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Communications

Synthesis and Structural Characterization of Novel Organometallic, Rh(III), Bis(acetylacetonate) Complexes

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Summary: Recently, we reported the first catalytic, intermolecular, anti-Markovnikov, hydroarylation of unactivated olefins by a homogeneous, bis-chelating, O-donor Ir(III) complex,[1] (acac)$_2$Ir(R)(L), based on the simplest β-diketonate, acetylacetonate, acac. With the ultimate objective of designing more active catalysts for this potentially useful reaction by structure−function studies, we embarked on developing a rational synthesis of the bis-acac Rh(III) organometallic analogues to the Ir complex. While many tris-acac, late transition metal complexes are known, no rational syntheses of bis-acac, organometallic analogues have been reported. Herein, we report the synthesis and full characterization of the organometallic complex (acac)$_2$Rh(Ph)(CH$_3$OH), ***III****, and related analogues. These complexes have all been found to be air and water stable.*

Recently, we reported the first catalytic, intermolecular, anti-Markovnikov, hydroarylation of unactivated olefins with unactivated arenes, by a homogeneous, bis-chelating, O-donor Ir(III) complex,[1] (acac)$_2$Ir(R)(L), based on the simplest β-diketonate, acetylacetonate, acac. Experimental and theoretical studies[2] suggest that (a) the trans-O-donor, bis-bidentate Ir(III) motifs are remarkably thermally stable to air and acids; (b) the bis-acac ligand motif can provide access via trans to cis isomerization to coordinatively unsaturated, five-coordinate, square pyramidal geometries that can be useful for catalysis; (c) the active species is the organometallic complex (acac)$_2$Ir(Ph)(L); (d) catalysis occurs by arene CH activation that involves an Ir(V) intermediate or transition state; and (e) the rate-determining step is olefin insertion. Intriguingly, while formation of olefins could be expected from facile β-hydride elimination reactions, no olefinic products are observed in stoichiometric or catalytic reactions with these O-donor Ir(III) systems. Calculations and experimental results suggest that this could be due to a combination of the high barrier for ligand dissociation from the cis-octahedral intermediates and the electron-withdrawing characteristics of the O-donor ligands that, while allowing olefin insertion and CH activation, destabilize the Ir(III) center to formation of stable olefinic complexes.[2] Both experimental and theoretical studies suggest that the trans to cis isomerization of the O-donor, bis-bidentate motif is required for reactivity and that this step may contribute to the overall reaction rate. Given the broad potential utility of efficient catalysts for olefin hydroarylation (such as heteroatom tolerance and regio- and stereocontrol), we have begun a systematic study of the structure−function relationships in this class of complexes by exploring variations in the metal center as well as the bis-bidentate, O-donor ligands.

The ultimate objectives of these studies will be to determine the fundamental requirements for effective catalysis with this promising class of complexes and to use this information to synthesize new, stable catalysts with higher rates and selectivities. On the basis of the general expectation that the steps contributing to the hydroarylation reaction, ligand loss, trans to cis isomerization, CH activation, and olefin insertion, could be expected to be faster on replacement of Ir(III) with Rh(III), we sought to synthesize the Rh(III) organometallic analogue, (acac)$_2$Rh(Ph)(L), of the active Ir(III) catalyst. While some steps could be expected to be more facile with Rh(III) compared to Ir(III), given the possible involvement of Ir(V) in the (acac)$_2$Ir(Ph)(L) catalyst[1,2] and the expected difficulty of accessing this oxidation state for Rh, the relative efficiencies of these catalysts is not obvious. Unfortunately, despite the ubiquity of these long-known β-diketonate ligands and while many late transition metal, tris-acac complexes have been reported, no rational syntheses of late transition metal, organometallic complexes with bis-acac ligands have been reported. We now report the first rational synthesis of the Rh(III) bis-acac, organometallic complex, **III**, and analogues of this material.

