

14-Electron Four-Coordinate Ru(II) Carbonyl Complexes and Their Five-Coordinate Precursors: Synthesis, Double Agostic Interactions, and Reactivity

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Abstract: The structure of five-coordinate Ru(II) complexes RuHCl(CO)(PⁱPr₃)₂, **1**, RuCl₂(CO)(PⁱPr₃)₂, **2**, and Ru(Ph)Cl(CO)(PⁱBu₂Me)₂, **12**, are reported. All three of these complexes have square-based pyramid geometry with the strongest σ -donor ligand trans to the vacant site. These 16-electron complexes do not show bona fide agostic interactions. This is attributed to the strong trans influence ligand (H, CO, and Ph) and π -donation of the Cl, which is further supported by the fact that two agostic interactions are present in the Cl⁻ removal product of **12**, i.e., the four-coordinate [RuPh(CO)L₂]BAR'₄ (L = PⁱBu₂Me, Ar' = 3,5-C₆H₃(CF₃)₂), **16**. Structural comparison of **16** and **12** reveals that removal of Cl⁻ does not change the remaining ligand arrangements but creates two low-lying LUMOs for agostic interactions, which persist in solution as evidenced by IR spectroscopy. Reactions of **16** with E–H (E = B, C(sp)) bonds cleave the Ru–Ph bond and form Ru–E/H bonds by different mechanisms. The reaction with catecholborane gives [RuH(CO)L₂]BAR'₄, which further reacts with catecholborane to give [Ru(BR₂)(CO)L₂]BAR'₄. However, the reaction with Me₃SiCCH undergoes a multistep transformation to give a PhCCSiMe₃- and Me₃SiCCH-coupled product, the mechanism of which is discussed. Reaction of RuCl₂(CO)L₂ with 1 equiv MeLi affords RuMeCl(CO)L₂, **5**, which further reacts with MeLi forming RuMe₂(CO)L₂, **7**. Variable-temperature ¹³C{¹H} NMR spectra reveal the two methyls in **7** are inequivalent and exchange by overcoming an energy barrier of 6.8 kcal/mol at –30 °C. The chloride of **5** can be removed to give [RuMe(CO)L₂]BAR'₄.

Introduction

Coordinatively and electronically unsaturated transition metal carbonyl complexes are key species in promoted reactions such as olefin polymerization, hydrogenation, hydrosilylation and hydroboration.¹ Particularly, complexes with formally 14-valence electrons, or 16-electron but bearing an extremely labile ligand (e.g., agostic bonding, weakly coordinating counterion or solvent) are recognized as the active catalytic component of olefin polymerization reactions and are extensively studied, both on early and late transition metals (III–IVB, Ni, Pd, Pt).² In sharp contrast, isolable 14-electron complexes of other transition metals are rare, although 14-electron species have been proposed often as active species in organometallic reactions.³ It has been proposed that a 14-electron complex has the advantage over its 16-electron counterpart since it provides two low-lying empty orbitals for substrate binding, and group (or atom) migration and bond formation.⁴ We wish to report our results on the synthesis and structure of four-coordinate Ru(II) carbonyl com-

plexes with a 14-electron count, [Ru(R)(CO)L₂]⁺ (R = CH₃, Ph, catecholboryl).⁵ The unusual structural feature of these complexes is the presence of two agostic interactions.

The geometry preference of five-coordinate d⁶ metal complexes has been well studied.⁶ The diamagnetic Ru or Os complexes with the general formula, MXY(CO)L₂ (X and Y are univalent ligands, L is usually a phosphine) adopt a square-based pyramidal geometry with the strongest trans influence ligand at the apical site so that the LUMO has the highest possible energy. When the X and Y are significantly different (e.g., H vs Cl) the geometry of the complex is rather obvious, but when the X and Y have similar trans influence (e.g., Me vs H or Ph), predicting the geometry is not straightforward. Although these complexes are fluxional, the primary reaction product is usually governed by the ground-state geometry.⁷ On the route to 14-electron Ru alkyl complexes, we have synthesized several five-coordinate precursors where X and Y are carbonyls of similar trans influence. Their geometry preferences

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Table 1. Crystallographic Data^a

	1	2	12	16
formula	C ₁₉ H ₄₃ ClOP ₂ Ru	C ₁₉ H ₄₂ Cl ₂ OP ₂ Ru	C ₂₅ H ₄₇ ClOP ₂ Ru	C ₅₇ H ₅₉ BF ₂₄ OP ₂ Ru
FW	485.99	520.44	562.12	1389.89
color	orange	red	orange	thermochromic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>T</i> (K)	173(2)	183(2)	103	103
<i>a</i> (Å)	8.0675(5)	21.867(4)	16.680(3)	18.176(3)
<i>b</i> (Å)	8.9312(7)	8.648(2)	17.037(4)	18.495(3)
<i>c</i> (Å)	16.6316(10)	15.033(2)	10.772(2)	18.090(3)
α (deg)	90	90	90.81(1)	90
β (deg)	92.492(5)	119.75(1)	92.85(1)	90
γ (deg)	90	90	112.68(1)	90
<i>Z</i>	2	4	4	4
<i>V</i> (Å ³)	1197.2(1)	2468.1(7)	2819.10	6081(46)
ρ_{calc} (g/cm ³)	1.348	1.401	1.324	1.518
λ (Å)	0.71073	0.71073	0.71069	0.71069
μ (cm ⁻¹)	6.85	9.88	7.66	4.23
wR ₂	0.069	0.0727	0.0464	0.062
<i>R</i> ₁	0.0264	0.0265	0.0655	0.061

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

Table 2. Geometric Parameters of RuHCl(CO)(PⁱPr₃)₂

Bond Lengths (Å)			
Ru–C(3)	1.752(6)	Ru–P(1)	2.3794(4)
Ru–Cl(2)	2.4219(18)	C(3)–O(3)	1.164(6)
Bond Angles (deg)			
P(1)–Ru–P(1)′	180	C(3)–Ru–Cl(2)	177.3(2)
P(1)–Ru–Cl(2)	89.34(5)	C(3)–Ru(1)–P(1)	90.04(14)
C(12)–P(1)–Ru	112.16(6)	C(13)–P(1)–Ru	113.62(7)
C(11)–P(1)–Ru	113.25(6)	Ru(1)–C(3)–O(3)	178.6(8)

are discussed based on spectroscopic data and X-ray structural data of related complexes.

Experimental Section

General Procedures. All reactions and manipulations were conducted using standard Schlenk and argon-filled glovebox techniques. Solvents were dried according to routine methods, distilled under argon, and stored in airtight solvent bulbs with Teflon closures. The solvents were also freshly degassed by freeze–pump–thaw cycles before use. All NMR solvents were dried, vacuum-transferred, and stored in an argon-filled glovebox. ¹H, ³¹P, ¹⁹F, and ¹³C NMR spectra were recorded on a Varian Gem XL300 or Unity I400 spectrometer. Chemical shifts are referenced to solvent peaks (¹H, ¹³C), or external H₃PO₄ (³¹P) and CFCl₃ (¹⁹F). Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. Elemental analyses were conducted on the Perkin-Elmer 2400 CHNS/O analyzer at the Department of Chemistry, Indiana University. RuHCl(CO)L₂⁸ and NaBAR₄⁹ are prepared following literature procedures. Other chemicals are commercially available and degassed before use.

X-ray Crystal Structure Determination of RuHCl(CO)(PⁱPr₃)₂, 1 (Tables 1 and 2). Orange crystals were obtained by slowly cooling a hot concentrated solution in a 3:1 MeOH/toluene mixture; Siemens four-circle diffractometer P4. Refinement used 209 parameters without constraints. Minimum and maximum peak of residual electron density in the final Fourier map $-0.450/0.921 \text{ e } \text{Å}^{-3}$. The structure was solved by direct methods (SHELXTL-Plus) and refined on *F*² (SHELXL93). Due to the special position of the ruthenium atom on a crystallographic inversion center, the CO and Cl ligand are disordered. The C(3), O(3), and Cl(2) atoms were refined as “half occupied” (50%). All non-H atoms were refined with anisotropic thermal parameters. All hydrogen atoms were introduced at their geometric positions and treated according to the “riding model” with isotropic thermal parameters fixed at 20% greater than that of the bonded C–H atom.

RuCl₂(CO)(PⁱPr₃)₂, 2. RuHCl(CO)(PⁱPr₃)₂ (200 mg, 0.41 mmol), PhCH₂Cl (1.0 g, 8.2 mmol), and 10 mL of toluene were mixed in a

Table 3. Geometric Parameters of RuCl₂(CO)(PⁱPr₃)₂

Bond Lengths (Å)			
Ru–C1	1.774(4)	Ru–Cl1	2.358(2)
Ru–P2	2.402(2)	Ru–P1	2.406(3)
C1–O1	1.164(5)	Ru–Cl2	2.382(3)
Bond Angles (deg)			
C1–Ru–Cl1	98.0(5)	Cl1–Ru–P1	90.99(9)
C1–Ru–P2	97.7(4)	C15–P1–Ru	114.6(3)
C1–Ru–P1	92.1(4)	C25–P2–Ru	116.8(3)
P2–Ru–P1	170.15(2)	Cl1–Ru–Cl2	165.97(3)
C18–P1–Ru	114.7(3)	Cl2–Ru–P2	90.89(9)
C28–P2–Ru	112.1(3)	Cl2–Ru–P1	87.66(9)
C1–Ru–Cl2	96.0(5)	C12–P1–Ru	110.2(3)
Cl1–Ru–P2	88.06(9)	C33–P2–Ru	106.7(3)

flask and heated at 80 °C for 4 h. The solution color changed from orange to brown. The volatiles were evaporated in vacuo, and the residue were extracted with diethyl ether. The diethyl ether solution was evaporated to a give brown solid, which was recrystallized from toluene at -40 °C. Yield: 150 mg (70%). Anal. Calcd for C₁₉H₄₂Cl₂OP₂Ru: C, 43.84, H, 8.07. Found: C, 44.29, H, 7.78. ¹H NMR (300 MHz, C₇D₈, 20 °C): δ 2.80 (m, 6H, PCH(CH₃)₂), 1.25 (vtd, *J*_{HH} = 6.5 Hz, *N* = 14.4 Hz, 36H, PCH(CH₃)₂). ³¹P{¹H} NMR (145 MHz, C₇D₈, 20 °C): 44.8 (s). IR(C₇D₈, cm⁻¹): 1937 (ν (CO)).

