

**The First η^2 -CH₂Cl₂ Adduct of
Ru(II):[RuH(η^2 -CH₂Cl₂)(CO)(P^tBu₂Me)₂][BAR'₄]
(Ar' = 3,5-C₆H₃(CF₃)₂) and Its
RuH(CO)(P^tBu₂Me)₂⁺ Precursor**

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The quest for the ideal noncoordinating solvent, like that for the ideal noncoordinating anion¹ has fallen upon hard times in that a sufficiently potent Lewis acid will find nucleophilicity in even the weakest of nucleophiles. Thus, Si(ⁱPr)₃⁺ interacts with toluene,² CH₄ interacts with Cr(CO)₅,³ HB(C₆F₅)₃⁻ interacts with Cp*₂ZrH⁺,⁴ and halocarbon solvents (CH₂Cl₂) have been shown to bind in a bidentate manner to Ag(I)⁵ and monodentate in [(ⁱPr₃P)₂PtH(η^1 -CH₂Cl₂)] [BAR'₄]⁶ and [Cp*Ir(PEt₃)(CH₃)(η^1 -CH₂Cl₂)] [BAR'₄].⁷ Indeed, this has led Strauss to suggest a redefinition of the concept of coordinative unsaturation (i.e., not simply having a 16-valence electron count).⁸ We report here our efforts to make and isolate a 14-electron species for metals earlier in the transition series than Cu⁺, Ag⁺, or Au⁺ (which often show 14-electron counts) and the consequent first observation of CH₂Cl₂ as a bidentate ligand⁹ to a single platinum group metal ion.

Reaction of RuHF(CO)L₂¹⁰ (L = P^tBu₂Me) with 1 equiv of Me₃SiOTf produces quantitatively RuH(OTf)(CO)L₂.¹¹ The latter undergoes metathesis with 1 equiv of NaBAR'₄ (Ar' = 3,5-C₆H₃(CF₃)₂)¹² in CH₂Cl₂ at room temperature to give [RuH(CO)(CH₂Cl₂)L₂][BAR'₄]¹³ in quantitative yield in 5 min. The orange complex is highly sensitive to the air. Moreover, filtration of the reaction mixture through Celite also causes

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- (11) Synthesis of RuH(OTf)(CO)L₂: RuH(CO)L₂ (2.0 g, 4.3 mmol) was dissolved in dry diethyl ether (30 mL). To the solution was added Me₃SiOTf (0.83 mL, 4.3 mmol) slowly via a syringe; exothermic reaction occurred immediately (which caused reflux of the solvent if the addition rate is fast). The solution color changed to bright yellow. After the addition (5 min), the solution was stirred for 10 min and the volatiles were removed in vacuo. The residue was recrystallized from diethyl ether (-40 °C) to yield yellow needles, 2.2 g (92%). Anal. Calcd for C₂₀H₃₃F₃O₄P₂RuS: C, 40.06; H, 7.23. Found: C, 40.40; H, 6.95. ¹H NMR (C₆D₆, 25 °C): 1.48 (vt, *N* = 5.1, PCH₃), 1.13 (vt, *N* = 13, 18H, PC(CH₃)₃), 1.00 (vt, *N* = 13, 18H, PC(CH₃)₃), -24.7 (t, *J*_{PH} = 19 Hz, 1H, Ru-H) ppm. ³¹P{¹H} NMR (C₆D₆, 25 °C): 56.4 ppm. ¹⁹F NMR (C₆D₆, 25 °C): -76.6 ppm. IR (C₆D₆): ν (CO) = 1923 cm⁻¹.
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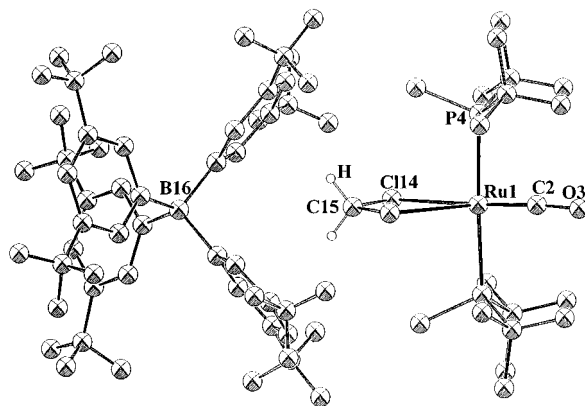


