chiral trisphospholane ligand N(CH$_2$DPP)$_3$ (**1**, DPP = 2,5-diphenylphospholane) proved to be "noninnocent" and exhibited a different reactivity.

Here we report the formation of a pentacoordinate ruthenium complex of **1** containing two cyclometalated phenyl groups along with its reactions with dihydrogen and diphenylsilane.

RESULTS AND DISCUSSION

Synthesis of the Double-Cyclometalated Ruthenium Complex. The $^{31}P\{^1H\}$ NMR spectrum recorded after heating a solution of N(CH$_2$DPP)$_3$ (**1**) and [Ru(η^4-COD)(η^3-methylallyl)$_2$] to 80 °C overnight displayed the presence of three species. A singlet at δ = 0.0 ppm corresponded to unreacted ligand, and two singlet resonances (δ = −1.9 and 51.6 ppm, intensities of 1:2) indicated the formation of a compound containing the ligand in its didentate binding mode (complex **2**, Scheme 1). An analogous complex was previously isolated as an intermediate in the formation of the ruthenium tmm complex of N(CH$_2$DMP)$_3$ (DMP = 2,5-dimethylphospholane).[7]

Further heating of the reaction mixture to 125 °C for 2 d resulted in complete conversion to the third species, which was represented by three doublets of doublets (δ = 29.7, 60.1, and 107.6 ppm) in the $^{31}P\{^1H\}$ NMR spectrum with relative intensities of 1:1:1. The formation of isobutene was observed by in situ ^1H NMR spectroscopy. In addition, the spectrum displayed aromatic proton resonances at unusual chemical shifts of δ = 5.23 (2 H), 8.65 (1 H), and 8.90 ppm (1 H), indicating that two phenyl rings had been transformed. Moreover the presence of two quaternary $^{13}C\{^1H\}$ NMR resonances at low field (δ = 178.7 and 185.3 ppm) exhibiting multiplet carbon−phosphorus couplings was indicative of the formation of Ru−C bonds. These observations led to the suggestion of structure **3**

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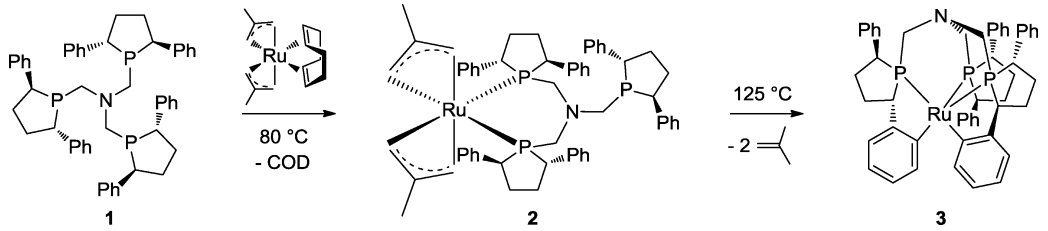
Scheme 1. Formation of Double-Cyclometalated Ruthenium Complex 3 via Intermediate 2



(Scheme 1), in which two of the phospholane-bound phenyl rings were *ortho*-metalated.

This was in accordance with the full set of 1D and 2D NMR data as well as mass spectrometry (HR-FAB) and elemental analysis. Compound **3** was isolated as a yellow powder in 91% yield after workup.

Reactivity of 3 with H_2. It is known that the Ru−C bond in cyclometalated complexes can be cleaved by hydrogen to form ruthenium hydride species.[4c,d,8] Consequently a solution of **3** was pressurized with H_2 (2 bar) in a high-pressure NMR tube. The yellow color of the solution faded immediately upon shaking, indicating a very rapid reaction. The $^{31}P\{^1H\}$ NMR spectrum exhibited the formation of two new species represented by a singlet (79%) at δ = 46.4 ppm and a set of three doublets of doublets (21%) at δ = 40.7 (1 P, ^2J(P,P) = 28.8 Hz), 42.2 (1 P, ^2J(P,P) = 28.3 Hz), and 78.6 ppm (1 P, ^2J(P,P) = 29.2 Hz). The equilibrium between the two compounds was shifted toward the main component by increasing the H_2 pressure. At 10 bar, a ratio of 95:5 in favor of the singlet species was observed. The pressure dependence of the relative amounts in solution is presented in Figure 1.

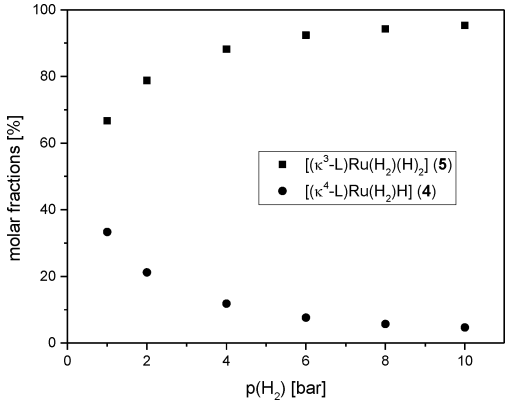
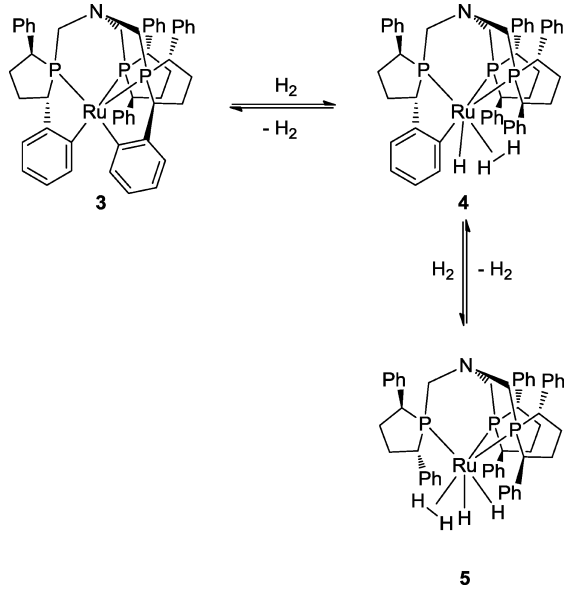


Figure 1. Hydrogen pressure dependence of the molar fractions of complexes **4** and **5** in solution, determined by $^{31}P\{^1H\}$ NMR. Broad signals of residual **3** were observed at $p(H_2)$ = 1 bar. These were not accounted for in the determination of the molar fractions of **4** and **5**.