X-ray Crystal Structure Determination of RuCl₂(CO)(PⁱPr₃)₂. Single crystals were obtained by slow cooling of a hot saturated methanol solution of the compound. The single crystals were taken from the mother liquors, separated under Nujol, and sealed in a glass capillary. The data collection was performed on a Siemens-P4 four-circle diffractometer. The structure was solved by the Patterson method, using the SHELXTL-Plus package. The refinement was carried out with SHELXL-93, employing full-matrix least-squares methods. Anisotropic thermal parameters were refined for all non-hydrogen atoms. All hydrogen atoms were constrained using a riding model with isotropic thermal parameters fixed at 20% greater than that of the bonded atom. The structure was refined (227 parameters) on *F*² (SHELXL93); the maximum and the minimum peaks in the final difference Fourier map corresponded to $-0.345/0.839 \text{ e } \text{Å}^{-3}$ (Tables 1 and 3).

Ru(CH₃)Cl(CO)(PⁱPr₃)₂, 4. RuCl₂(CO)(PⁱPr₃)₂ (150 mg, 0.3 mmol) was dissolved in benzene (5 mL). To the solution, MeLi (1.4 mol/L in diethyl ether, 0.21 mL) was added, and the solution was stirred for 5 h. The solvent was removed, and the residue was extracted with pentane and filtered. The filtrate was concentrated to 3 mL and cooled to -40 °C for 1 day to give orange crystals. ¹H NMR (C₆D₆, 20 °C): 2.60 (m, 6H, PCH(CH₃)₂), 1.52 (t, *J* = 5 Hz, 3H, Ru–CH₃), 1.25 (vtd, *N* = 13.5 Hz, *J*_{HH} = 7 Hz, 18H, PCH(CH₃)₂), 1.20 (vtd, *N* = 13.5 Hz, *J* = 7 Hz, 18H, PCH(CH₃)₂). ³¹P{¹H} NMR: 37.7 (s).

NMR Study of the Reaction of RuCl₂(CO)(PⁱPr₃)₂ with MeLi. RuCl₂(CO)(PⁱPr₃)₂ (10 mg, 0.019 mmol) was dissolved in C₆H₆ (0.5

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as the crystal was cooled. A check of the unit cell parameters at -55 °C indicated no significant change from those measured at -164 °C however, so any phase change that may have taken place occurred above -55 °C.

Ru(Ph)F(CO)(P'Bu₂Me)₂, 13. Ru(Ph)Cl(CO)(P'Bu₂Me)₂ (200 mg, 0.36 mmol) and CsF (100 mg, 0.66 mmol) were mixed with acetone (5 mL) and stirred for 12 h. The mixture was filtered and the residue was washed with pentane. The combined filtrate was evaporated to dryness in vacuo. The crude product was recrystallized from pentane (-40 °C). Yield: 150 mg (77%). ¹H NMR (300 MHz, C₆D₆, 20 °C): 8.44 (d, $J_{\text{HH}} = 6.6$ Hz, 1H, ortho H of Ph), 7.50 (d, $J_{\text{HH}} = 8.1$ Hz, 1H, ortho H of Ph), 6.92 (m, 1H, para H of Ph), 6.90 (m, meta H of Ph), 6.83 (m, meta H of Ph), 1.31 (vt, $N = 5.7$ Hz, 6H, PCH₃), 1.08 (vt, $N = 13.2$ Hz, 18H, P'Bu), 0.99 (vt, $N = 12.6$ Hz, 18H, P'Bu). ³¹P{¹H} NMR (121 MHz, C₆D₆, 20 °C): 42.0 (d, $J_{\text{PF}} = 24$ Hz, Ru-P). ¹⁹F NMR (376 MHz, C₆D₆, 20 °C): -204.5 (t, $J = 24$ Hz, Ru-F). IR (C₆D₆, cm⁻¹): $\nu(\text{CO}) = 1890$.

Ru(Ph)OTf(CO)(P'Bu₂Me)₂, 14. (a) From Ph₂Hg. RuH(OTf)(CO)(P'Bu₂Me)₂ (0.50 g, 0.83 mmol) and Ph₂Hg (0.50 g, 1.4 mmol) were mixed in toluene (10 mL). The mixture was refluxed for 12 h, during which time mercury metal precipitates. The solution was cooled to room temperature and filtered through a Celite pad. The filtrate was evaporated to dryness. The resulting orange solid was heated in vacuo at 80 °C to sublime away excess Ph₂Hg. The remaining orange solid was dissolved in diethyl ether and filtered. The filtrate was concentrated to 3 mL and layered with pentane. Orange crystals were formed over 1 week. Yield: 0.45 g (80%).

(b) From Ru(Ph)F(CO)(P'Bu₂Me)₂ and Me₃SiOTf. RuPhF(CO)(P'Bu₂Me)₂ (150 mg, 0.28 mmol) was dissolved in cyclohexane (10 mL). To the solution, Me₃SiOTf (54 μ L, 0.28 mmol) was added. The mixture was stirred for 10 min and freed of volatiles. Recrystallization from toluene layered with pentane gave orange crystals. Yield: 110 mg (58%). ¹H NMR (300 MHz, C₆D₆, 20 °C): 8.0 (d, $J_{\text{HH}} = 7.8$ Hz, 1H, ortho H of Ph), 7.31 (d, $J_{\text{HH}} = 7.8$ Hz, 1H, ortho H of Ph), 6.90 (t, $J_{\text{HH}} = 7.4$ Hz, 1H, para H of Ph), 6.73 (m, 1H, meta H of Ph), 6.72 (m, 1H, meta H of Ph), 1.50 (br, s, 6H, PCH₃), 1.04 (vt, $N = 13.2$ Hz, 18H, P'Bu), 0.76 (vt, $N = 13.2$ Hz, 18H, P'Bu). ³¹P{¹H} NMR (121 MHz, C₆D₆, 20 °C): 40.5 (s, Ru-P). ¹⁹F NMR (282 MHz, C₆D₆, 20 °C): -77.7 (s, O₃SCF₃). IR (C₆D₆, cm⁻¹): $\nu(\text{CO}) = 1921$.

Ru(Ph)(CH₃)(CO)(P'Bu₂Me)₂, 15. RuPh(OTf)(CO)(P'Bu₂Me)₂ (200 mg, 0.36 mmol) was dissolved in toluene (10 mL). To the solution, MeLi (1.6 mol/L in diethyl ether, 200 μ L, 0.32 mmol) was added. The mixture was stirred for 5 min, and the volatiles were evaporated to dryness. The residue was dissolved in tetramethylsilane and filtered. Removal of the solvent results in a viscous oil, which was recrystallized from bis(trimethylsilyl) ether to give orange crystals. Yield: 40%. ¹H NMR (300 MHz, C₆D₆, 20 °C): 7.65 (d, $J_{\text{HH}} = 5.7$ Hz, 1H ortho H of Ph), 7.45 (d, $J_{\text{HH}} = 5.7$ Hz, 1H, ortho H of Ph), 6.72 (m, 3H, meta and para H of Ph), 1.42 (vt, $N = 12$ Hz, 18H, PCCCH₃), 1.05 (t, $J_{\text{PH}} = 4$ Hz, 3H, PCH₃), 0.99 (vt, $N = 12$ Hz, 18H, P(C(CH₃)₃)). ¹³C{¹H} NMR (C₇D₈, 100 MHz, 20 °C): 203.7 (t, $J_{\text{PC}} = 13$ Hz, Ru-CO), 158.5 (s, Ru-C_{ipso}), 144.0, 139.4, 126.6, 120.4 (s, Ph), 37.5 (vt, $N = 15$ Hz, PC(CH₃)₃), 36.4 (vt, $N = 16$ Hz, PC(CH₃)₃), 30.0, 29.5 (s, PC(CH₃)₃), 9.5 (br, Ru-CH₃), 5.1 (br, PCH₃). IR (C₆D₆, cm⁻¹): 1883 ($\nu(\text{CO})$). Anal. Calcd for C₂₆H₅₀OP₂Ru: C, 57.64, H, 9.30. Found: C, 57.38, H, 9.48.

