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Formation of a Ruthenium(II) Dicyclohexyl(η^2-cyclohex-3-enyl)phosphine Hydride Complex from an Alkylidene Precursor

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*Summary: Treatment of Ru(=CHPh)Cl_2(PCy_3)$_2$ (Cy = cyclohexyl) with K[N(i-Pr_2PS)$_2$] afforded a mixture of Ru(=CHPh)[N(i-Pr_2PS)$_2$](PCy_3)Cl (**1**) and Ru(=CHPh)-[N(i-Pr_2PS)$_2$]$_2$ (**2**). Reaction of **1** with TlOPh gave Ru(=CHPh)[N(i-Pr_2PS)$_2$](PCy_3)(OPh) (**3**), whereas that with NaOMe yielded the Ru(II) hydride compound Ru(H)[N(i-Pr_2PS)$_2$][PCy_2(η^2-C_6H_9)] (**4**), in which the dicyclohexyl(cyclohex-3-enyl)phosphine ligand binds to Ru via the phosphorus atom and the C=C bond of the cyclohex-3-enyl ring. The structures of complexes **3** and **4** have been established by X-ray crystallography.*

Introduction

Ruthenium alkylidene complexes have attracted much attention due to their applications in alkene metathesis and organic synthesis.[1] While Ru alkylidene complexes supported by phosphine, N-heterocyclic carbene, and nitrogen ligands are well documented, relatively few Ru alkylidene complexes with sulfur ligands have been isolated.[2,3] Organoruthenium complexes with sulfur ligands are of interest because of their possible involvement as intermediates in RuS_2-based catalytic processes, e.g., hydrodesulfurization.[4]

Dichalcogenoimidodiphosphinates $[N(R_2PQ)_2]^-$ (R = alkyl, aryl; Q = O, S, Se) have been recognized as chalcogen analogues of acetylacetonate (Chart 1). Unlike acetylacetonate, $[N(R_2PQ)_2]^-$ can bind to metal ions in various binding modes with high electronic and structural flexibilities.[5] Previously, we found that the Ru[$N(R_2PS)_2$]$_2$ core can form stable complexes with a variety of ligands including carbene, diazene, and sulfur monoxide.[2,6] Ru(=CHPh)[$N(R_2PS)_2$]$_2$ can catalyze ring-opening polymerization of norbornene.[2] As an extension of this work, we sought to explore the organometallic chemistry of monochelated Ru alkylidene complexes of the type Ru(=CHPh)[$N(R_2PS)_2$](PR_3)X.

We are particularly interested in Ru alkoxide and aryloxide derivatives because late transition-metal alkoxide and aryloxide complexes are known to exhibit nucleophilic reactivity[7] and may find applications in C−H activation.[8] Additionally, Ru alkylidene aryloxide complexes were found to be active catalysts for ring-closing metathesis.[9] Herein, we describe the synthesis of Ru(=CHPh)[N(*i*-Pr_2PS)$_2$](PCy_3)Cl (**1**) (Cy = cyclohexyl) and its reactions with TlOPh and NaOMe. The formation of a Ru(II) hydride complex containing a dicyclohexyl(η^2-cyclohex-3-enyl)phosphine ligand from the reaction of **1** with NaOMe will be reported.

Experimental Section

General Considerations. All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300, 75.5, and 121.5 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H and ^{13}C) and H_3PO_4 (^{31}P). Elemental analyses were performed by Medac Ltd., Surrey, UK.

The compound Ru(=CHPh)Cl_2(PCy_3)$_2$ (Grubbs first-generation catalyst) was purchased from Aldrich and used as received. The ligand K[N(*i*-Pr_2PS)$_2$] was synthesized according to a literature method.[10]

Preparations of Ru(=CHPh)[N(*i*-Pr_2PS)$_2$](PCy_3)Cl (1) and Ru(=CHPh)[N(*i*-Pr_2PS)$_2$]$_2$ (2). To a solution of Ru(=CHPh)-(PCy_3)$_2$$Cl_2$ (60 mg, 0.061 mmol) in tetrahydrofuran (THF) (10 mL) was added 1.3 equiv of K[N(*i*-Pr_2PS)$_2$] (33 mg, 0.079 mmol), and the reaction mixture was stirred at room temperature for 40 h, during which the purple solution turned dark

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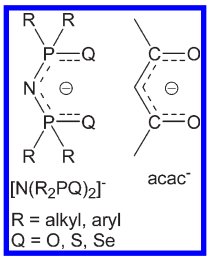
Chart 1



yellow. The solvent was pumped off, and the residue was extracted with hexane. The filtrate was concentrated to ca. 2 mL and allowed to stand at room temperature to give brown crystals of **1**. Concentration of the mother liquor and cooling at −10 °C afforded light green solid of **2**.