The syntheses of new, trans bis-diketonate complexes of Rh(III) with the simplest β-diketonate, acetylacetonate, acac, are summarized in Scheme 1. To our knowledge this is the first rational route for the direct syntheses of bis-acac Rh(III) complexes. It is noted that the products of the reaction of RhCl$_3$·XH$_2$O with β-diketonate ligands strongly depend on the reaction temperature and solvent. Well-defined products include Rh-

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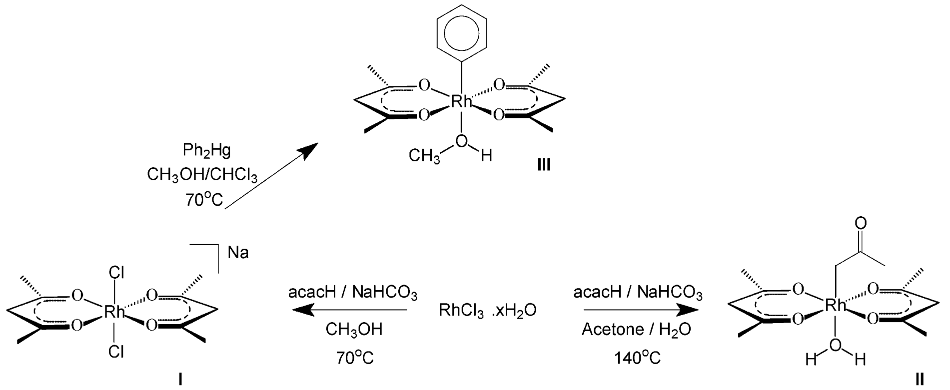
Scheme 1. Synthesis of $(acac)_2Rh(III)$ Complexes



$(acac)_3$[4] and $Rh(acac)(H\text{-}acac)Cl_2$[5] (where H-acac is the acetylacetone) when different reaction conditions are used. Previous attempts to synthesize trans bis-acac Rh(III) complexes have failed.[6] However, we note that complex **I** is the same compound that has been reported earlier as a trace product from the synthesis of Rh-$(acac)_3$. The only characterization reported was an X-ray diffraction structure.[6]

Heating $RhCl_3{\cdot}XH_2O$ with 2 equiv of H-acac and 2 equiv of $NaHCO_3$ in a mixture of H_2O/CH_3COCH_3 at 70 °C for 16 h led to Na[*trans*-$(acac)_2RhCl_2$], **I**. Complex **I** is an orange-yellow, air and water stable microcrystalline compound. Complex **I** was precipitated from a concentrated methanol solution of the reaction mixture at −30 °C. The ^{1}H NMR spectrum of **I** shows single resonance signals for the methyl and methine proton of the acac ligand at their usual chemical shifts, which implies a symmetric environment for the two acac ligands, as expected for the trans geometry. It was not anticipated that this could be a mono-acac Rh complex, as these typically show rather complicated ^{1}H NMR spectra due to the existence of isomers in solution. This assignment was confirmed by a low-temperature, single-crystal X-ray diffraction study of **I**.[8] The molecular structure of **I** is shown in Figure 1. Each Rh atom adopts octahedral coordination geometry, with four O atoms of the two acac ligands in the same plane. Two O atoms from adjacent octahedra are simultaneously in contact with Na^+ ions, together with two CH_3OH molecules at cis positions, to form a distorted Na octahedron with a - -Rh- -Na- -Rh- - polymeric chain structure, in which neighboring $Rh(acac)_2$ equatorial planes are inclined to each other at an angle of 77°. It is noted that although the geometry of the Rh core is the same as that reported by others,[6] the cell composition is different because of the different number and types of solvent molecules in the unit cell.

Interestingly, when the reaction of $RhCl_3{\cdot}H_2O$ with 2 equiv of H-acac and 2 equiv of $NaHCO_3$ in a H_2O/CH_3COCH_3 mixture was carried out at 140 °C for 2 h, a new organometallic species, $Rh(acac)_2(CH_2COCH_3)(H_2O)$ (**II**), separated as a yellow and air and water stable microcrystalline solid with 59% yield. The X-ray structure of **II** is shown in Figure 2. The analogous acetonyl Ir analogue can be obtained by CH activation of acetone,[1a] and if a similar CH activation reaction is responsible for the formation of this Rh analogue, this suggests that the Rh analogues could be active for CH activation. This is being investigated. The molecular structure of this complex is also octahedral, with two acac ligands in a trans relationship. The average Rh−O