[Ru(Ph)(CO)(P'Bu₂Me)₂]BAR'₄, 16. RuPh(OTf)(CO)(P'Bu₂Me)₂ (150 mg, 0.22 mmol) and NaBAR'₄ (201 mg, 0.23 mmol) were mixed in fluorobenzene (5 mL) in a test tube under argon. The mixture was shaken for 10 min and centrifuged. The liquid was transferred to a Schlenk flask and layered with pentane. After 2 days, red crystals were obtained. Yield: 160 mg (52%). Anal. Calcd for C₅₇H₅₉BF₂₄OP₂Ru: C, 48.59; H, 4.22. Found: C, 48.61; H, 4.10. ¹H NMR (CD₂Cl₂, 20 °C): 7.73 (s, 8H, BAR'₄), 7.57 (s, 4H, BAR'₄), 7.15 (br, s, 2H, Ph), 7.01 (br, s, 2H, Ph), 6.88 (m, 1H, para H of Ph), 1.22 (vt, $N = 4.8$ Hz, 6H, PCH₃), 1.18 (vt, $N = 13.2$ Hz, 18H, P'Bu), 1.12 (vt, $N = 14.4$ Hz, 18H, P'Bu). ¹⁹F NMR (CD₂Cl₂, 20 °C): -65.2 (s, BAR'₄). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): 41.4 (s). IR (CD₂Cl₂ or fluorobenzene, cm⁻¹): $\nu(\text{CO}) = 1958$, $\nu(\text{C-H}_{\text{agostic}}) = 2722$, 2672.

Crystal Structure of [Ru(Ph)(CO)(P'Bu₂Me)₂]BAR'₄ X-ray quality crystals were grown from a fluorobenzene/pentane mixture at room

Table 5. Selected Geometric Parameters of [RuPh(CO)(P'Bu₂Me)₂]⁺

Bond Lengths (Å)			
Ru1-P10	2.3920(22)	Ru1-P20	2.3653(28)
Ru1-C4	2.058(12)	Ru1-C2	1.799(14)
C2-O3	1.163(16)		
Bond Angles (deg)			
P10-Ru1-P20	167.98(14)	P10-Ru1-C2	93.0
P10-Ru1-C4	96.532(28)	P20-Ru1-C2	95.5(3)
P20-Ru1-C4	91.5(3)	C2-Ru1-C4	93.7(8)
Ru1-P10-C11	98.1(3)	Ru1-P10-DFC15	126.1(4)
Ru1-P10-C19	109.4(4)	Ru1-P20-C29	114.6(5)
Ru1-P20-C21	121.7(6)	Ru1-P20-C25	96.6(3)

temperature. If the crystals were grown at -20 or -40 °C in the same solvent system, only twinned crystals were obtained. The highly air-sensitive compound was handled in a nitrogen atmosphere glovebag. The crystals were mounted using silicone grease and were then transferred to a goniostat equipped with a nitrogen vapor cold stream at -170 °C. No decomposition was evident for the crystal at the low temperature. A preliminary automated search for peaks and then analysis using programs DIRAX and TRACER revealed a primitive orthorhombic cell. Following intensity data collection, the only conditions observed were $h = 2n$ for $h00$, $k = 2n$ for $0k0$, and $l = 2n$ for $00l$ which uniquely determined space group $P2_12_12_1$. Data processing produced a set of 4419 unique intensities and an $R_{\text{av}} = 0.098$ for the averaging of 4109 of these which had been observed more than once. Four standards measured every 300 data points had considerable random scatter, but they showed no systematic trends. No correction was made for absorption ($\mu = 4.2$ cm⁻¹). The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. The positions of the Ru atom and the P and C atoms bonded to it were obtained from an initial E-map. The positions of the remaining non-hydrogen atoms were obtained from iterations of a least-squares refinement and difference Fourier calculation. Hydrogens were included in fixed calculated positions with thermal parameters fixed at one plus the isotropic thermal parameter of the parent carbon atom. Four of the carbon atoms, C(24) and C(27) in a *tert*-butyl group and C(75) and C(77) in the anion, had thermal parameters that refined to nonpositive definite anisotropic values. In the final cycles of refinement, these four atoms were varied with isotropic thermal parameters and the remaining 82 non-hydrogen atoms were varied with anisotropic thermal parameters to give a final $R(F) = 0.062$ for the 756 total variables (Tables 1 and 5). The largest peak in the final difference map was 0.95, and the deepest hole was -1.15 e/Å³.

Reaction of [RuPh(CO)(P'Bu₂Me)₂]BAR'₄ with C₆H₄O₂B-H. [RuPh(CO)(P'Bu₂Me)₂]BAR'₄ (10 mg, 7.2×10^{-3} mmol) and catecholborane (0.76 μ L, 7.2×10^{-3} mmol) were mixed in CD₂Cl₂ (0.5 mL). After 1 h, NMR analysis of the reaction solution reveals the formation of [RuH(CO)(P'Bu₂Me)₂]⁺ and C₆H₄O₂B-Ph, which was confirmed by comparing the NMR spectra with authentic samples.

Ru(BO₂C₆H₄)(OTf)(CO)(P'Bu₂Me)₂, 17. RuH(OTf)(CO)(P'Bu₂Me)₂ (0.50 g, 8.3×10^{-4} mol) and catecholborane (97 μ L, 1.0×10^{-3} mmol) were mixed with C₆H₆ (10 mL) and heated at 80 °C for 4 h. The mixture was evaporated to give a yellow solid, which was recrystallized from pentane/benzene mixture to give light-yellow crystals. Yield: 0.40 g (67%). Anal. Calcd for C₂₆H₄₀BF₃O₆P₂RuS: C, 43.50, H, 5.62. Found: C, 44.01, H, 6.64. ¹H NMR (300 MHz, C₆D₆, 20 °C): 7.00 (m, 2H, O₂C₆H₄), 6.70 (m, 2H, O₂C₆H₄), 1.57 (vt, $N = 5.9$ Hz, 6H, PCH₃), 1.12 (vt, $N = 13.3$ Hz, 18H, PC(CH₃)₃), 0.85 (vt, $N = 13$ Hz, 18H, PC(CH₃)₃). ³¹P{¹H} NMR (C₆D₆, 20 °C): 53.6 (s, $w_{1/2} = 194$ Hz) ¹⁹F NMR (C₆D₆, 20 °C): -78.6 (s, CF₃). ¹¹B NMR (C₆D₆, 20 °C): 44.5 (br s). IR (C₆D₆, cm⁻¹): 1939 ($\nu(\text{CO})$).

[Ru(BO₂C₆H₄)(CO)(P'Bu₂Me)₂, 18. Ru(BO₂C₆H₄)(OTf)(CO)(P'Bu₂Me)₂ (10 mg, 0.014 mmol) and NaBAR'₄ (12.4 mg, 0.014 mmol) were mixed in CD₂Cl₂ to give a yellow solution. NMR analysis of the mixture revealed clean formation of [Ru(BO₂C₆H₄)(CO)(P'Bu₂Me)₂]-BAR'₄. ¹H NMR: 7.73 (s, 8H, ortho H of Ar'), 7.57 (s, 4H, para H of Ar'), 7.21 (m, 2H, O₂C₆H₄), 7.05 (2H, O₂C₆H₄), 1.44 (vt, $N = 5.1$ Hz, 6H, PCH₃), 1.21 (vt, $N = 13.5$ Hz, 38H, PC(CH₃)₃), 1.21 (vt, $N =$

13.5 Hz, 18H, PC(CH₃)₃). ³¹P{¹H} NMR: 43.3 (br s), ¹⁹F NMR: -64.1 (s). ¹¹B NMR: 42.8 (br,s). IR: 1981 (ν(CO)).

Reaction of Ru(Ph)(OTf)(CO)(P^tBu₂Me)₂ with Catecholborane. Ru(Ph)(OTf)(CO)(P^tBu₂Me)₂ (10 mg, 0.015 mmol) and catecholborane (2.0 μL, 0.023 mmol) were mixed in C₆D₆ (0.5 mL) and heated at 80 °C for 8 h. ¹H NMR spectroscopic analysis revealed formation of RuH-(OTf)(CO)(P^tBu₂Me)₂ and Ru(BO₂C₆H₄)(OTf)(CO)(P^tBu₂Me)₂ with a ca. 1:1 ratio along with PhBO₂C₆H₄. If one more equivalent of catecholborane was added and heated for 4 h, only Ru(BO₂C₆H₄)(OTf)(CO)L₂ was observed.

Reaction of [Ru(Ph)(CO)(P^tBu₂Me)₂]BAR'₄ with Me₃SiCCH. When [Ru(Ph)(CO)(P^tBu₂Me)₂]BAR'₄ (10 mg, 7.6 × 10⁻³ mmol) and Me₃-SiCCH (1 μL, 7.6 × 10⁻³ mmol) were dissolved in CD₂Cl₂, the solution color changed to red immediately. NMR analysis revealed partial consumption of [Ru(Ph)(CO)(P^tBu₂Me)₂]BAR'₄ and formation of [Ru((Me₃-SiCH=C-CH=CH(SiMe₃)(CO)(P^tBu₂Me)₂)]BAR'₄¹¹ and trace [Ru-(CH=CHSiMe₃)(CO)(P^tBu₂Me)₂]BAR'₄. ¹H NMR (300 MHz, CD₂Cl₂, 20 °C): 7.71 (s, 8 H, ortho H of Ar'), 7.51 (d, J_{HH} = 12.3 Hz, 1 H, RuCH), 5.50 (dt, J_{HH} = 12.3 Hz, J_{PH} = 2 Hz, 1 H, RuCH=CH), 1.39 (vt, N = 4.5 Hz, 6 H, PCH₃), 1.28 (vt, N = 13.2 Hz, 18 H, P^tBu), 1.19 (vt, N = 13.2 Hz, 18 H, P^tBu). 0.038 (s, 9 H, SiCH₃)₃. ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, 20 °C): δ 40.8 (s). IR (Nujol, cm⁻¹): 2726, 2677 (ν(C-H_{agostic})), 1944 (ν(CO)). If two more equivalents of Me₃SiCCH are added, clean formation of [Ru((Me₃SiCH=C-CH=CH(SiMe₃)-CO)(P^tBu₂Me)₂)]BAR'₄ was achieved. Analysis of the volatiles revealed the presence of PhCCSiMe₃ as the only product that contains the Ph group.