A quartet at δ = −7.34 ppm (4 H) in the ^{1}H NMR spectrum was attributed to the major ^{31}P NMR resonance. This suggests the formation of the tetrahydride **5**, as shown in Scheme 2, in which the four hydrides rapidly interchange, resulting in a pseudo-C_3-symmetric structure. The multiplicity of the hydride resonance (^2J(H,P) = 10 Hz) which is completely resolved above −30 °C was explained by the coupling to the three chemically equivalent phosphorus donors. Accordingly, the quartet simplified to a singlet in the $^1H\{^{31}P\}$ NMR spectrum.

The ^{1}H and $^{13}C\{^1H\}$ NMR resonances are in accordance with the proposed structure. No extreme low-field carbon

Scheme 2. Complex 3 Reacted with H_2 to Reversibly Form Trishydride 4 and Tetrahydride 5



resonances similar to the one found for **3** were observed, confirming that both Ru−C bonds were cleaved.

As mentioned above, the minor species present in solution was represented by three doublets of doublets in the ^{31}P NMR spectrum. A ^{1}H NMR signal at δ = −4.82 ppm (3 H) was attributed to this complex. One single quaternary multiplet at δ = 175.9 ppm in the $^{13}C\{^1H\}$ NMR spectrum characteristic for a ruthenium-coordinated aromatic carbon atom was assigned to this compound.

These findings are consistent with the structure **4** shown in Scheme 2. Cleavage of one Ru−C bond followed by η^2-coordination of a second equivalent of dihydrogen led to the formation of the trishydride.

Remarkably, release of the hydrogen pressure and purging with argon led to complete recovery of the initial complex **3**. Such reversibility of a Ru−C bond cleavage by hydrogen or deuterium has been observed before[4d,8,9] and is most likely due to both entropic effects and steric properties of the ligand. The phospholane-bound phenyl groups are preorientated toward the metal center, facilitating metalation.

The NMR spin−lattice relaxation time (T_1) has proved to be an important criterion for the distinction between classical and nonclassical hydrides.[10] The presence of η^2-H_2 in fluxional ruthenium polyhydrides usually gives rise to a short T_1^{min} of <100 ms.[11] The temperature dependence of T_1 of complexes **4** and **5** was determined by inversion−recovery measurements at 400 MHz. Trishydride complex **4** exhibited a T_1^{min} of 15 ms, strongly suggesting the presence of a fluxional nonclassical structure. In the case of **5**, a minimum of the relaxation time

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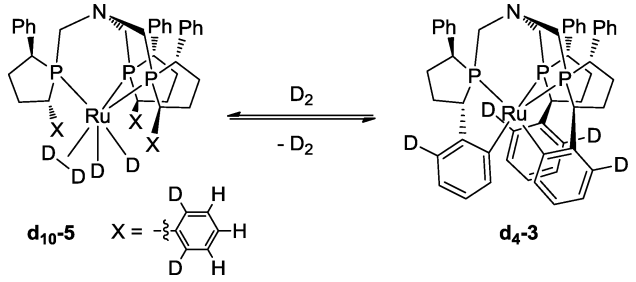
was not reached even at temperatures as low as −90 °C. However, given that the actual T_1^{min} will be shorter than the lowest observed T_1 value of 50 ms, one can confidently assume a nonclassical nature of the hydrido ligands.

The spectral data and relaxation time of of **5** are comparable to the well-known analogue $[Ru(H_2)H_2(PPh_3)_3]$.[9,10,11e,12] Further derivatives of this system including various coligands have been reported.[10c,11c,13]

Deuteration Experiment. Due to the reversible nature of the formation of the hydrido complexes **4** and **5**, these species cannot be isolated and characterized by any technique other than NMR spectroscopy. Deuterium labeling has proved to be a valuable tool for structural and mechanistic investigations related to such species.[14] In order to provide additional evidence for the assumed structures of complex **3** and tetrahydride **5**, a solution of **3** was pressurized with 10 bar of D_2.

Compared to the spectra of nondeuterated tetrahydride complex **5**, the NMR data of $\mathbf{d_{10}}$**-5** (Scheme 3) lack one very

Scheme 3. Reaction of Cyclometalated Complex 3 with D_2 to Form Deuterated Complexes $\mathbf{d_{10}}$-5 and $\mathbf{d_4}$-3