Figure 1. ORTEP drawing of the intimate ion pair [RuH(CO)(CH₂Cl₂)(P^tBu₂Me)₂][BAR'₄]. Only the CH₂Cl₂ hydrogens are shown. \angle Cl14–Ru1–C2 = 125.4 and 171.6°.

partial decomposition. The reaction solution therefore was centrifuged, and the solution was decanted and layered with pentane. Crystals were obtained after the solution was kept 2 days at -20 °C. Proton NMR of this complex at 25 °C in CD₂Cl₂ shows two virtual triplets for diastereotopic ¹Bu, one virtual triplet for the PCH₃ protons and a triplet at -19 ppm for the Ru hydride. Proton chemical shifts show a single BAR'₄ environment, and ³¹P{¹H} and ¹⁹F NMR each give a sharp singlet. Attempts to detect the coordinated CD₂Cl₂ by ¹³C{¹H} NMR at -90 °C were not successful, indicating that even at this temperature the coordinated CD₂Cl₂ undergoes rapid exchange with free CD₂Cl₂.

A well-formed single crystal from CH₂Cl₂/pentane used for X-ray study of [RuH(CO)L₂][BAR'₄] \cdot 2CH₂Cl₂ (L = P^tBu₂Me) shows¹⁴ the unit cell to contain one CH₂Cl₂ molecule in the lattice, in the general region of the Ar' rings and the other CH₂Cl₂ donating both chlorines to Ru(II), to complete a six-coordinate octahedral geometry about the metal (Figure 1). The Ru/Cl distances are long (2.74 Å) and the C–Cl distances (1.756(27) Å) are not lengthened from those in free CH₂Cl₂. The Cl–Ru–Cl angle is quite acute (63°). This “salt” is sufficiently soluble in benzene to obtain NMR spectra, which is probably because the BAR'₄ anion interacts in a pairwise space-filling manner with the cation: two phenyl rings adopt an atypical rotational conformation about their B–C(*ipso*) bonds to form a crevice, into which the CH₂Cl₂ ligand fits like a knife edge. This directs each (acidic) dichloromethane hydrogen toward the center of a phenyl ring, to form a hydrogen bond to the arene π -system (the distances from dichloromethane hydrogens to the centers of phenyl rings are 2.71 Å). Thus, even in the solid state, an intimate ion pair is formed.

The carbonyl stretching frequency (1951 cm⁻¹) in CD₂Cl₂ is much higher than that of RuH(OTf)(CO)L₂ (1923 cm⁻¹), revealing much weaker π -donor ability of the metal in the former. Upon standing in vacuum for 12 h, a CH₂Cl₂-free complex is obtained. Elemental analysis of that solid supports the solvent-free form.¹⁵ Furthermore, the much higher CO stretching frequency (1971 cm⁻¹) of this solid than that in CD₂Cl₂ solution also substantiates even lower electron density of the metal center, consistent with the solvent-free (i.e., ligand

(13) Spectroscopic data for [RuH(η^2 -CD₂Cl₂)(CO)L₂][BAR'₄]: ¹H NMR (CD₂Cl₂, 20 °C): δ 7.70 (br, s, 8H, BAR'₄), 7.50 (br, s, 4H, BAR'₄), 1.54 (vt, *N* = 4.8 Hz, 6H, PCH₃), 1.30 (vt, *N* = 14.4 Hz, 18H, P^tBu), 1.13 (vt, *N* = 13.2 Hz, 18H, P^tBu), -19.4 (br, t, *J*_{PH} = 17 Hz, 1H, Ru-H). ³¹P{¹H} NMR (CD₂Cl₂, 20 °C): 49 (s). ¹⁹F NMR (CD₂Cl₂, 20 °C): 62.0 (s). IR (CD₂Cl₂, cm⁻¹): ν (CO) = 1951.

(14) Crystallographic data for C₅₃H₅₈BCl₄F₂₄OP₂Ru (-170 °C): *a* = 13.639(1) Å and *c* = 34.558(3) Å with *Z* = 4 in space group P41212. *R*(*F*) = 0.0462 for 1845 data with *F* > 2.33 σ (*F*) and a fully anisotropic refinement model with idealized hydrogens. A crystallographic C₂ axis passes through Ru and B; consequently, the hydride and CO ligands are disordered.