General Procedure for Low-Temperature NMR Spectroscopic Study. [Ru(Ph)(CO)(P^tBu₂Me)₂]BAR'₄ (10 mg) was placed in an NMR tube with Teflon valve closure and carefully covered with CD₂Cl₂ (0.5 mL) so that the crystals were settled at the bottom of the tube. To the headspace of the tube, Me₃SiCCH (1 μL) was added. The tube was then promptly taken out of glovebox and placed in a dry ice acetone bath. The tube was then shaken thoroughly and transferred to a precooled NMR probe for observation.

Results and Discussion

Structure of RuHCl(CO)(PⁱPr₃)₂, **1.** This complex was originally synthesized by Werner and co-workers.¹² The chemical reactivity has been extensively studied mainly by Esteruelas and co-workers.¹³ The rich reactivity ranges from highly regioselective hydrosilylation catalysis to synthesis of cyclopentadienyl complexes such as CpRuCl(CO)(PⁱPr₃). Compounds with different phosphine ligands (PCy₃ and P^tBu₂Me) have also been synthesized by a similar method.¹⁴ The structure assignment of **1** was based solely on spectroscopic data. These data, however, do not provide any information on the weak interactions such as agostic bonding. Therefore, we carried out the X-ray single-crystal structure determination of **1**. The ORTEP plot (Figure 1) shows a square-based pyramidal geometry with hydride trans to the vacant site and the π-donor (Cl) and the π-acceptor (CO) ligands trans to each other, benefiting from push-pull stabilization. Although there is disorder around a center of symmetry, all three Ru-P-C(methine) angles are normal (around 113°) and the shortest distance from Ru to (CH₃) carbon (3.5 Å) is too long for agostic interaction. Therefore, **1** is authentically coordinatively unsaturated. Other features of the structure are normal for Ru(II) complexes and deserve no further

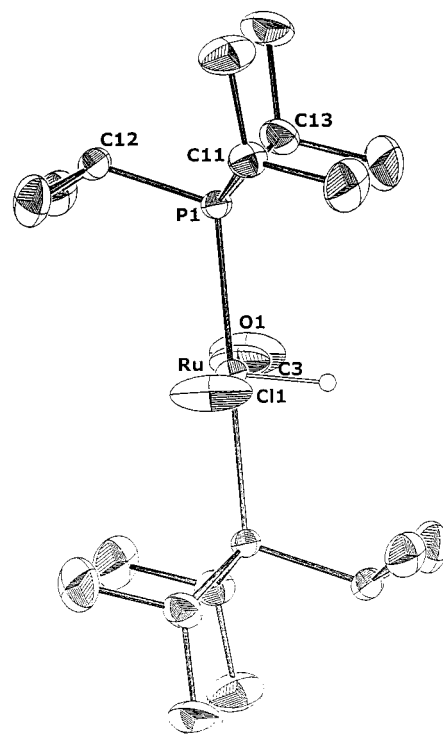
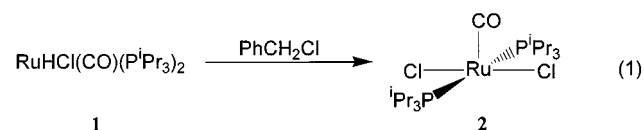


Figure 1. ORTEP diagram (50% probability level) of RuHCl(CO)-(PⁱPr₃)₂, **1**. Hydrogen atoms are omitted except those bound to Ru.

comment. The structure of **1** is similar with that of Os analogue OsHCl(CO)(PCy₃)₂, which also has no agostic interaction.¹⁵

Synthesis and X-ray Crystal Structure of RuCl₂(CO)L₂ (L = PⁱPr₃), **2.** The hydride in **1** is replaced by chloride using PhCH₂Cl (80 °C, 4 h) to give **2** in good yield (eq 1). The



complex has been reported as a byproduct (12% yield) in the synthesis of **1**.¹⁶ The method reported here gives a rational synthesis, which is also a quite specific one, since benzyl chloride does not transform RuHCl(CO)(P^tBu₂Me)₂ to RuCl₂(CO)(P^tBu₂Me)₂, **3**. The latter has been synthesized by reaction with CHCl₃, and the reactivity has been reported.^{7b} The spectroscopic data of **2** includes only one virtual triplet of doublets for the methyl group, indicative of the two symmetry elements to make all CH₃ of ⁱPr magnetically equivalent. Moreover, the much higher CO stretching frequency (1937 vs 1908 cm⁻¹ of **1**) suggests geometry differences between them. These results support the geometry with CO trans to the vacant site, which is proved by X-ray single-crystal structure analysis. The ORTEP plot of **2** is depicted in Figure 2 and the geometric parameters are collected in Table 3. Like **1**, **2** also adopts a square-based pyramidal geometry, but with two mutually trans chlorides and phosphines at the basal and CO at the apical site. This arrangement is in agreement with the computational prediction on the geometry preference of five-coordinate d⁶ metal complexes; the highest trans influence ligand occupies the apical site, which raises the energy of the LUMO. In **2**, the

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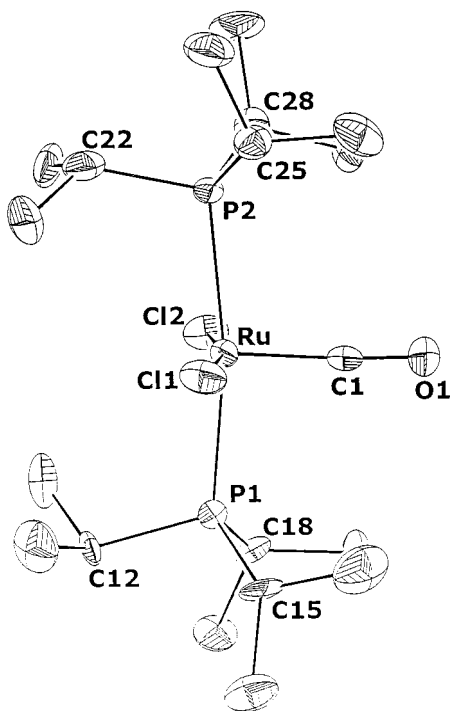
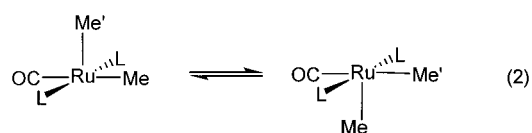


Figure 2. ORTEP diagram (50% probability level) of $\text{RuCl}_2(\text{CO})(\text{P}^i\text{Pr}_3)_2$, **2**. Hydrogen atoms are omitted.

P–Ru–P and Cl–Ru–Cl angles significantly deviate from 180° . A similar structure is adopted by $\text{RuCl}_2(\text{CHR})\text{L}_2$.¹⁷ The bending of Cl–Ru–Cl suppresses filled–filled repulsion between the Cl lone pair and the metal $d\pi$ electron. One $i\text{Pr}$ group of phosphine bends toward to the vacant site so that the Ru–P2–C22 is as much as 10° smaller than that of Ru–P2–C28 (or C25). This may indicate weak agostic interaction, since all corresponding angles in nonagostic **1** are nearly identical. However, the long distance of Ru to the nearest CH_3 carbon (3.6 Å) and Ru/H (2.98 Å) speaks against any bonding interactions. This is in marked contrast with $\text{RuCl}_2(\text{CO})(\text{PCy}_3)_2$, which has an agostic interaction between ortho CH_2 of cyclohexyl and Ru(II) (Ru/C is 3.0 Å, and Ru/H is 2.3 Å).¹⁸ For comparison, in $\text{Rh}(\text{mesityl})_3$, distances to agostic ortho methyl groups are Rh/C = 2.8 Å and Rh/H = 2.25–2.37 Å.¹⁹ The interplay of steric effects and the trans influence has been addressed in recent theoretical calculations.²⁰