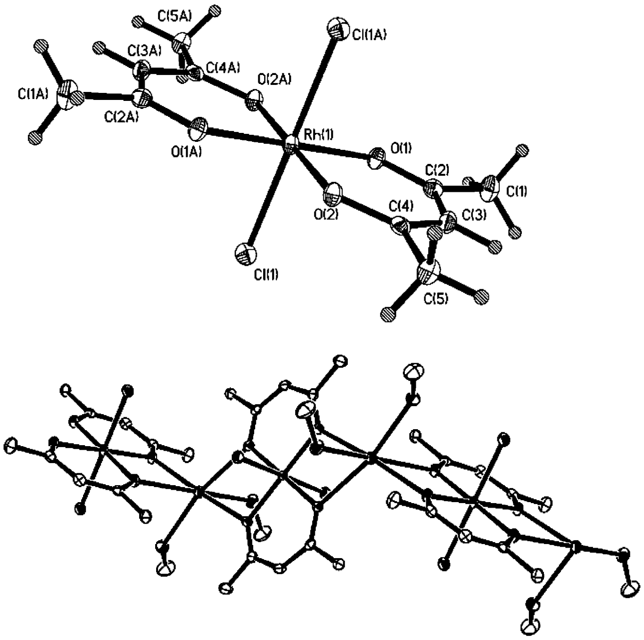


Figure 1. Thermal ellipsoid plot of **I** (50% probability thermal ellipsoids), showing the $[Rh(acac)_2Cl_2]^-$ complex anion (top). Each complex is bridged to the next by a cis-$[Na(CH_3OH)_2]^+$ in the crystal lattice (bottom).

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(8) Crystal data for **I**: an orange prism-shaped crystal of dimensions 0.295 × 0.045 × 0.045 mm was grown from methanol at −30 °C. $C_{12}Cl_2NaO_6Rh{-}H_2O$: monoclinic, group $C2/c$, $a = 19.476(4)$ Å, $b = 8.9430(14)$ Å, $c = 13.154(3)$ Å, $V = 1812.1(6)$ Å^3, $Z = 4$, $T = 85(2)$ K, $D_{calcd} = 1.675$ Mg/m^3, $R(F) = 2.61$ for 5334 observed reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full crystallographic information is given in the Supporting Information. Crystal data for **II**: a yellow prism-shaped crystal of dimensions 0.082 × 0.08 × 0.06 mm was grown from diethyl ether at −30 °C. $C_{13}H_{19}O_6Rh$: monoclinic, group $P2(1)/n$, $a = 8.7436(12)$ Å, $b = 14.715(2)$ Å, $c = 11.9556(16)$ Å, $V = 1456.1(3)$ Å^3, $Z = 3$, $T = 85(2)$ K, $D_{calcd} = 1.695$ Mg/m^3, $R(F) = 5.49$ for 8814 observed reflections. Full crystallographic information is given in the Supporting Information. Crystal data for complex **III**$\cdot 2CHCl_3$: a yellow prism-shaped crystal of dimensions 0.474 × 0.248 × 0.092 mm was grown from a 50/50 mixture of methanol/chloroform at −30 °C. $C_{19}H_{24}C_{16}O_5Rh$: triclinic, group $P\bar{1}$, $a = 10.2645(5)$ Å, $b = 11.0621(6)$ Å, $c = 11.7027(7)$ Å, $V = 1307.84(12)$ Å^3, $Z = 2$, $T = 149(2)$ K, $D_{calcd} = 1.645$ Mg/m^3, $R(F) = 4.21$ for 7846 observed reflections. Full crystallographic information is given in the Supporting Information.

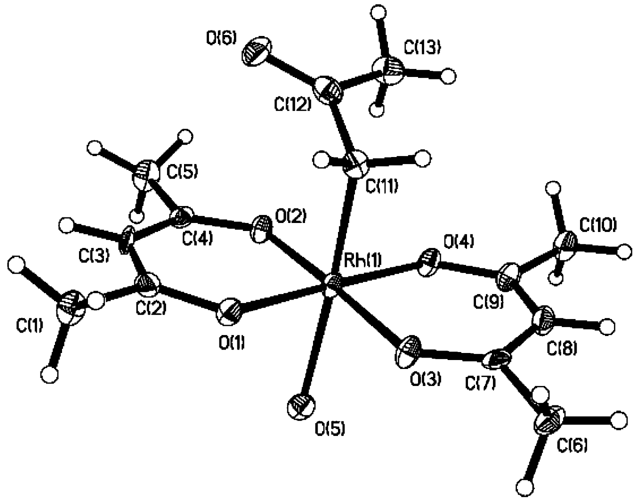

Figure 2. Thermal ellipsoid plot of **II** (50% probability), showing the σ-bonded $-CH_2COCH_3$ ligand and a water ligand in axial positions. The hydrogen atoms of the aqua ligand have not been located and were omitted.