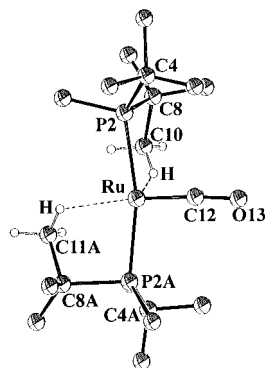


Figure 2. ORTEP drawing of $[\text{RuH}(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2]^+$. Only the hydrogens of the agostic methyl groups are shown. The (undetected) hydride ligand points toward the viewer.

loss) form. The ^1H NMR of the solid in CD_2Cl_2 does not show a signal of the CH_2Cl_2 (CH_2Cl_2 in CD_2Cl_2 is a singlet at 5.34 ppm, while CDHCl_2 is a triplet at 5.33 ppm); this supports the claim that CH_2Cl_2 removal is complete. CH_2Cl_2 is not essential in the synthesis since the same CH_2Cl_2 -free solid can also be obtained by executing the synthesis in $\text{C}_6\text{H}_5\text{F}$ layered with pentane.

An X-ray diffraction study of the CH_2Cl_2 -free material¹⁶ (Figure 2) shows no interaction of either the lattice $\text{C}_6\text{H}_5\text{F}$ or the BAR'_4 anion with the coordination complex cation. The $\text{RuH}(\text{CO})\text{L}_2^+$ ion has thus been authentically "isolated", although the cation in the crystal is disordered around a center of symmetry, which limits the quantitative features which we can learn about structure. The phosphines bend toward one another ($\angle\text{P}-\text{Ru}-\text{P} = 166.3(5)^\circ$), and for each phosphine, one ^iBu group bends inward, toward Ru ($\angle\text{Ru}-\text{P}-\text{C} = 100.3(5)$ and $96.4(5)^\circ$ compared to $119.7(8)$ and $116.4(8)^\circ$ for the second ^iBu groups). As a result, there are two short $\text{Ru}-\text{CH}_3(^i\text{Bu})$ distances (2.74(2) and 2.85(2) Å) which speak for the 14-electron cation $\text{RuH}(\text{CO})(\text{P}^i\text{Bu}_2\text{Me})_2^+$ forming two agostic interactions to methyl C-H bonds. This gives $\text{Ru}\cdots\text{H}(\text{CH}_3)$ distances of approximately 2.17 Å. The authentic 14-electron species is thus too electron deficient to exist when $\text{L} = \text{P}^i\text{Bu}_2\text{Me}$.

The structure of the model species $\text{RuH}(\text{CO})(\text{PH}_3)_2^+$ was optimized with DFT/Becke3LYP calculations with C_s symmetry.¹⁷ This four-coordinate 14-electron species was found to have the (nonintuitive) nonplanar structure¹⁸ which is a fragment of an octahedron ($\text{H}-\text{Ru}-\text{C} = 87^\circ$; $\text{P}-\text{Ru}-\text{P} = 173^\circ$) with two empty sites trans to the ligands of largest trans effect. This unusual structure is preferred because it permits the six electrons in the d shell to be in d orbitals which are nonbonding with respect to the ligands, or which are even stabilized by back-donation into CO, and it also creates the largest HOMO-LUMO gap since all empty orbitals are strongly antibonding with the

ligands. Making the structure more planar, for instance, would result in the occurrence of a low-lying LUMO, z^2 . Making the structure more tetrahedral would create a d splitting of two orbitals lower in energy than the other three, which is inappropriate for low-spin d^6 complexes. $[\text{RuH}(\text{CO})\text{L}_2]^+$ thus has two empty orbitals which are symmetric and antisymmetric with respect to the plane bisecting the $\text{H}-\text{Ru}-\text{C}$ angle. These two orbitals are adapted to make bonds to the two Cl atoms of CH_2Cl_2 or to two agostic C-H bonds. The dissociation energy for loss of CH_2Cl_2 (based on DFT/Becke 3LYP calculations on $\text{Ru}(\text{H})(\text{CO})(\text{CH}_2\text{Cl}_2)(\text{PH}_3)_2^+$) is calculated to be 22.2 kcal/mol, which is in accord with the facile loss of dichloromethane under vacuum. The C-Cl bonds are calculated to be negligibly stretched (1.80 Å) with respect to free CH_2Cl_2 (1.77 Å). The Ru-Cl bond trans to H is longer (2.89 Å) than that trans to CO (2.67 Å), in accord with the relative trans influence of H and CO, and their average value is close to the experimental, 2.74 Å. The H-Ru-CO angle (85°) is not significantly modified by binding to CH_2Cl_2 . The experimental and calculated Cl-Ru-Cl angles are almost identical (63 and 64° , respectively). This good agreement between several experimental and calculated geometrical parameters allows reliance on the calculated hydride position; crystallographic disorder prevents experimental determination.