Ru(Me)Cl(CO)L₂ and RuMe₂(CO)L₂. Addition of 1 equiv of MeLi to **2** in toluene results in immediate formation of equal amounts of $\text{RuMeCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$, **4**, and $\text{RuMe}_2(\text{CO})(\text{P}^i\text{Pr}_3)_2$, **6**, along with some starting materials (Scheme 1). After 3 h, **4** is the dominant product (>90%) with a small amount of starting material. Apparently, ligand redistribution between **2** and **6** occurs. Ligand scrambling of similar complexes has been examined before and is considered to be an associative process even though there are two sterically demanding phosphine ligands.²¹ If one more equivalent of MeLi is added, clean conversion to **6** results. The reaction also succeeds with the $\text{P}^i\text{Bu}_2\text{Me}$ analogue. $\text{RuMeCl}(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$, **5**, has been syn-

thesized independently by treatment of $\text{RuHCl}(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$ with diazomethane, but this reaction fails to convert **1** to **4**.^{7a} The CO stretching frequency (1898 cm^{-1}) of **5** is close to that of $\text{RuHCl}(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$ (1906 cm^{-1}), suggesting that they have similar geometry. Since methyl has the strongest trans influence among the ligands, one may reasonably assume that the complex has a square-based pyramidal geometry with Me trans to the vacant site. In agreement with this, the carbon resonance of the Ru–CH₃ of **5** appears at unusually high field (-11.0 ppm). Similarly, the (Os)–CH₃ $^{13}\text{C}\{^1\text{H}\}$ NMR resonance of $\text{Os}(\text{CH}_3)\text{Cl}(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$ appears at unusually high field (-38 ppm).^{7a} The high field shift of the hydride has been a diagnostic feature of five-coordinate Ru and Os complexes with hydride trans to the vacant site, and perhaps the same is true of the ^{13}C chemical shift in such a site. The dimethyl complex $\text{RuMe}_2(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$, **7**, shows only one ruthenium methyl proton (or carbon) resonance at room temperature as well as one ^iBu signal, indicating that the two (Ru)–CH₃ and all the ^iBu methyls are equivalent. However, at -90°C , two ^1H and $^{13}\text{C}\{^1\text{H}\}$ Ru–CH₃ signals (^{13}C , -15.7 and 17.5 ppm) are observed along with two ^iBu peaks (^1H or ^{13}C). Therefore, the ground-state geometry of the complex has one methyl in the apical site and the other trans to CO in the basal plane. On the basis of the decoalescence temperature of the ^{13}C signals of the Ru–CH₃, the energy barrier (ΔG^\ddagger) of the conversion is calculated as 6.8 kcal/mol at -30°C . Since it is an intramolecular process, the entropy change (ΔS^\ddagger) is expected to be small such that the ΔG^\ddagger value is close to that of ΔH^\ddagger . The hydride site exchange of $\text{Ru}(\text{H})_2(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$ has the ΔH^\ddagger of 7.6 kcal/mol and ΔS^\ddagger of 6.5 eu, so ΔG^\ddagger for $\text{Ru}(\text{H})_2(\text{CO})\text{L}_2$ at -30°C is 6.0 kcal/mol.²² This number compares well to the barrier of $\text{Ru}(\text{CH}_3)_2(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$, indicating a similar process for methyl site exchange as that of hydride site exchange of $\text{Ru}(\text{H})_2(\text{CO})\text{L}_2$, which is calculated to go through an intermediate with CO trans to the vacant site and the two hydride trans to each other (eq 2).



Synthesis of RuMeF(CO)L₂, RuMe(OTf)(CO)L₂, RuMe(BF₄)(CO)L₂, and [RuMe(CO)L₂]BAR⁺4. Halide exchange of $\text{RuMeCl}(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2$ with CsF in acetone for 4 h gives $\text{RuMeF}(\text{CO})\text{L}_2$, **8** (Scheme 1), in quantitative yield as judged by NMR and in 54% isolated yield. The complex is characterized by the doublet of the ^{31}P NMR signal ($J_{\text{PF}} = 22\text{ Hz}$) and a triplet of quartets of the ^{19}F resonance (-201 ppm , $J_{\text{PF}} = 22\text{ Hz}$, $J_{\text{HF}} = 4\text{ Hz}$). The fluoride readily reacts with 1 equiv of $\text{BF}_3\cdot\text{OEt}_2$ (in Et_2O) to give $\text{RuMe}(\text{BF}_4)(\text{CO})\text{L}_2$, **10** (Scheme 1), which is not soluble in diethyl ether and precipitates from the reaction solution. However, it is soluble in benzene or toluene, thus BF_4^- is likely to be coordinating. Consistent with this, the ^{19}F NMR spectrum of the BF_4^- is an extremely broad peak (-210 ppm , $\omega_{1/2} = 1396\text{ Hz}$) at 20°C , due to exchange of coordinated BF_4^- . The CO stretching frequency of **10** is higher than that of the $\text{Ru}(\text{Me})\text{Cl}(\text{CO})\text{L}_2$ (1919 vs 1898 cm^{-1}). The fluoride in **8** is also readily replaced by trifluoromethane sulfonate (triflate) using Me_3SiOTf (diethyl ether, 10 min) to give $\text{RuMe}(\text{OTf})(\text{CO})\text{L}_2$, **9** (Scheme 1). The CO stretching frequency of this complex is higher (1914 cm^{-1}) than that of **4**, in accordance

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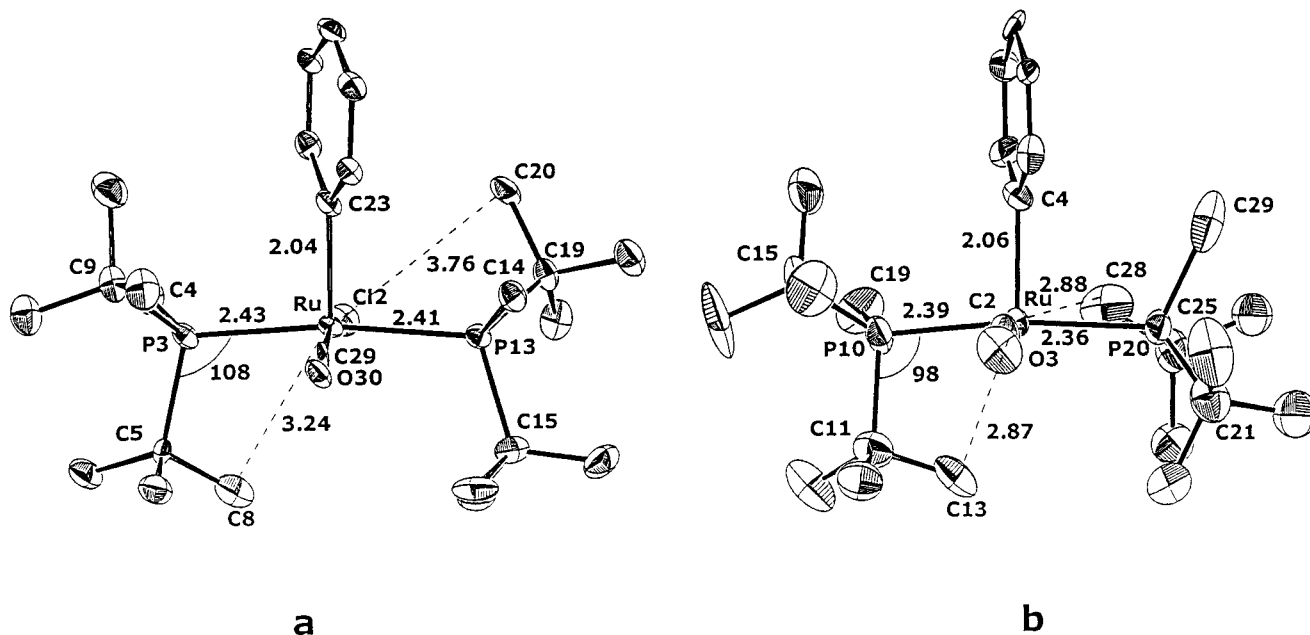
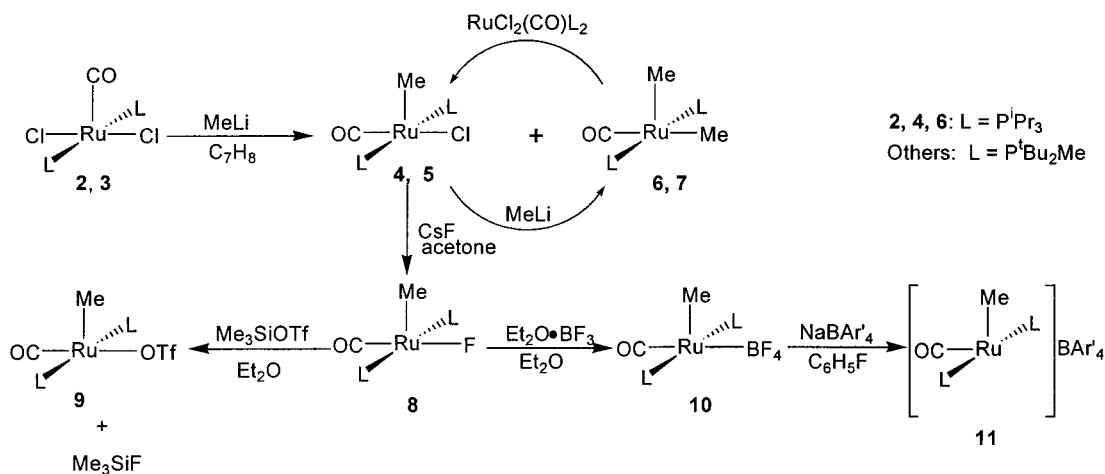


Figure 3. ORTEP diagrams of Ru(Ph)Cl(CO)(PⁱBu₂Me)₂, **12** (a), and [RuPh(CO)(PⁱBu₂Me)₂]BAR'₄, **16** (b). Hydrogen atoms are omitted.