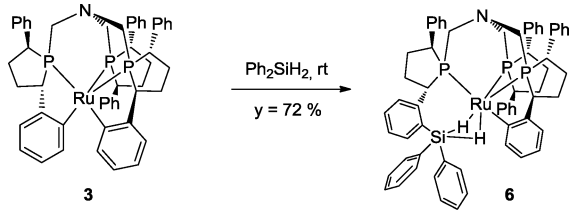
broad ^{1}H resonance at δ = 8.11 ppm and one broad $^{13}C\{^1H\}$ signal at δ = 129.9 ppm. This was explained by the H/D exchange of the aromatic *ortho*-protons of three phenyl groups oriented toward the ruthenium. This was backed up by the observation of a hydridic ^{1}H resonance of low intensity despite the use of pure D_2. As a result of the fast equilibrium between **5**, starting complex **3**, and trihydride **4**, four aromatic protons are distributed statistically within the available positions in the complex and the deuterium gas. The ^{2}H NMR spectrum of $\mathbf{d_{10}}$-**5** provided additional evidence, showing a broad aromatic resonance at 7.37 ppm (6 *ortho*-D) and a deuteride signal at −7.35 ppm (4 D). Release of D_2 afforded the deuterated compound $\mathbf{d_4}$-**3** (Scheme 3). The disappearance of three aromatic proton resonances respectively clearly showed that H/D exchange occurred in the *ortho* positions of all three phenyl groups that are oriented toward the metal. Again, this was expected, as compounds $\mathbf{d_4}$-**3** and $\mathbf{d_{10}}$-**5** are in equilibrium under a hydrogen atmosphere. The three phenyl groups that, due to the chirality, are located on the opposite side of the phospholane rings with respect to the ruthenium, thus pointing away from the metal center, do not undergo H/D exchange.

Reactivity with Silanes. Hydrosilanes react with most transition metals to form stable metal silyl complexes.[15] The scope of bonding modes ranges from nonclassical σ-complexes to classical structures containing two-center-two-electron M−Si bonds. A wide variety of isolated intermediates exist in which the Si−H bond cleavage is "arrested" along the oxidative addition pathway.[16] Tilley and co-workers have recently published η^3-silane complexes $[(PhBPPh_3)RuH(\eta^3\text{-}H_2SiRR')]$ (RR′ = PhMe, Ph_2) containing two M−H−Si σ-bonding interactions.[17] There are only a few other examples of structures containing this H_2Si motif.[18] A common feature of these compounds is the presence of phosphorus coligands.

Given the structural similarity of Tilley's tridentate phosphine ligand[19] with our trisphospholane **1** and the observation that the Ru−C bonds in complex **3** are easily cleaved by dihydrogen, we investigated its reactivity toward hydrosilanes.

Indeed, reaction of **3** with diphenylsilane proceeded smoothly at room temperature. Insertion into one of the two Ru−C bonds affords the ruthenium silyl dihydrido complex **6** (Scheme 4). The $^{31}P\{^1H\}$ NMR spectrum exhibited three

Scheme 4. Insertion of Diphenylsilane into One Ru−C Bond to Form 6



doublets of doublets, owing to the P−P coupling of the three inequivalent phosphorus nuclei. Compound **6** was isolated as an off-white powder in a yield of 72% and fully characterized by NMR spectroscopy, mass spectrometry, and elemental analysis.

Its molecular structure determined by X-ray diffraction is depicted in Figure 2. The ruthenium center is coordinated in a

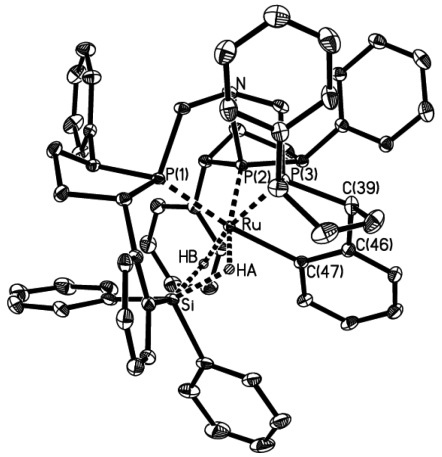


Figure 2. Thermal ellipsoids (50% probability level; nonhydridic hydrogen atoms omitted for clarity) of the molecular structure of complex **6**. Principal bond lengths [Å] and angles [deg]: Ru−P(1) 2.3076(5), Ru−P(2) 2.3586(4), Ru−P(3) 2.2952(5), Ru−C(47) 2.1324(17), Ru−HA 1.58(3), Ru−HB 1.60(3), Ru−Si 2.3850(5), Si−HA 1.84(3), Si−HB 1.87(3), P(1)−Ru−P(2) 89.53(2), P(3)−Ru−P(1) 87.90(2), P(3)−Ru−P(2) 91.27(2), Si−Ru−HA 50.3(10), Si−Ru−HB 51.5(9).

slightly distorted octahedral fashion, the two agostic hydrogen atoms being *cis* to the metalated carbon atom C(47). The η^3-H_2Si moiety is symmetrically bound to the metal, the Ru−H−Si angles being very similar. The Ru−H distances are in accord with those found previously in ruthenium complexes containing a hypervalent $[H_2SiPh_3]^-$ fragment (1.47(4)−1.568(16) Å).[18e,j] Both the Si−H and Ru−Si bond lengths are in the range of the

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literature data (Si−H: 1.72(3)−2.016(14); Ru−Si 2.3816(5)−2.4006(5) Å). The five-membered ring formed by coordination of the cyclometalated phenyl group (Ru−P(3)−C(39)−C(46)−C(47)) is virtually planar (RMSD = 0.0150 Å).

In the ^{1}H NMR spectrum of **6**, only one broad hydridic resonance was observed at δ = −6.08 ppm, equivalent to two protons. Given the C_1 symmetry of the complex, a fast exchange must account for the equivalence of the two bridging hydrides. As the silicon moiety is covalently attached to one phospholane ring via a phenyl group, exchange between the two hydride atoms by simple rotation of the silyl fragment[18g] is not possible (see discussion below). A T_1^{min} of 424 ms was found at 0 °C (400 MHz). This is well in the characteristic range of classical hydride structures[10d] and in agreement with the value of 436 ms (400 MHz) found for [TpRu(PPh$_3$)(η^3H$_2$SiR$_3$)].[18g,j] ^{1}H NMR spectra acquired at various temperatures showed coalescence of the hydride signal at −20 °C ($\Delta G^{\ddagger}$ = 46 kJ/mol). Two doublets of doublets are observed at lower temperature, and one doublet of doublets represented the high-temperature limit. The multiplicities are due to the coupling to two nonequivalent phosphorus nuclei. Accordingly, the ^{1}H{^{31}P} NMR spectra displayed singlet hydride signals with ^1J(Si,H) values of 47 Hz.