1: Yield: 33 mg, 56%. ^{1}H NMR (C_6D_6): δ 0.83−2.62 (m, 61H, Cy and *i*-Pr), 7.19−7.31 (m, 3H, H_m and H_p of Ph), 8.74 (d, J_{HH} = 8.1 Hz, 2H, H_o of Ph), 18.74 (d, $^3J_{PH}$ = 13.2 Hz, 1H, H_α). ^{31}P{^{1}H} NMR (C_6D_6): δ 40.77 (dd, J_{PP} = 9.7, 3.6 Hz, PCy_3), 57.38 (dd, J_{PP} = 19.6, 9.7 Hz, [N(*i*-$Pr_2PS)_2]^-$), 59.12 (dd, J_{PP} = 19.6, 3.6 Hz,). ^{13}C{^{1}H} NMR (C_6D_6): δ 292.02 (s, C_α).

2: Yield: 9 mg, 18%. ^{1}H NMR (C_6D_6): δ 1.19−1.25 (m, 24H, $(CH_3)_2CH$), 1.30−1.64 (m, 24H, $(CH_3)_2CH$), 2.13 (m, 4H, $(CH_3)_2CH$), 2.30 (m, 4H, $(CH_3)_2CH$), 7.46 (t, J_{HH} = 7.5 Hz, 2H, H_m of Ph), 7.59 (t, J_{HH} = 7.5 Hz, 1H, H_p of Ph), 8.61 (d, J_{HH} = 7.5 Hz, 2H, H_o of Ph), 20.20 (s, 1H, H_α). ^{31}P{^{1}H} NMR (C_6D_6): δ 61.74 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 294.64 (s, C_α).

Preparation of Ru(=CHPh)[N(*i*-$Pr_2PS)_2$](PCy$_3$)(OPh) (3). To a solution of **1** (30 mg, 0.037 mmol) in THF (10 mL) was added TlOPh (12 mg, 0.040 mmol), and the reaction mixture was stirred at room temperature for 5 h, during which the dark yellow solution turned yellowish-green. The solvent was pumped off and the residue was extracted with hexane. Concentration and cooling at −10 °C afforded dark green crystals. Yield: 21 mg, 67%. ^{1}H NMR (C_6D_6): δ 1.12−2.61 (m, 61H, Cy and *i*-Pr), 7.06 (t, J_{HH} = 7.2 Hz, 1H, H_p of OPh), 7.29 (d, J_{HH} = 7.8 Hz, 2H, H_o of OPh), 7.51−7.63 (m, 5H, H_m and H_p of CHPh and H_m of OPh) 8.76 (d, J_{HH} = 7.2 Hz, 2H, H_o of CHPh), 18.78 (d, $^3J_{PH}$ = 15.6 Hz, 1H, H_α). ^{31}P{^{1}H} NMR (C_6D_6): δ 36.69 (dd, J_{PP} = 11.3, 6.6 Hz, PCy_3), 57.39 (dd, J_{PP} = 11.3 Hz, J = 19.7 Hz, L), 60.31 (dd, J = 19.7, 6.6 Hz, [N(*i*-$Pr_2PS)_2]^-$). ^{13}C{^{1}H} NMR (C_6D_6): δ 286.52 (s, C_α).

Preparation of Ru(H)[N(*i*-$Pr_2PS)_2$][PCy$_2$(η^2-C_6H_9)] (4). A mixture of **1** (82 mg, 0.10 mmol) and excess sodium methoxide (32 mg, 0.60 mmol) was heated in THF (10 mL) at 45 °C for 0.5 h, during which the dark yellow solution turned orange. The solvent was pumped off and the residue was extracted with hexane. Concentration and cooling at −30 °C afforded orange crystals. Yield: 35 mg, 52%. ^{1}H NMR (C_6D_6): δ −22.84 (d, $^2J_{PH}$ = 36 Hz, 1H, Ru*H*), 1.11−2.89 (m, 31H, Cy and C_6H_9), 1.50 (m, 24H, $(CH_3)_2CH$), 2.25 (m, 4H, $(CH_3)_2CH$), 4.56 (m, 1H, olefinic proton), 4.72 (m, 1H, olefinic proton). ^{31}P{^{1}H} NMR (C_6D_6): δ 60.01 (d, J_{PP} = 4.7 Hz, [N(*i*-$Pr_2PS)_2]^-$), 80.14 (t, J_{PP} = 4.7 Hz, PCy_2). Anal. Calcd for $C_{30}H_{60}NP_3RuS_2$: C, 52.0; H, 8.7; N, 2.0. Found: C, 52.0; H, 8.8; N, 2.1.