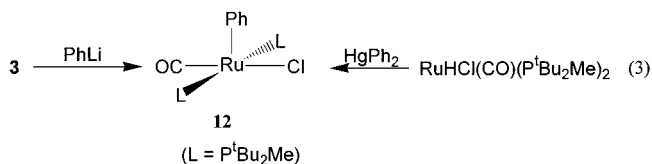
Scheme 1



with the weaker donating ability of OTf than of chloride. However, OTf cannot be completely replaced by weakly coordinating BAR'₄⁻ (Ar' = 3,5-trifluoromethyl phenyl). Thus, stirring equimolar **9** and NaBAR'₄ in CH₂Cl₂ for 12 h only results in partial replacement of OTf, as evidenced by IR spectroscopy to give a solution having two CO bands (1951 and 1914 cm⁻¹) with similar intensity. The higher frequency band is assigned to [RuMe(CO)L₂]BAR'₄, **11**, which was synthesized (Scheme 1) from salt metathesis of NaBAR'₄ and **10** (C₆H₅F, 10 min). **11** is a rare example of a 14-electron four-coordinate Ru(II) alkyl complex. It might be possible to have two agostic interactions as we observed for the similar complex [Ru(Ph)(CO)L₂]BAR'₄ (vide infra). Alternatively, the Ru–methyl group could have an α-agostic interaction with the metal, which would cause higher field shift of the methyl proton. However, at 20 °C, this CH₃ proton has a normal chemical shift (1.14 ppm in C₆D₅F/C₇D₈ 1:2). This signal does not change position upon cooling to -70 °C, and therefore, no α-agostic interaction is substantiated. The solvent, C₆D₅F and toluene-*d*₈, is not likely to be coordinating to the metal, since [RuH(CO)L₂]BAR'₄ does not coordinate these solvents.²³ The two vacant sites of **11** are likely

to be occupied by C–H bonds from the ^tBu methyl on the phosphine ligands.

Synthesis and Structure of Ru(Ph)Cl(CO)(PⁱBu₂Me)₂. PhLi reacts with **3** at low temperature with clean formation of RuPhCl(CO)L₂, **12** (eq 3). Excess PhLi, however, does not cause

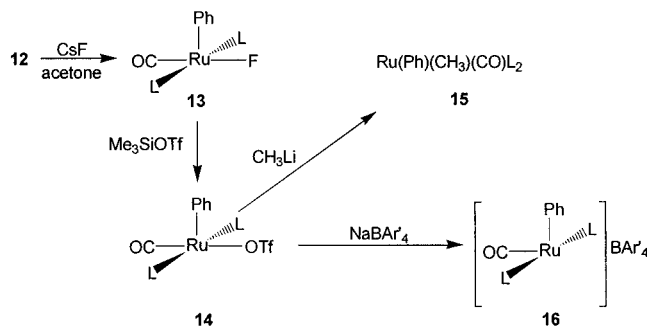


further replacement of the other chloride, probably due to steric crowding in **12**. Reaction of RuH(Ph)(CO)L₂ with excess *N*-chlorosuccinimide (NCS) also gives **12** in moderate yield.²⁴ Alternatively, refluxing RuHCl(CO)L₂ with Ph₂Hg in toluene gives **12** in excellent yield (>80%).²⁴ **12** is moderately air stable and can be recrystallized from methanol (!). The spectroscopic data of **12** have been reported and discussed before.²³ A single crystal of **12** grown from methanol was chosen for the X-ray study. The ORTEP drawing of **12** is shown in Figure 3a, and

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Scheme 2



the geometric parameters are in Table 4. Similar to **3** and **4**, **12** has a square-based pyramidal geometry but with Ph trans to the vacant site, consistent with the stronger trans influence of Ph than CO. Moreover, with CO trans to Cl, push–pull stabilization is maximized. Although two ^tBu groups on phosphine ligands point toward the vacant site, the shortest distance of the phosphine carbon to Ru is 3.24 Å, and the Ru–P–C(CH₃)₃ angles do not deviate much from the normal value of 115°; therefore, there is no agostic interaction. The structure of the related complex Ru(*p*-tolyl)Cl(CO)(PPh₃)₂ shows weak agostic donations from one ortho phenyl of both phosphines (Ru/H = 2.77–2.85 Å Ru/C = 3.41 Å) to the site trans to the *p*-tolyl in a square pyramidal structure.²⁵ Such weak interactions to PPh₃ are absent in RuCl(*o*-tolyl)(CO)(PPh₃)₂, where the *o*-tolyl methyl appears to form an agostic interaction to Ru (Ru/H = 1.9 Å) and *o*-tolyl is no longer in the apical site of a square pyramid.¹⁰

Halide Replacement of 12. The Cl of **12** can be replaced with F by salt metathesis with CsF (acetone, 20 °C, 12 h) to give RuPhF(CO)L₂, **13** (Scheme 2). **13** is isolated as orange crystals from pentane or by sublimation at 140 °C at 5 × 10⁻² mmHg. The ³¹P{¹H} NMR of **13** shows a doublet (*J*_{PF} = 24 Hz) and, correspondingly, the ¹⁹F spectrum is a triplet close (–204 ppm) to the ¹⁹F chemical shift of **8** (–201 ppm). There are also five distinct phenyl proton resonances, indicative of slow rotation of Ph around the Ru–C(ipso) bond.

The CO stretching band appears at lower frequency (1890) than that of **12** (1902) since F is a stronger π-donor than Cl.²⁶ Replacement of F by triflate occurs under mild conditions using Me₃SiOTf (Et₂O, 20 °C, immediate reaction) to give Ru(Ph)(OTf)(CO)L₂, **14**, quantitatively. Ligand exchange of Me₃Si–X with metal fluoride has been reported on several occasions.²⁷ Surprisingly, salt metathesis using AgOTf does not give the same product; instead, decomposition of **12** yields [AgL₂]OTf. **14** can also be synthesized in high yield from RuH(OTf)(CO)L₂²³ and Ph₂Hg in refluxing toluene. **14** is soluble in nonpolar solvents such as benzene and pentane, indicative of coordinated triflate. Moreover, similar to **12** and **13**, **14** also has five distinct proton NMR signals for Ph, indicative of slow rotation of Ph. Consistent with weak donation by OTf, the CO stretching frequency (1921 cm⁻¹) of **14** is higher than those of **12** and **13**.

Ru(Ph)(CH₃)(CO)L₂. As a better leaving group, OTf of **14** is readily replaced by MeLi to give RuPh(Me)(CO)L₂, **15**, at

20 °C in benzene within the time of mixing (Scheme 2). In contrast, substitution of Cl by Me in **12** requires a 10-fold excess of MeLi and prolonged reaction time (3 days).²⁸ **15** (like **6**) is a rare example of a 16-electron Ru(II) complex devoid of π-basic ligands. Similar to **14**, **15** shows five distinct phenyl proton chemical shifts, revealing the slow rotation of the Ph ring on the ¹H NMR time scale. The Ru–CH₃ protons appear as a triplet at 1.07 ppm (*J*_{PH} = 7 Hz). Unlike the high-field ¹³C chemical shifts of methyl of **4** (–11 ppm) and one methyl of **6** (–15 ppm), the methyl ¹³C chemical shift of **15** is at lower field (9.5 ppm), in agreement with CH₃ trans to CO, not the vacant site. Although not trans to a π-donor ligand, the CO stretching frequency is low (1883 cm⁻¹), due probably to the strong σ-donating powers of CH₃ and Ph. **15** contains three strong trans influencing ligands, Ph, Me, and CO, and they are all good candidates to occupy the apical site. On the basis of the NMR spectral data, we conclude that Ph of **15** lies at the apical site, where it is sterically constrained from rotating easily. Ru(H)(Ph)(CO)L₂, on the other hand, has Ph in the basal plane since the hydride resonance is at very high field (–28 ppm) and only three proton chemical shifts for Ph are observed, indicating fast rotation of the phenyl.²³ These results, along with the geometry of the methyl complexes, permit us to conclude that the trans influence of the σ-donor ligands has the order of H > Ph > Me > CO.

16-electron, five-coordinate Ru(II) complexes without π-donor ligands are rare. So far, only one such compound, RuH(SiHPh₂)(CO)L₂, was structurally characterized.²⁹ Similar complexes Ru(H)₂(CO)L₂ and RuH(Ph)(CO)L₂ are not long-lived species since they tend to eliminate H₂ or benzene. In contrast, **15** remains unchanged in toluene for 2 days at 20 °C. Generally, since metal carbon bonds are weaker than metal hydrogen bonds, the persistence of **15** should be attributed to the kinetic barrier for reductive elimination to form a C–C bond.