Reactivity of 6 with Hydrogen. It was expected that in analogy with the reaction of **3** with dihydrogen the remaining Ru−C bond of **6** might be easily cleaved upon pressurization. Indeed, the in situ ^{31}P{^{1}H} NMR spectrum of a solution of **3** under 2 bar of H$_2$ revealed a mixture of starting complex (22%) and a new species (78%). The relative amount of the latter went up to 96% upon increasing the pressure to 10 bar (Figure 3). ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra recorded under these conditions agreed with structure **7** shown in Scheme 5.

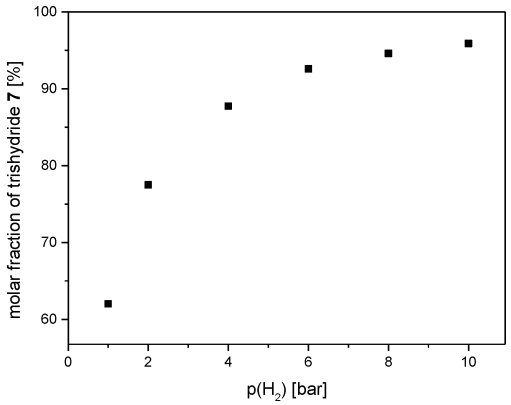
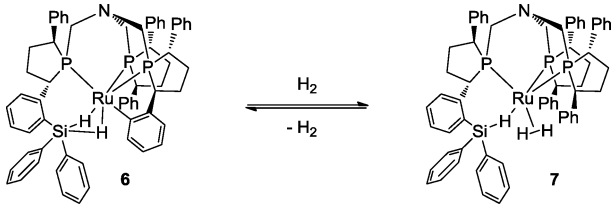


Figure 3. Hydrogen pressure dependence of the molar fraction of complex **7** in solution, determined by ^{31}P{^{1}H} NMR.

Scheme 5. Reaction of the Dihydridosilicato Complex 6 with H$_2$ to Reversibly Form the Trihydride 7

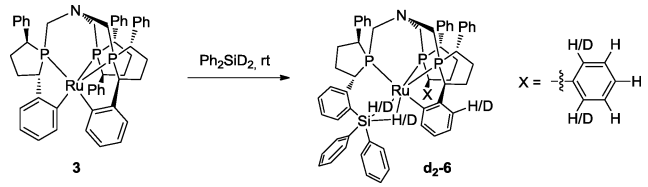


A series of low-temperature ^{1}H NMR spectra of **7** exhibited a broadening of the hydridic resonance at δ = −7.48 ppm; however coalescence was not observed even at −90 °C. Given a T_1^{min} of 38 ms at 0 °C (400 MHz), the hydrides were again considered to be of fluctuating nonclassical nature. This is in accordance with the T_1 value of 22 ms (250 MHz) found for [(η^2-H$_2$)(PCy$_3$)$_2$RuH(η^3-H$_2$SiPh$_3$)].[18c−f]

As in the case of **5**, release of the hydrogen and purging with argon led to complete backreaction to the initial dihydrido complex **6**.

Mechanism of Hydride Exchange in 6. A mechanism rendering the two hydrides in complex **6** equivalent was considered to consist in a fast reductive elimination−oxidative addition process involving the metalated phenyl group. Consequently, H/D scrambling was expected to occur when employing d$_2$-diphenylsilane in the synthesis of **d$_2$-6** (Scheme 6). Indeed, the low-field hydride signal also detected for **6**

Scheme 6. Deuterium Labeling Experiment with d$_2$-Diphenylsilane



appeared in the ^{1}H NMR spectrum. This proved the proposed exchange of the deuterides and the aromatic protons. A relative intensity of this resonance of 2/3 would be indicative of an H/D exchange involving one proton in the *ortho* position of the metalated phenyl ring. The observed intensity of around 6/5 led to the conclusion that also the previously noncoordinating phenyl group pointing toward the metal takes part in the process.

In order to further corroborate this hypothesis, a solution of **d$_2$-6** was pressurized with D$_2$. Subsequent gas release led to the formation of a species that was identified as **d$_5$-6** by NMR spectroscopy. Two ^{13}C{^{1}H} resonances corresponding to the nonequivalent aromatic *ortho*-carbons that underwent H/D exchange converted from doublets in nondeuterated **6** (124.9 and 131.7 ppm) to broad quaternary signals in **d$_5$-6** (124.6 and 131.4 ppm). Given these findings, participation of the phospholane-bound phenyl groups in the fast exchange between the hydride ligands in **6** is likely.

Addition of an excess of d$_2$-diphenylsilane to **3** led to the detection of HDSiPh$_2$ and H$_2$SiPh$_2$ in the ^{1}H NMR spectrum. Obviously, exchange occurs between hydridic protons in **6** on the one hand and deuterides in noncoordinated silane on the other hand. No reaction was observed upon heating solutions of **3** and tris(isopropyl)silane or triphenylsilane at elevated temperatures of 80 or 95 °C, respectively.