The structure of this complex is especially interesting in that the 14-electron species only rather weakly binds dichloromethane, without reacting further (e.g., oxidative addition); the weak bonding is in agreement with the poor basicity (nucleophilicity) of CH_2Cl_2 . The structure observed for $\text{RuH}(\text{CO})(\text{CH}_2\text{Cl}_2)_2^+$ is thus associated with strong Lewis acidic properties and weak reducing ability of the $\text{Ru}(\text{H})(\text{CO})\text{L}_2^+$ moiety.

Since CH_2Cl_2 is a very poor base, the $\text{M}-\text{ClCH}_2\text{Cl}$ dative bond has always been presumed to be weak and labile. The only previous reports on structurally characterized bidentate CH_2Cl_2 complexes (of $\text{Ag}(\text{I})$) show that the structure of coordinated CH_2Cl_2 only slightly deforms from that of free CH_2Cl_2 . The other common feature is that all CH_2Cl_2 complexes are cationic. In contrast, Waters et al. reported an Ru_3 cluster with a bridging CH_2Cl_2 .¹⁹ The CH_2Cl_2 is bound tightly to the three Ru by donating four lone pairs (two from each Cl), and thus, significant structural change of this CH_2Cl_2 is observed.

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Supporting Information Available: Tables giving full crystallographic details and anisotropic thermal parameters for the two structures reported (15 pages). See any current masthead page for ordering or Internet access instructions.

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(15) Synthesis of $[\text{RuH}(\text{CO})\text{L}_2][\text{BAR}'_4]$: $\text{RuH}(\text{OTf})(\text{CO})\text{L}_2$ (200 mg, 0.33 mmol) and NaBAR'_4 (300 mg, 0.34 mmol) were mixed with CH_2Cl_2 (10 mL) in a test tube in an Ar-filled glovebox. The mixture was shaken for 5 min before it was centrifuged. The resulting clear solution was carefully decanted to a Schlenk flask (also in an Ar-filled glovebox). The solution was then layered with pentane and stored at -20°C for 3 days. Large orange crystals were formed, which were filtered and washed with pentane. The solid was dried under vacuum for 12 h to obtain CH_2Cl_2 free form (240 mg, 55%). Anal. Calcd for $\text{C}_{51}\text{H}_{55}\text{BF}_2\text{OP}_2\text{Ru}$: C, 46.57; H, 4.22. Found: C, 46.15; H, 4.33. IR (Nujol mull, cm^{-1}): $\nu(\text{CO}) = 1971$. If the solid is dissolved in CD_2Cl_2 , the NMR spectra are the same as the ones described.¹³

(16) Crystal data for $\text{C}_{57}\text{H}_{59}\text{BF}_2\text{OP}_2\text{Ru}$ (-170°C): $a = 18.744(3)$ Å, $b = 17.870(3)$ Å, $c = 18.608(3)$ Å, and $\beta = 95.48(1)^\circ$ with $Z = 4$ in space group $\text{C}2/c$. $R(F) = 0.0789$ for 2133 reflections with $F > 4\sigma(F)$. Agostic hydrogens were placed in idealized (sp^3) locations with $\text{C}-\text{H} = 0.96$ Å and a staggered rotational conformation; distances involving these hydrogens are thus unreliable.

(17) The calculations were performed with the Gaussian 94 package. The pseudopotential and basis sets for Ru, P, C, O, and hydride are those of LANL2DZ. Polarization functions were added to P, C, O, and the hydride. The hydrogens of PH_3 are calculated with a minima basis set. Optimization was carried out at the DFT (B3LYP) level. Gaussian 94. Revision D. I.: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

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