Synthesis and Structure of [RuPh(CO)L₂]BAR₄. Triflate can be removed from **14** using NaBAR₄ to give [RuPh(CO)L₂]BAR₄, **16**, in either methylene chloride or in fluorobenzene at room temperature in the time of mixing (Scheme 2). The highly air-sensitive complex **16** is purified by recrystallization as orange crystals from a pentane/fluorobenzene mixture with strict exclusion of air and moisture. At room temperature, the NMR of the Ph protons show only three peaks, including one sharp triplet for the para proton and one broad peak for the meta and one broad peak for the ortho protons. Therefore, the Ph rotation is faster as compared to **12** with Ph at the apical site. Upon cooling to –70 °C, each broad peak decoalesces to two multiplets. The phosphine peak remains a sharp singlet in the same temperature range; therefore, slow rotation around the Ru–P bond is not observed, which might have given rise to two magnetically different phosphines, as is seen for **12**.³⁰ Two virtual triplets for ^tBu groups reveal the nonplanar arrangement of the four ligands. The CO stretching frequency is high (1958 cm⁻¹), and two bands with medium strength are also found at the agostic C–H stretch region (2722 and 2672 cm⁻¹). These two bands disappear after **16** is saturated with excess CO, which replaces the agostic interacting C–H bonds (Figure 4). These agostic interactions are highly fluxional and cannot be frozen out on the NMR time scale as in the other agostic interactions between unsaturated metal and the phosphine ligand C–H bond.³¹ To gain solid evidence for the structure of **16**, an X-ray

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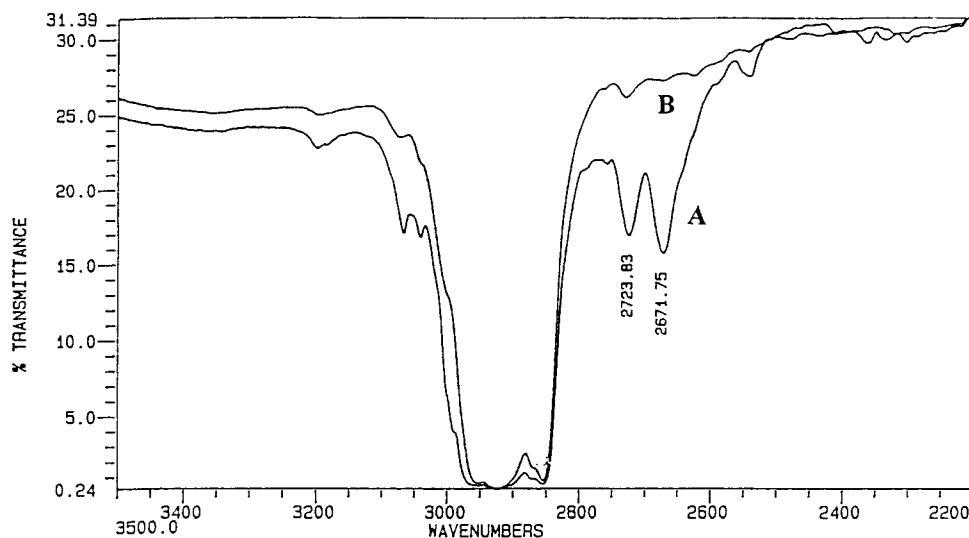


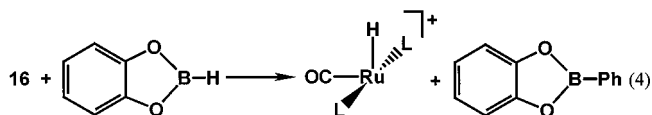
Figure 4. IR spectra of $[\text{Ru}(\text{Ph})(\text{CO})(\text{P}'\text{Bu}_2\text{Me})_2]\text{BAR}'_4$, **16** (curve A), and the reaction product of **16** with carbon monoxide (curve B). The bands due to agostic interactions disappear when **16** is treated with CO.

crystal structure study was carried out. The ORTEP diagram is shown in Figure 3b and the geometric parameters are in Table 5. Four-coordinate **16** adopts a sawhorse geometry with two phosphine ligands trans and the Ph and CO cis to each other. The two vacant sites are occupied by agostic C–H bonds from two ^tBu on different phosphines. The Ru/C_{agostic} distances are short (2.88 and 2.87 Å, respectively), indicative of relatively strong interactions. Comparing the structural differences of **16** and **12** (Figure 3a,b) provides some insight into the impact of the structural changes upon removal of the X ligand. Removal of the X ligand does not cause any large disturbance to the remaining four atoms bound to Ru; they remain approximately in the same relative position. The P–Ru–P angles and CO–Ru–C angles are comparable between **16** and **12**. The Ru–P distances are shorter in **16**. In sharp contrast to small movements of atoms directly bound to Ru, the substituents on phosphine have been disturbed significantly. The angle Ru–P3–C5 of **12** is 108°, while it is 10° smaller in **16**. In **12**, the angle Ru–P13–C19 is 119°; in contrast, upon removal of the Cl, this angle decreases to 97° (Ru–P20–C25). Accordingly, the Ru/C_{agostic} distances are shortened by 0.375 and 0.874 Å, respectively, compared to the corresponding Ru/C distance in **12**. Thus, the removal of the Cl creates two agostic interactions. The absence of agostic interaction in **12** and the presence of two agostic interactions in **16** show that agostic interaction is not solely determined by the nature of the ligand trans to the empty site. If that were the case, one should have observed an agostic interaction trans to Ph in **12**. Going from a 16e Ru(Ph)Cl(CO)L₂ to 14e RuPh(CO)L₂⁺ is likely to lower all empty metal orbitals, even those which in first approximation should not have been influenced by the presence of the removed ligand (Cl[−]); there is a general increase in electrophilicity.

Reactivity of 16. Surprisingly, this highly electrophilic complex is thermally robust in solvents such as benzene or toluene. Upon heating in toluene-*d*₈ (100 °C) for 24 h, no significant decomposition or reaction is evidenced by NMR spectroscopy. The ¹H NMR spectrum remains unchanged. Moreover, the two diastereotopic ^tBu groups do not decoalesce at 100 °C (toluene-*d*₈), thus there is no phosphine dissociation or unimolecular inversion through a square-planar intermediate.

On the other hand, it shows reactivity of the Ru–Ph with E–H bonds (E = boryl, H, and C(sp)).

(A) With Catecholborane, Synthesis of [RuB(C₆H₄O₂)(CO)L₂]BAR'**₄.** A mixture of 1 equiv catecholborane and **16** in methylene chloride produces exclusively [RuH(CO)L₂]**BAR'**₄ and (C₆H₄O₂)B–Ph in 1 h at room temperature (eq 4). The

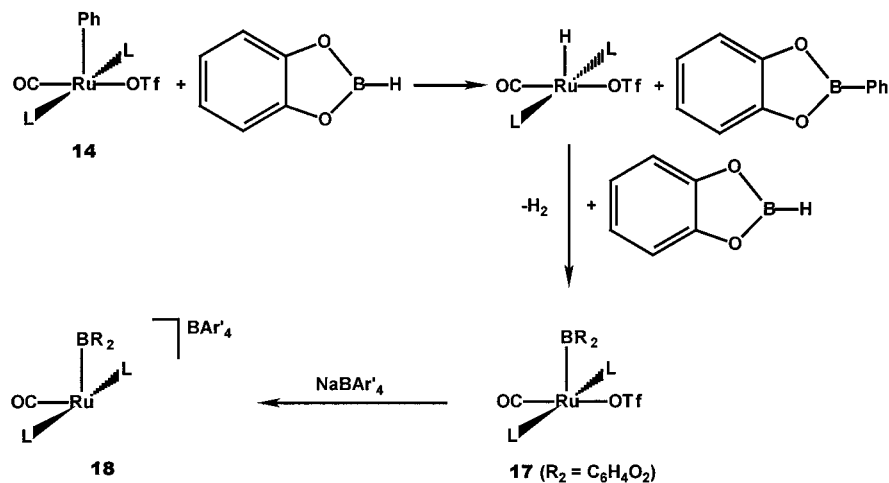


products are identified by comparing the ¹H and ³¹P NMR spectra with the known values for the two compounds. **14** also reacts (Scheme 3) with 1 equiv catecholborane, albeit at higher temperature (80 °C, 4 h), to give RuH(OTf)(CO)L₂ (90%), trace Ru(BR₂)(OTf)(CO)L₂, **17**, and (C₆H₄O₂)B–Ph. If one more equivalent of catecholborane is added to the reaction mixture, clean conversion to **17** is achieved. Therefore, the formation of **17** from **14** involves two steps to release (C₆H₄O₂)B–Ph and H₂ separately (Scheme 3). Indeed, reaction of RuH(OTf)(CO)L₂ with 1 equiv catecholborane cleanly yields **17**. **17** has two ^tBu virtual triplets and a broad singlet for ³¹P and ¹¹B (44.5 ppm) signals. The CO stretching band appears at higher frequency (1939 cm^{−1}) than that of **6**, in agreement with the presence of the π-acidic boryl ligand. The mechanism of this reaction can be oxidative addition followed by reductive elimination or σ-bond metathesis. In either mechanism, the reaction is highly selective for the formation of M–BR₂. Hartwig and co-workers studied the mechanism of the reaction of saturated CpRu(PPh₃)₂Me and catecholborane (giving metal hydride and methylcatecholborane) and concluded that the reaction proceeds by a four-centered transition state (σ-bond metathesis), not by oxidative addition.³² Although a similar mechanism may be operative in eq 4, since the Ru of **16** is already π-electron deficient and oxidative addition to give aRu(IV) species is not favored, highly unsaturated **16** is likely to coordinate catecholborane before further reaction occurs. Recently, Roper and co-workers reported that the reaction of either RuHCl(CO)(PPh₃)₃ or Ru(Ph)Cl(CO)(PPh₃)₂ with catecholborane gives Ru(boryl)Cl(CO)(PPh₃)₂ as the sole product. How-

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Scheme 3



ever, no experimental details concerning the reaction of $\text{Ru}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ are given. Therefore, it is not clear if the reaction is also a two-step process, with initial formation of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_2$, which then further reacts with catecholborane. In contrast, the Os analogue $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ does not react with catecholborane, while $\text{Os}(\text{Ph})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ does, to give the boryl complex $\text{Os}(\text{BR}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and benzene.³³ Saturated $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ may not undergo a ligand dissociation under the reaction conditions, which is a prerequisite for the reaction to occur, while $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ may have a labile phosphine.