CONCLUSION AND OUTLOOK

In summary, we have provided a rare example of a ruthenium complex including a *double*-cyclometalated ligand. Moreover a hydridosilicate complex comprising a κ^3-H$_2$Si fragment was synthesized, again exhibiting reversible incorporation of dihydrogen. Ruthenium hydride species are involved in a variety of catalytic carbon−carbon bond formations,[1a,b] and investigations into the activity of these compounds with particular focus on asymmetric transformations are currently under way. The reversibility of the formation of **5** might be beneficial for future applications of this compound as a catalyst

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in stereoselective reactions. Many catalyst precursors need to be activated by irreversible elimination of a leaving group such as COD. As a consequence, after complete conversion of the substrate, these catalysts may decompose due to the absence of coordinating species. In principle, the cyclometalated ligand itself might act as an internal protecting group, which might prove useful in terms of catalyst recovery.

EXPERIMENTAL SECTION

General Experimental Methods and Procedures. All reactions were carried out in air- and moisture-free conditions. Argon was used as inert gas after drying over Granusic phosphorus pentoxide granulate. Standard Schlenk and glovebox techniques were employed to handle the substances. Solvents were dried according to literature known procedures,[20] degassed by several successive freeze−pump−thaw cycles, and stored under argon in Teflon-capped glass ampules. Tris((2*S*,5*S*)-2,5-diphenylphospholanomethyl)amine (**1**) was prepared according to a literature method.[6a] All other chemicals were received from commercial suppliers and used without further purification.

Nuclear magnetic resonance spectra were recorded on Bruker Avance II (400 MHz) and Bruker Avance III (600 MHz) instruments. Chemical shifts are given in parts per million (ppm) and are referenced to the residual proton solvent signals (^{1}H: C_6D_6 = 7.16 ppm) or carbon resonances (^{13}C: C_6D_6 = 128.06 ppm).[21] H_3PO_4 (^{31}P NMR) and $SiMe_4$ (^{29}Si NMR) were used as external standards. The appearance of the signals was described using the following abbreviations: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiplet), b (broad signal). T_1 relaxation data were recorded by inversion−recovery experiments at 400 MHz, and relaxation times were calculated using the standard nonlinear three-parameter fitting routine provided by the spectrometer software.[22] Mass spectra were acquired on Bruker ApexQe hybrid 9.4 T FT-ICR (HR-ESI) and JEOL JMS-700 magnetic sector (HR-FAB) spectrometers at the mass spectrometry facility of the Institute of Organic Chemistry of the University of Heidelberg. Elemental analyses were carried out in the Microanalysis Laboratory of the Heidelberg Chemistry Department.

Synthesis of [(N(CH$_2$DPP)$_3$-κ^3*P*,κ^2*C*)Ru] (3). A solution of ligand N(CH$_2$DPP)$_3$ (**1**) (482 mg, 0.623 mmol) and [(COD)Ru(methylallyl)$_2$] (209 mg, 0.654 mmol) in toluene was heated to 125 °C for 2 days in an ACE pressure tube, whereupon a yellow precipitate formed. Removal of the solvent in vacuo and addition of pentane (6 mL) to the oily residue produced a yellow solid, which was washed with pentane (3 × 5 mL) and dried in vacuo (496 mg, 0.568 mmol, 91%). ^{1}H NMR (C_6D_6, 600.13 MHz, 295 K): δ 1.18−1.54 (m, 5 H, 4 × C*H*$_2$, C*H*), 1.55−1.77 (m, 4 H, 3 × C*H*$_2$, NC*H*$_2$P), 1.90 (m, 1 H, C*H*$_2$), 1.96−2.07 (m, 3 H, 2 × C*H*$_2$, NC*H*$_2$P), 2.12 (m, 1 H, C*H*$_2$), 2.26 (d, ^2J(H,H) = 15.4 Hz, 1 H, NC*H*$_2$P), 2.37−5.52 (m, 2 H, C*H*$_2$, NC*H*$_2$P), 2.88 (d, ^2J(H,H) = 15.4 Hz, 1 H, NC*H*$_2$P), 2.91 (m, 1 H, C*H*), 3.19 (dd, ^3J(H,H) = 10.5 Hz, ^3J(H,H) = 6.6 Hz, 1 H, C*H*), 3.24 (m, 1 H, C*H*), 3.29 (m, 1 H, C*H*), 3.40 (d, ^2J(H,H) = 15.4 Hz, 1 H, NC*H*$_2$P), 3.65 (m, 1 H, C*H*), 5.23 (bs, 2 H, *o*-*H*^{Ar}), 6.54−7.60 (m, 24 H, *H*^{Ar}), 8.65 (m, 1 H, *H*^{Ar}), 8.90 ppm (m, 1 H, *H*^{Ar}). ^{13}C{^{1}H} NMR (C_6D_6, 150.92 Hz, 295 K): δ 34.6 (d, ^2J(C,P) = 4.0 Hz, *C*H$_2$), 34.8 (d, ^2J(C,P) = 6.6 Hz, *C*H$_2$), 35.4 (s, *C*H$_2$), 36.5 (s, *C*H$_2$), 36.5 (s, *C*H$_2$), 38.2 (d, ^2J(C,P) = 3.1 Hz, *C*H$_2$), 43.4 (m, *C*H), 45.3 (m, *C*H), 46.1 (m, *C*H), 50.6 (m, NC*H*$_2$P), 50.8 (m, NC*H*$_2$P), 51.4 (m, NC*H*$_2$P), 55.7 (m, *C*H), 57.5 (m, *C*H), 60.0 (m, *C*H), 121.9 (s, *C*H^{Ar}), 122.2 (b, *C*H^{Ar}), 123.1 (s, *C*H^{Ar}), 123.9 (m, *C*H^{Ar}), 124.5 (m, *C*H^{Ar}), 125.2 (m, *C*H^{Ar}), 125.8 (s, *C*H^{Ar}), 126.2 (s, *C*H^{Ar}), 126.4 (m, *C*H^{Ar}), 126.5 (s, *C*H^{Ar}), 127.1 (s, *C*H^{Ar}), 128.2 (m, *C*H^{Ar}), 128.5 (s, *C*H^{Ar}), 128.6 (s, *C*H^{Ar}), 129.0 (s, *C*H^{Ar}), 129.5 (m, *C*H^{Ar}), 130.5 (m, *C*H^{Ar}), 134.1 (s, *C*H^{Ar}), 139.2 (m, *C*H^{Ar}), 140.3 (d, J(C,P) = 4.2 Hz, *C*^{Ar}), 140.6 (m, *C*H^{Ar}), 141.8 (d, J(C,P) = 5.0 Hz, *C*^{Ar}), 143.4 (d, J(C,P) = 7.1 Hz, *C*^{Ar}), 152.1 (m, *C*^{Ar}), 152.3 (m, *C*^{Ar}), 153.9 (d, J(C,P) = 24.7 Hz, *C*^{Ar}), 178.7 (m, *C*^{Ar}), 185.3 ppm (m, *C*^{Ar}). ^{31}P{^{1}H} NMR (C_6D_6, 242.92 Hz, 295 K): δ 29.7 (dd, ^2J(P,P) = 29.3 Hz, ^2J(P,P) = 19.3 Hz, 1 P), 60.1 (dd, ^2J(P,P) = 27.7 Hz, ^2J(P,P) = 19.4 Hz, 1 P), 107.6 ppm (dd, ^2J(P,P) = ^2J(P,P) = 28.5 Hz, 1 P). Anal. Calcd for $C_{51}H_{52}NP_3Ru$: C, 70.17; H, 6.00; N, 1.60. Found: C, 69.93; H, 6.48; N, 1.64. HRMS (ESI): *m*/*z* calcd for $C_{51}H_{53}NP_3Ru$ ([M + H]) 874.2434, found 874.2485.