X-ray Crystallography. Crystallographic data and experimental details for **3** and **4** are summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were corrected for absorption using the program SADABS.[11] Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[12]

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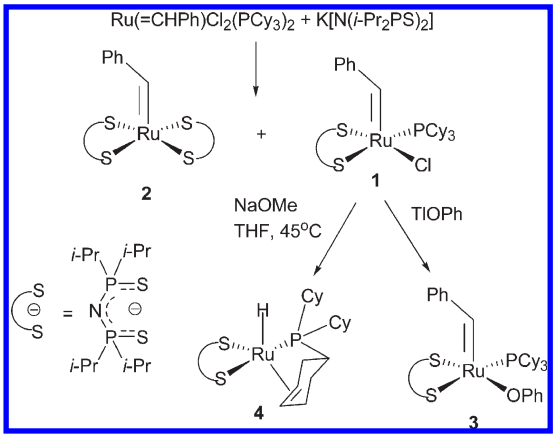
Table 1. Crystallographic Data and Experimental Details for Ru(=CHPh)[N(*i*-$Pr_2PS)_2$](PCy$_3$)(OPh)·C_6H_{12} (3·C_6H_{12}) and Ru(H)[N(*i*-$Pr_2PS)_2$][PCy$_2$(η^2-C_6H_9)] (4)

	3·C_6H_{12}	4
empirical formula	$C_{49}H_{84}NOP_3RuS_2$	$C_{30}H_{60}NP_3RuS_2$
fw	961.27	692.89
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	18.3351(13)	9.6266(10)
b, Å	14.4241(10)	11.5208(12)
c, Å	19.9515(14)	16.9307(18)
α, deg		95.7840(10)
β, deg	106.697(1)	102.7490(10)
γ, deg		108.0770(10)
V, Å^3	4967.8(6)	1711.8(3)
Z	4	2
ρ_{calcd}, g cm^{-1}	1.285	1.344
temp, K	100(2)	100(2)
F(000)	2056	736
μ(Mo Kα), mm^{-1}	0.532	0.740
total reflns	24418	17612
indep reflns	8629	6629
R_{int}	0.0430	0.0220
GoF[a]	0.979	1.050
R_1[b], wR_2[c] ($I > 2\sigma(I)$)	0.0380, 0.0810	0.0239, 0.0587
R_1, wR_2 (all data)	0.0557, 0.0862	0.0283, 0.0602

[a] GoF = $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$. [b] $R_1 = (\sum(|F_o| - |F_c|)/\sum|F_o|$. [c] $wR_2 = [\sum w^2(|F_o| - |F_c|)^2/\sum w^2F_o|^2]^{1/2}$.

Scheme 1. Synthesis of 3 and 4



Results and Discussion

Ru Alkylidene Complexes. The syntheses and reactivity of Ru[N(*i*-$Pr_2PS)_2$] benzylidene complexes are summarized in Scheme 1. Previously, we reported the synthesis of Ru(=CHPh)[N($Ph_2PS)_2$]$_2$ by the reaction of Ru(=CHPh)Cl$_2$(PCy$_3$)$_2$ with 2 equiv of K[N($Ph_2PS)_2$].[2] In this work, we found that the reaction of Ru(=CHPh)Cl$_2$(PCy$_3$)$_2$ with 1 equiv of K[N(*i*-$Pr_2PS)_2$] gave a mixture of the monochelated Ru(=CHPh)[N(*i*-$Pr_2PS)_2$](PCy$_3$)Cl (**1**) and bis-chelated Ru(=CHPh)[N(*i*-$Pr_2PS)_2]_2$ (**2**) complexes, which could be separated by fractional recrystallization from hexane. The yield of **1** was optimized to be around 56% when 1.3 equiv of K[N(*i*-$Pr_2PS)_2$] was used. Complexes **1** and **2** are soluble in most organic solvents including hexane, and air stable in both the solid state and solutions. In the ^{1}H NMR spectrum of **1** the carbene proton appeared as a doublet at δ 18.74 ($^3J_{PH}$ = 13.2 Hz), which is more upfield than that of **2** (δ 20.2 (s)). The ^{31}P{^{1}H} NMR spectrum of **1** displayed two doublets of doublets at δ 57.38 and 59.12 and a doublet of doublets at δ 40.77 that are assigned to the coordinated [N(*i*-$Pr_2PS)_2]^-$