distance (1.993(3) Å) is slightly shorter than that in complex **I** (2.009(2) Å). The Rh−C distance (2.042(5) Å) is similar to those in other Rh(III) complexes having different ligands.[7] The ^{1}H NMR spectrum of **II** is consistent with its solid state structure. The resonances of the acac ligands are very similar to those in complex **I** but shifted to higher field because of replacement of the Cl with the more electron-rich acetonyl ligand in **II**. The most diagnostic feature in the spectrum is the doublet resonance of the Rh-bonded CH_2 group at 3.63 ppm, with a coupling of 3 Hz ($^2J_{Rh-H}$, Rh−C−H coupling). The $^{13}C\{^1H\}$ NMR resonance of this Rh-bonded CH_2 group appears at 31 ppm as a doublet.

Treatment of **I** with Ph_2Hg in $CHCl_3/CH_3OH$ at 70 °C gave the air and water stable organometallic complex $(acac)_2Rh(Ph)(CH_3OH)$, **III**. The structure of **III** was confirmed by X-ray diffraction as shown in Figure 3. The geometry of the Rh atom in **III** is very similar to that in **I** and the Ir analogue. The Rh- - -C(of Ph) distance, 1.970(3) Å, in **III** is slightly shorter than the Rh- -C(of CH_2COMe) distance, 2.042(5) Å, in **II**, presumably due to the difference in covalent radii between C(sp^2) and C(sp^3) atoms. The ^{1}H NMR spectrum of **III** is consistent with this structure and shows simple singlets for both the methyl and the methine groups of the acac ligands. The resonance of the Ph group appears at about 6.8 ppm, which is comparable to that of its Ir analogue.[1a]

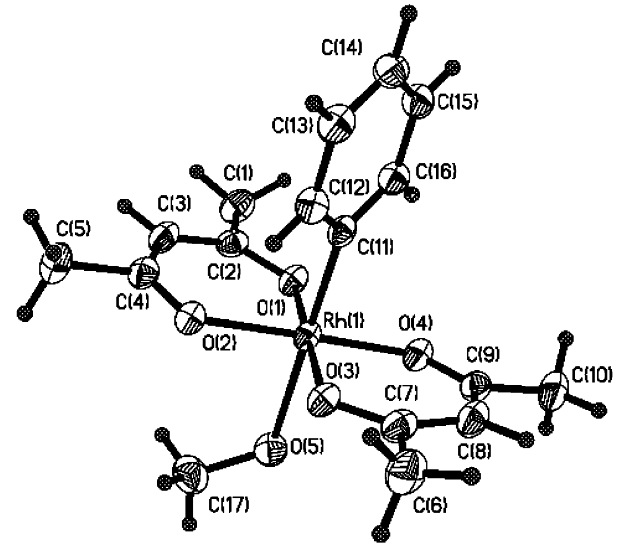

Figure 3. Thermal ellipsoid plot of **III** (50% probability). Two molecules of cocrystallized $CHCl_3$ have been omitted for clarity. The hydrogen atom of the methanol ligand was not located and was omitted.

In conclusion, we have prepared several novel bisacetylacetonate Rh(III) compounds with the same structure and composition as the Ir catalysts we previously reported for the hydroarylation of olefins.[1] Encouragingly, preliminary studies show that these complexes are both thermally stable and active for CH activation of arenes in reactions with acetic acid. With the development of a general, rational synthesis to the class of O-donor Rh(III) arylated and alkylated complexes in hand, efforts are now underway to explore the scope of catalytic and reaction chemistry of these O-donor, bis-bidentate, Rh(III) complexes.

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Supporting Information Available: The preparative procedures, spectroscopic and elemental analysis data for compounds **I**−**III**, and crystallographic data sets for **I**, **II**, and **III** are available free of charge via the Internet at http// www.pubs.acs.org.

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