Synthesis of [(N(CH$_2$DPP)$_3$-κ^3*P*)RuH$_4$] (5). A solution of **5** (6.2 mg, 0.0071 mmol) in C_6D_6 (0.45 mL) was pressurized with H_2 (10 bar) in a pressure NMR tube. The product forms within seconds upon shaking. The reaction is reversible, and the product is in equilibrium with complex **4** (5% based on ^{31}P{^{1}H} NMR). Purging of the NMR tube with argon leads to the back-formation of the starting complex. As the product is stable only under a hydrogen atmosphere, it cannot be isolated. ^{1}H NMR (C_6D_6, 600.13 MHz, 295 K): δ −7.34 (q, ^2J(H,P) = 9.8 Hz, 4 H, hydride), 1.37−1.48 (m, 6 H, C*H*, C*H*$_2$), 1.99 (m, 3 H, C*H*$_2$), 2.46−2.55 (m, 6 H, NC*H*$_2$P, C*H*$_2$), 2.65 (m, 3 H, C*H*$_2$), 3.02 (d, ^2J(H,H) = 15.3 Hz, 3 H, NC*H*$_2$P), 3.45 (m, 3 H, C*H*), 6.79 (t, ^3J(H,H) = 7.3 Hz, 3 H, *H*^{Ar}), 6.82 (d, ^3J(H,H) = 7.7 Hz, 6 H, *H*^{Ar}), 7.00 (b, 6 H, *H*^{Ar}), 7.06 (t, ^3J(H,H) = 7.3 Hz, 3 H, *H*^{Ar}), 7.15 (m, 6 H, *H*^{Ar}), 8.11 ppm (b, 6 H, *H*^{Ar}). ^{13}C{^{1}H} NMR (C_6D_6, 150.92 Hz, 295 K): δ 26.7 (m, *C*H$_2$), 30.0 (m, *C*H$_2$), 42.8 (m, *C*H), 46.6 (m, NC*H*$_2$P), 52.1 (m, *C*H), 125.9 (s, *C*H^{Ar}), 126.7 (s, *C*H^{Ar}), 128.0 (s, *C*H^{Ar}), 128.9 (s, *C*H^{Ar}), 129.1 (b, *C*H^{Ar}), 129.9 (b, *C*H^{Ar}), 140.1 (s, *C*^{Ar}), 143.4 ppm (m, *C*^{Ar}). ^{31}P{^{1}H} NMR (C_6D_6, 242.92 Hz, 295 K): δ 46.4 ppm (s).