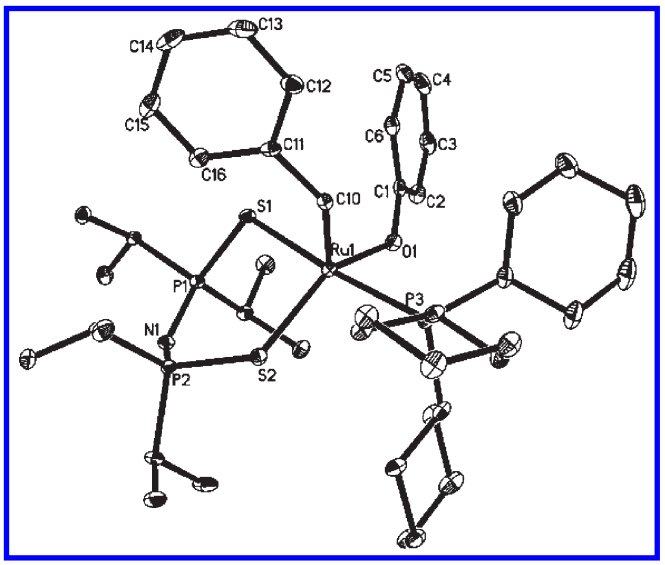


Figure 1. Molecular structure of Ru(=CHPh)[N(*i*-$Pr_2PS)_2$](PCy_3)(OPh) (**3**). Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at a 30% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)−C(10) 1.852(3), Ru(1)−S(1) 2.4529(7), Ru(1)−S(2) 2.3250(7), Ru(1)−P(3) 2.3648(8), Ru(1)−O(1) 1.9953(18), S(1)−P(1) 2.0116(10), S(2)−P(2) 2.0494(10), N(1)−P(1) 1.607(2), N(1)−P(2) 1.573(2); C(10)−Ru(1)−S(1) 94.06(9), C(10)−Ru(1)−S(2) 103.40(8), C(10)−Ru(1)−P(3) 89.59(9), C(10)−Ru(1)−O(1) 109.47(10), S(1)−Ru(1)−S(2) 97.19(3), S(1)−Ru(1)−P(3) 170.69(3), S(1)−Ru(1)−O(1) 85.44(6), S(2)−Ru(1)−P(3) 90.28(3), S(2)−Ru(1)−O(1) 146.77(6), P(3)−Ru(1)−O(1) 85.26(6), Ru(1)−O(1)−C(11) 132.29(17), P(1)−N(1)−P(2) 131.30(16).

and PCy_3 ligands, respectively, whereas that of **2** showed a singlet at δ 61.74. The carbene carbons in **1** and **2** resonate at δ 292.02 and 294.64, respectively, which are similar to those of reported Ru benzylidene complexes.[2,13]

Reaction of 1 with TlOPh. Treatment of **1** with TlOPh in THF yielded the phenoxide complex Ru(=CHPh)[N(*i*-$Pr_2PS)_2$](PCy_3)(OPh) (**3**). Unlike **1**, complex **3** is air sensitive in both solutions and the solid state. The $^{31}P\{^1H\}$ spectrum of **3** displayed three doublets of doublets at δ 36.69, 57.39, and 60.31, which are assigned to PCy_3 and $[N(i\text{-}Pr_2PS)_2]^-$, respectively. The carbene carbon resonates at δ 286.52, which is more upfield than that of **1**.