[RuB(O₂C₆H₄)(CO)L₂]BAR'₄. Salt metathesis of **17** with NaBAR'_4 in methylene chloride or fluorobenzene gives $[\text{Ru}(\text{BR}_2)(\text{CO})\text{L}_2]\text{BAR}'_4$, **18**, in quantitative yield (Scheme 3). Like other four-coordinated $\text{RuR}(\text{CO})\text{L}_2^+$, **18** exhibits two virtual triplets for the ^tBu groups indicative of nonplanar geometry with two phosphines mutually trans. Only two proton chemical shifts are observed for catecholboryl, indicating fast rotation of the boryl group. ¹¹B NMR and ³¹P{¹H} NMR spectra are broad singlets probably caused by the quadrupolar ¹¹B. The CO stretching band of **18** (1981 cm⁻¹) is higher than any other $[\text{RuR}(\text{CO})\text{L}_2]\text{BAR}'_4$ owing to the π-acidic boryl group. To our knowledge, **18** is the first example of a highly electron-deficient (14e) Ru(II) boryl complex, the reactivity of which is still under investigation and will be reported separately.

(B) Reaction with Me₃SiCCH. Addition of 1 equiv of Me₃SiCCH to a methylene chloride solution of **16** at room temperature gives in the time of mixing partial conversion to PhCCSiMe_3 , $[\text{Ru}\{\eta^3\text{-(Me}_3\text{SiCH=C-CH=CH(SiMe}_3)\}\text{CO})\text{L}_2]\text{BAR}'_4$, **19**, and a trace amount of $[\text{Ru}(\text{CH=CH(SiMe}_3)\text{CO})\text{L}_2]\text{BAR}'_4$, **20** (Scheme 4). If two more equivalents of Me₃SiCCH are added, clean conversion to **19** is observed. **19** can be synthesized independently from $\text{RuH}(\text{CO})\text{L}_2^+$ with 2 equiv of Me₃SiCCH, and its structure has been determined.¹¹ Therefore, it is likely that the reaction of **16** with Me₃SiCCH forms $\text{RuH}(\text{CO})\text{L}_2^+$, which further reacts with Me₃SiCCH to give **19**. The most straightforward mechanism of the first step is that Me₃SiCCH and **16** undergo σ-bond metathesis to give Me₃SiCCPh and $\text{RuH}(\text{CO})\text{L}_2^+$, which then reacts with Me₃SiCCH to give **19** and **20**. Alternatively, oxidative addition of the C(sp)-H bond to Ru(II) followed by exclusive reductive elimination of Me₃SiCCPh would also account for the first step. To gain more information on this reaction, a low-temperature NMR spectroscopic study was carried out. One equivalent of Me₃SiCCH and

16 were mixed at -70 °C in an NMR tube in CD₂Cl₂. At temperatures below -40 °C, there is no detectable interaction between **16** and Me₃SiCCH. As the temperature rises, one new product starts to form, which has a characteristic vinyl proton triplet ($J_{\text{PH}} = 2$ Hz) at 5.87 ppm. At -5 °C, this product is the dominant one (>70%, based on ³¹P NMR integration). ³¹P NMR of this product is a sharp singlet and two virtual ^tBu triplets (¹H NMR) are also identified in addition to a singlet for Me₃Si. Therefore, it has two trans phosphines with diastereotopic ^tBu groups. On the basis of these data, we propose that the product has structure **21**. The formation of **21** requires that one Me₃SiCCH isomerized to vinylidene before the Ph migratory insertion occurs. Further warming in the presence of free Me₃SiCCH converts some **21** to PhCCSiMe_3 , **19** and **20** until all Me₃SiCCH is consumed (judging from ¹H NMR). **21** then isomerizes at room temperature to **22**, which has been synthesized independently from $\text{RuH}(\text{CO})\text{L}_2^+$ and PhCCSiMe_3 and characterized by X-ray diffraction.³⁴ The transformation of **21** to **22** is likely to go through β-hydrogen migration via an unobserved intermediate, the η²-Ph-CC-SiMe₃ adduct **23**. The final reaction mixture gives over 80% **22**, and small amounts of **19** and **20**. Although **22** might have been formed via direct addition of Ru-Ph to the C≡C bond, this cannot account for the complexity of the observed intermediates. Consistently, if the same reaction is carried out using 3 equiv Me₃SiCCH, at low temperature (<-5 °C), **21** is the dominant product, which releases PhCCSiMe_3 and transforms to **19**. No **22** is observed. The high migrating ability of the silyl, hydrogen, and phenyl groups makes this reaction complicated and likely leads to the thermodynamic product.

Conclusion

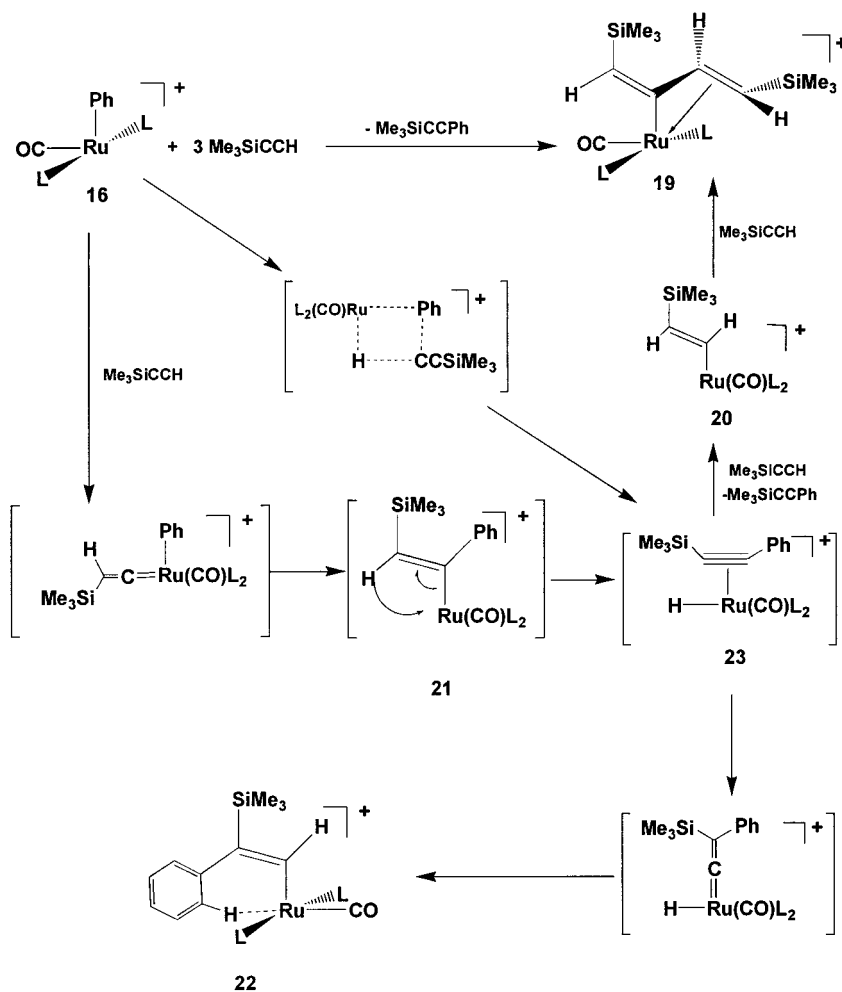
We have demonstrated the synthesis and structural characterization of the 16-electron five-coordinate Ru(II) complexes and 14-electron four-coordinate $\text{Ru}(\text{Ph})(\text{CO})\text{L}_2^+$, and their reactivity toward E-H bonds is also examined. On the basis of the results gathered here, several conclusions can be reached.

(1) Synthesis of the 14-electron four-coordinate complex, $[\text{RuR}(\text{CO})\text{L}_2]\text{BAR}'_4$, is achieved by salt metathesis of its triflate precursor and NaBAR'_4 . The cation adopts a sawhorse geometry with two sterically demanding phosphine ligands trans and the two strong trans influencing ligands cis to each other so that the unsaturated metal gains the most steric protection. This also

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Scheme 4



raises the energy of the empty valence orbitals. The two vacant sites are occupied by agostic interactions, which is directly proved, in the case of R = Ph, by X-ray single-crystal structure analysis and the solid-state IR spectrum. Structural comparison of Ru(Ph)(CO)L₂⁺ with its five-coordinated precursor Ru(Ph)Cl(CO)L₂ reveals that halide removal does not cause a major geometry change of the remaining fragment; on the other hand, two agostic interactions are created.

(2) 16-electron Ru(II) carbonyl complexes RuR₂(CO)L₂ without π -donor ligands are persistent species. This is in sharp contrast to the hydride complexes, Ru(H)(Ph)(CO)L₂ and RuH(Me)(CO)L₂, which readily undergo reductive elimination even at -40°C (RuH(Me)(CO)L₂). The persistence of the carbonyl complexes can be attributed to kinetic sluggishness of reductive elimination.

(3) On the basis of the geometry preference of five-coordinate complexes, the magnitude of trans influence has the following order: H > Ph > CH₃ > CO > Cl.

The sawhorse geometry of Ru(R)(CO)L₂⁺ places a vacant site cis to the M-R bond. In combination with the Lewis acidity of the metal (as demonstrated by the two agostic interactions), we can envision some interesting reactivity between an incoming ligand and M-R. The detailed reactivity study will be pursued and reported in due course.

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Supporting Information Available: Full crystallographic details, positional and thermal parameters, and distances and angles on four compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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