Synthesis of [(N(CH$_2$DPP)$_3$SiPh$_2$H$_2$-κ^3*P*,κ^1*C*,κ^2*SiH*$_2$)Ru] (6). To a solution of [Ru(*C*$_3$DPP)] (50.1 mg, 0.0574 mmol) in THF (2 mL) was added diphenylsilane (11 μL, 0.0593 mmol). After stirring for 20 min at room temperature, the solvent was removed in vacuo. Addition of diethyl ether to the oily residue produced a solid, which was washed with diethyl ether and dried in vacuo (43.9 mg, 0.0415 mmol, 72%). ^{1}H NMR (C_6D_6, 600.13 MHz, 295 K): δ −6.08 (b, 2 H, hydrides), 1.15−1.30 (m, 2 H, 2 × C*H*$_2$), 1.30−1.50 (m, 5 H, 4 × C*H*$_2$), 1.52−1.62 (m, 2 H, C*H*$_2$, NC*H*$_2$P), 1.75 (d, ^2J(H,H) = 15.2 Hz, 1 H, NC*H*$_2$P), 1.78−1.85 (m, 2 H, C*H*$_2$, NC*H*$_2$P), 1.90 (m, 1 H, C*H*$_2$), 2.00 (m, 1 H, C*H*$_2$), 2.21 (m, 1 H, C*H*$_2$), 2.32 (m, 1 H, C*H*$_2$), 2.50 (m, 1 H, C*H*), 2.62 (d, ^1J(H,H) = 5.5 Hz, 1 H, C*H*), 3.15−3.24 (m, 2 H, C*H*, NC*H*$_2$P), 3.35 (d, ^1J(H,H) = 10.8 Hz, 1 H, C*H*), 3.42 (m, 1 H, C*H*), 3.65 (d, ^2J(H,H) = 15.2 Hz, 1 H, NC*H*$_2$P), 3.72 (m, 1 H, C*H*), 3.78 (d, ^2J(H,H) = 15.5 Hz, 1 H, NC*H*$_2$P), 6.77−7.76 ppm (m, 38 H, *H*^{Ar}). ^{13}C{^{1}H} NMR (C_6D_6, 150.92 Hz, 295 K): δ 32.4 (d, ^2J(C,P) = 9.2 Hz, *C*H$_2$), 34.6 (s, *C*H$_2$), 37.0 (s, *C*H$_2$), 37.1 (m, *C*H$_2$), 38.7 (s, *C*H$_2$), 39.0 (s, *C*H$_2$), 44.2 (m, *C*H), 48.6 (m, *C*H), 49.0 (m, NC*H*$_2$P), 50.4 (m, *C*H), 50.7 (m, NC*H*$_2$P), 52.1 (m, *C*H), 54.2−54.4 (m, *C*H, NC*H*$_2$P), 54.7 (m, *C*H), 122.2 (s, *C*H^{Ar}), 124.9 (d, J(C,P) = 17.9 Hz, *C*H^{Ar}), 125.1 (s, *C*H^{Ar}), 125.3 (m, *C*H^{Ar}), 126.4 (s, *C*H^{Ar}), 126.7 (s, *C*H^{Ar}), 126.8 (s, *C*H^{Ar}), 127.0−127.1 (m, 2 × *C*H^{Ar}), 127.5 (s, *C*H^{Ar}), 127.9 (m, *C*H^{Ar}), 128.1−128.3 (m, 4 × *C*H^{Ar}), 128.7 (s, *C*H^{Ar}), 129.1 (s, *C*H^{Ar}), 129.3 (m, *C*H^{Ar}), 130.7 (b, 2 × *C*H^{Ar}), 131.1 (d, J(C,P) = 9.3 Hz, *C*H^{Ar}), 131.7 (d, J(C,P) = 9.6 Hz, *C*H^{Ar}), 135.4 (s, *C*H^{Ar}), 137.1 (b, *C*H^{Ar}), 137.5 (m, *C*H^{Ar}), 141.7 (d, J(C,P) = 1.8 Hz, *C*^{Ar}), 141.9 (d, J(C,P) = 6.7 Hz, *C*^{Ar}), 142.6 (d, J(C,P) = 4.6 Hz, *C*^{Ar}), 142.8 (d, J(C,P) = 5.1 Hz, *C*^{Ar}), 143.8 (m, *C*^{Ar}), 147.1−147.3 (m, 2 × *C*^{Ar}), 147.8 (m, *C*H^{Ar}), 148.1 (d, J(C,P) = 6.9 Hz, *C*^{Ar}), 156.0 (m, *C*^{Ar}), 170.2 ppm (m, *C*^{Ar}). ^{31}P{^{1}H} NMR (C_6D_6, 242.92 Hz, 295 K): δ 20.2 (dd, ^2J(P,P) = 37.5 Hz, ^2J(P,P) = 29.3 Hz, 1 P), 32.0 (dd, ^2J(P,P) = 37.4 Hz, ^2J(P,P) = 33.2 Hz, 1 P), 54.4 ppm (dd, ^2J(P,P) = 32.9 Hz, ^2J(P,P) = 29.5 Hz, 1 P). ^{19}Si NMR (C_6D_6, 79.44 Hz, 296 K, resonance detected by ^{1}H, ^{19}Si-HMBC): 4.8 ppm. Anal. Calcd for $C_{63}H_{64}NP_3RuSi$: C, 71.57; H, 6.10; N, 1.32. Found: C, 71.29; H, 5.85; N, 1.33. HRMS (ESI): *m*/*z* calcd for $C_{63}H_{62}NP_3{}^{102}RuSi$ ([M − H_2]) 1055.2908, found 1055.2919.

Synthesis of [(N(CH$_2$DPP)$_3$SiPh$_2$H$_2$-κ^3*P*,κ^3*SiH*$_2$)RuH] (7). A solution of [Ru(*C*$_3$DPPSiPh$_2$)H$_2$] (11.1 mg, 0.0105 mmol) in C_6D_6 (0.5 mL) was pressurized with H_2 (10 bar) in a pressure NMR tube. The product forms within seconds upon shaking. The reaction is reversible, and the product is in equilibrium with the starting complex (4% based on ^{31}P{^{1}H} NMR). Purging of the NMR tube with argon leads to the back-formation of the starting complex. As the product is stable only under a hydrogen atmosphere, it cannot be isolated. ^{1}H NMR (C_6D_6, 600.13 MHz, 295 K): δ −7.48 (m, 3 H, hydrides), 0.98 (m, 1 H, C*H*$_2$), 1.35−1.53 (m, 3 H, C*H*, 2 × C*H*$_2$), 1.63 (m, 1 H, C*H*), 1.81 (m, 1 H, C*H*$_2$), 1.97 (m, 1 H, C*H*$_2$), 2.02−2.38 (m, 7 H, 5