Figure 1 shows the structure of **3**. The geometry around Ru is pseudo-square-pyramidal with the benzylidene ligand at the apical position. The Ru−C distance of 1.852(3) Å is typical for Ru alkylidene complexes. The Ru−S(trans to P) distance (2.4529(7) Å) is longer than the Ru−S(trans to O) distance (2.3250(7) Å) due to the trans influence of the phosphine ligand. The Ru−O distance of 1.9953(18) Å is similar to that in *cis,trans*-Ru(dtbpy)($CH_2SiMe_3)_2$(NO)(OPh) (dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl) (2.0212(9) Å).[14] The rather large Ru−O−C angle (132.29(17)°) in **3** is indicative of d_π(Ru)−p_π(O) interaction [cf. 128.72(9)° in *cis*, *trans*-Ru(dtbpy)($CH_2SiMe_3)_2$(NO)(OPh)].

Reaction of 1 with NaOMe. No reaction was found between **1** and K(O-*t*-Bu). Reaction of **1** with sodium methoxide in THF at 45 °C led to isolation of the hydride complex Ru(H)[N(*i*-$Pr_2PS)_2$][$PCy_2(\eta^2$-$C_6H_9)$] (**4**) containing a dicyclohexyl-

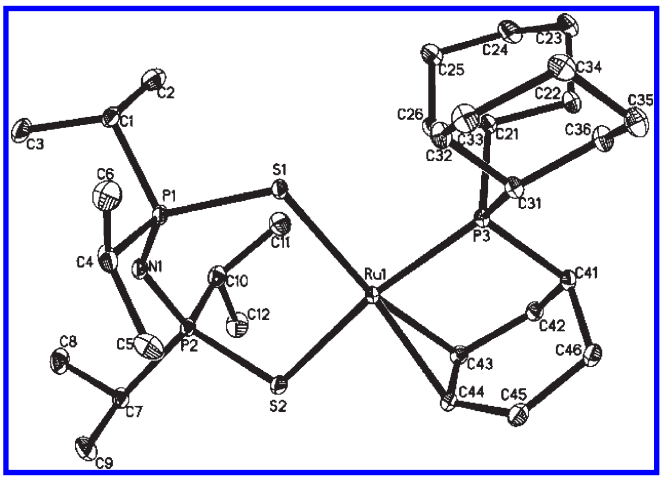


Figure 2. Molecular structure of Ru(H)[N(*i*-$Pr_2PS)_2$][$PCy_2(\eta^2$-$C_6H_9)$] (**4**). Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at a 30% probability level. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) 2.3957(5), Ru(1)−S(2) 2.4771(5), Ru(1)−P(3) 2.2460(5), Ru(1)−C(43) 2.1604(17), Ru(1)−C(44) 2.1671(17), P(1)−S(1) 2.0301(6), P(2)−S(2), 2.0084(7), N(1)−P(1) 1.5866(15), N(2)−P(2) 1.5936(15); S(1)−Ru(1)−S(2) 100.076(16), S(1)−Ru(1)−P(3) 91.197(17), S(2)−Ru(1)−P(3) 165.940(17), P(1)−N(1)−P(2) 134.06(10).

(η^2-cyclohex-3-enyl)phosphine ligand. The ^1H NMR spectrum of **4** displayed a doublet at δ −22.84 (d, $^2J_{PH}$ = 36 Hz) assignable to the hydride ligand. The olefinic protons in the η^2-cyclohex-3-enyl group appeared as two multiplets at δ 4.56 and 4.72. The $^{31}P\{^1H\}$ spectrum displayed a doublet at δ 60.01 and a triplet at δ 80.14, attributable to $[N(i\text{-}Pr_2PS)_2]^-$ and $PCy_2(\eta^2\text{-}C_6H_9)$, respectively.

Figure 2 shows the structure of **4**. The geometry around Ru is pseudo-square-pyramidal with the hydride occupying the apical position. The dicyclohexyl(cyclohex-3-enyl)phosphine ligand binds to Ru via the phosphorus atom and the C=C double bond in the cyclohex-3-enyl group. Such a binding mode of a tricycloalkylphosphine ligand has been found in Ru(η^2-C_2H_4)[$PCyp_2(\eta^2$-$C_5H_7)]_2$ and *trans*-Ru(H)$_2$[$PCyp_2(\eta^2$-$C_5H_7)]_2$ (Cyp = cyclopentyl) prepared from the reaction of Ru(η^2-$H_2)_2(PCyp_3)_2$ with C_2H_4.[15] The Ru−S(trans to P) distance (2.4771(5) Å) is obviously longer than Ru−S(trans to C), indicating that the phosphine has a stronger trans influence than the olefin group. The Ru−P distance in **4** (2.2460(5) Å) is considerably shorter than that in **3** presumably due to the chelate effect of the C=C bond in the cyclohex-3-enyl group. The C=C distance (1.404(3) Å) is similar to that in Ru(H)$_2$(CO)[$PCyp(\eta^2$-$C_5H_7)$]($PCyp_3$) (1.408(8) Å).[16] The Ru−C distances (2.1604(17) and 2.1671(17) Å) are shorter than those in Ru(H)$_2$(CO)[$PCyp(\eta^2$-$C_5H_7)$]($PCyp_3$) (2.301(6) and 2.276(6) Å) because the C=C bond in the latter is trans to a hydride ligand.

Degradation of Ru carbene complexes to hydride species is well documented.[17,18] Ruthenium hydrides have also been

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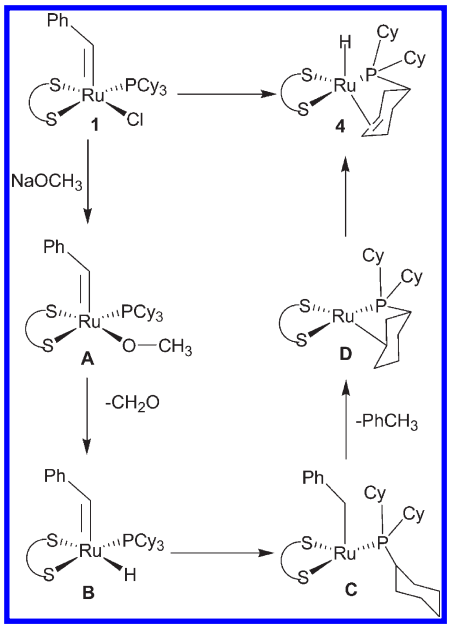
Scheme 2. Possible Mechanism for Formation of 4



proposed as reactive intermediates in the isomerization of alkenes, silylation of alcohols, and hydrosilylation of alkynes catalyzed by the Grubbs catalyst.[19] It seems reasonable to assume that the hydride **4** is derived from a Ru methoxide precursor. A possible mechanism for the formation of **4** is shown in Scheme 2. The first step involves the formation of a methoxide precursor (**A**) from **1** and NaOMe. β-Hydrogen elimination of **A** affords a benzylidene hydride intermediate (**B**) and formaldehyde. Hydride migration to the alkylidene group in **B** gives a benzyl species (**C**). A similar process has been found for the reaction of $Ru(=CHPh)Cl_2(PCy_3)_2$ with sodium dihydrobis(methimidazolyl)borate, which resulted in migration of the hydrogen in a B−H group to the alkylidene ligand and subsequent transfer of the benzyl fragment to boron.[20] Intramolecular C−H activation of a cyclohexyl group in the PCy_3 ligand and reductive elimination of toluene gives the cyclometalated Ru hydride species (**D**). Further C−H activation of the η^1-bound cyclohexyl group yields the Ru hydride product containing a dicyclohexyl(η^2-cyclohex-3-enyl)phosphine ligand. Consistent with this proposal, ^{1}H NMR spectroscopy confirmed that toluene was produced from the reaction of **1** with NaOMe in C_6D_6. It may also be noted that a similar pathway has been suggested by Dinger and Mol for the formation of $Ru(H)(CO)Cl(PCy_3)_2$ and toluene from the reaction of $Ru(=CHPh)Cl_2(PCy_3)_2$ with methanol in the presence of Et_3N.[17a] However, contrary to the reaction reported by Dinger and Mol, in which the carbonyl hydride was generated by decarbonylation of formaldehyde, in our system a carbonyl hydride species was not produced, and the hydride in **4** was derived from cyclometalation of a cyclohexyl ring.

In summary, we have synthesized and characterized a Ru benzylidene complex containing a dithiolate ligand, $Ru(=CHPh)[N(i\text{-}Pr_2PS)_2](PCy_3)Cl$ (**1**), which can serve as a starting material for Ru aryloxide/alkoxide complexes. Reaction of **1** with TlOPh gave a Ru phenoxide complex, whereas that with NaOMe led to formation of a Ru(II) hydride complex with a dicyclohexyl(η^2-cyclohex-3-enyl)phosphine ligand, presumably via hydride migration to the alkylidene group and subsequent dehydrogenation of a cyclohexyl ring in PCy_3.

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Supporting Information Available: Tables of crystal data, final atomic coordinates, anisotropic thermal parameters, complete bond lengths and angles for complexes **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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