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× CH_2, NCH_2P, CH), 2.42−2.59 (m, 4 H, 2 × CH_2, 2 × NCH_2P), 2.73 (d, ^2J(H,H) = 15.2 Hz, 1 H, NCH_2P), 2.92 (d, ^2J(H,H) = 15.0 Hz, 1 H, NCH_2P), 3.04 (d, ^2J(H,H) = 15.6 Hz, 1 H, NCH_2P), 3.46 (m, 1 H, CH), 3.59 (m, 1 H, CH), 3.69 (m, 1 H, CH), 6.74−7.69 (m, 34 H, H^{Ar}), 7.95 (d, ^3J(H,H) = 7.3 Hz, 1 H, H^{Ar}), 8.29 (d, ^3J(H,H) = 7.4 Hz, 2 H, H^{Ar}), 8.52 ppm (m, 2 H, H^{Ar}). $^{13}C\{^1H\}$ NMR (C_6D_6, 150.92 Hz, 295 K): δ 26.6 (d, ^2J(C,P) = 9.9 Hz, CH_2), 29.2 (d, ^2J(C,P) = 8.6 Hz, CH_2), 30.7 (d, ^2J(C,P) = 17.7 Hz, CH_2), 31.1 (d, ^2J(C,P) = 6.6 Hz, CH_2), 34.5 (d, ^2J(C,P) = 14.3 Hz, CH_2), 36.5 (d, ^2J(C,P) = 12.1 Hz, CH_2), 42.7 (dd, ^1J(C,P) = 20.8 Hz, ^3J(C,P) = 2.3 Hz, CH), 43.1 (dd, ^1J(C,P) = 14.7 Hz, ^3J(C,P) = 3.1 Hz, CH), 46.5 (d, ^1J(C,P) = 11.5 Hz, NCH_2P), 47.1 (d, ^1J(C,P) = 10.1 Hz, CH), 48.8 (dd, ^1J(C,P) = 14.13 Hz, ^3J(C,P) = 7.8 Hz, NCH_2P), 50.2 (dd, ^1J(C,P) = 15.1 Hz, ^3J(C,P) = 5.7 Hz, NCH_2P), 51.1−51.3 (m, CH, CH), 53.6 (m, CH), 126.2 (s, CH^{Ar}), 126.2 (s, CH^{Ar}), 126.3 (s, CH^{Ar}), 126.9 (s, CH^{Ar}), 127.1 (s, CH^{Ar}), 127.1 (s, CH^{Ar}), 127.3 (s, CH^{Ar}), 127.5 (s, CH^{Ar}), 128.2−128.4 (m, 3x CH^{Ar}), 128.5 (b, CH^{Ar}), 128.7 (s, CH^{Ar}), 128.8−129.0 (m, 3 × CH^{Ar}), 129.6 (s, CH^{Ar}), 129.8 (m, CH^{Ar}), 130.5 (m, CH^{Ar}), 131.6 (d, J(C,P) = 7.5 Hz, CH^{Ar}), 137.0 (s, CH^{Ar}), 137.8 (s, CH^{Ar}), 138.4 (s, CH^{Ar}), 139.3 (d, J(C,P) = 2.4 Hz, C^{Ar}), 141.4 (d, J(C,P) = 4.5 Hz, C^{Ar}), 142.4 (d, J(C,P) = 9.3 Hz, C^{Ar}), 144.0 (d, J(C,P) = 8.7 Hz, C^{Ar}), 144.3−144.4 (m, 2x C^{Ar}), 148.6 (d, J(C,P) = 4.0 Hz, C^{Ar}), 149.6 (m, C^{Ar}), 151.6 ppm (m, C^{Ar}). $^{31}P\{^1H\}$ NMR (C_6D_6, 242.92 Hz, 295 K): δ 33.0 (dd, ^2J(P,P) = ^2J(P,P) = 31.6 Hz, 1 P), 33.4 (dd, ^2J(P,P) = ^2J(P,P) = 32.1 Hz, 1 P), 57.6 ppm (dd, ^2J(P,P) = ^2J(P,P) = 31.9 Hz, 1 P). ^{19}Si NMR (C_6D_6, 79.44 Hz, 296 K, resonance detected by ^1H, ^{19}Si-HMBC): 23.4 ppm.

X-ray Crystal Structure Determinations. *Crystal data of complex* ***6****:* $C_{63}H_{64}NP_3RuSi$, orthorhombic, space group $P2_12_12_1$, a = 11.90299(5) Å, b = 19.06264(8) Å, c = 22.67018(10) Å, V = 5143.92(4) Å^3, Z = 4, λ = 0.71073, μ = 0.464 mm^{-1}, F_{000} = 2208, T = 110(2) K, θ range 3.2 to 32.4°, index ranges h, k, l −17...17, −28...28, −34...34, 614 554 reflections measured, 18 157 independent reflections (R_{int} = 0.0960), 17 253 observed reflections ($I > 2\sigma(I)$), final R indices ($F_o > 4\sigma(F_o)$) $R(F)$ = 0.0243, $R_w(F^2)$ = 0.0547, GOF = 1.05.

Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Mo Kα radiation, microfocus tube, multilayer mirror optics). Data were corrected for air and detector absorption, Lorentz, and polarization effects;[23] absorption by the crystal was treated analytically.[23,24] The structure was solved by the charge flip procedure[25] and refined by full-matrix least-squares methods based on F^2 against all unique reflections.[26] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally placed at calculated positions and refined with a riding model. The positions of the hydrogen atoms involved in the RhHSi agostic interactions were taken from difference Fourier syntheses and fully refined.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures showing the temperature dependences of the spin−lattice relaxation times (T_1) for **4**, **5**, **6**, and **7**. Temperature-dependent ^1H NMR spectra for **6**. CIF files giving crystallographic data for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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