Heterobimetallic Polyhydride Complex Containing Ruthenium and Iridium. Synthesis and Site-Selectivity in the Reaction with Unsaturated Hydrocarbons

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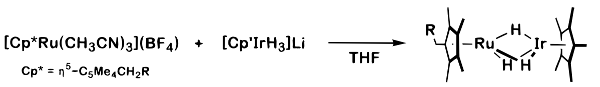
*Summary: The first heterobimetallic trihydride complex containing ruthenium and iridium having C_5Me_5 groups as ancillary ligands was synthesized, and its structure was determined by X-ray studies. The reactions of **3** with $CH_2{=}CH_2$, PhC≡CMe, and PhC≡CPh proceed site-selectively.*

The reactivity of transition metal cluster complexes has been of special interest because of their capability of multiple coordination of a substrate and multielectron transfer between the substrate and the cluster. In the multimetallic reaction site generated on the cluster complex, substrates can, therefore, be activated in an effective, and sometimes unusual, manner due to the cooperative action of the metal centers. We have demonstrated several typical examples of the concerted activation of organic substrates on the multimetallic site by using ruthenium polyhydride clusters $(Cp'Ru)_2(\mu\text{-}H)_4$ (**1**) and $(Cp'Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**2**) ($Cp' = \eta^5\text{-}C_5Me_5$) as precursors of the active species for *multimetallic activation*.[1]

As an extension of *multimetallic activation* on homonuclear cluster complexes, we have recently focused on the substrate activation on the electronically anisotropic reaction site of heteronuclear cluster complexes. Substitution of one of the metals in a homonuclear cluster with a different kind of metal is responsible for the electron density gradient between the metal centers. A heteronuclear polyhydride complex is expected to be a suitable precursor of an active species for concerted activation due to different kinds of metals, that is, *heterometallic activation*, as ruthenium polyhydride cluster complexes **1** and **2** are precursors for *homometallic activation*. Although a number of heterobimetallic polyhydride cluster complexes have been synthesized,[2] there have been only a few reported examples of achievement of heterobimetallic activation.[3] We report herein the first synthesis of the heterometallic polyhydride complex containing group VIII and IX transition metals, $Cp'Ru(\mu\text{-}H)_3IrCp'$ (**3**), which has only Cp′ groups as ancillary ligands. Remarkable site-selectivity between the ruthenium and iridium centers observed in the reaction of the heterobimetallic cluster **3** with alkenes and alkynes is also reported.

The reaction of $[Cp'Ru(CH_3CN)_3](BF_4)$[4] with anionic iridium hydride complex $Li[Cp'IrH_3]$[5] in tetrahydrofuran at ambient temperature resulted in the exclusive formation of a new hydride cluster **3** (eq 1). The new compound **3** was isolated as a red-brown crystalline solid in 62% yield and assigned as a dinuclear mixed-metal polyhydride-bridged complex based on the observation of three singlet signals at δ 1.90 (15H), 1.85 (15H), and −17.37 (3H) in the ^1H NMR spectrum for the Cp′ group bound to Ru, that bound to Ir, and the bridging hydrides, respectively. The ^1H and ^{13}C resonance signals for the Cp′ ligands were unequivocally assigned in comparison with those of $(C_5Me_4Et)Ru(\mu\text{-}H)_3IrCp'$ (**3′**), which was derived by the reaction of the corresponding C_5Me_4Et analogue of the cationic acetonitrile complex, $[(C_5Me_4Et)Ru(CH_3CN)_3](BF_4)$, with $Li[Cp'IrH_3]$.



(1)

3, R = H
3', R = Me

The longitudinal relaxation time T_1 for the hydride ligands in **3** was determined to be 3.34 s at 193 K by

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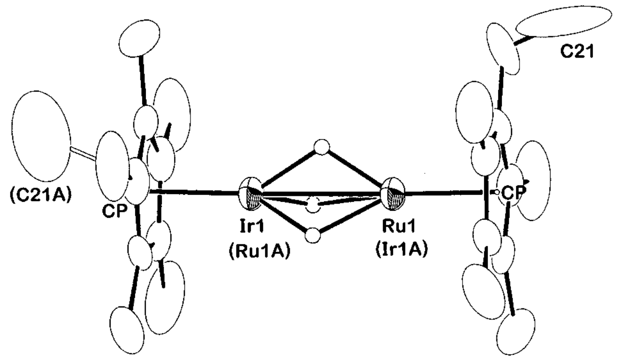

Figure 1. Molecular structure of (η^5-C_5Me_4Et)Ru(μ-H)$_3$Ir(η^5-C_5Me_5) (**3′**). Selected bond distances (Å) and angles (deg): Ru1−Ir1 2.4858(4); CP−Ir1−Ru1 178.8, CP−Ru1−Ir1 177.6 (CP = Cp′ centroid).

using the inversion−recovery method. The observed T_1 value is sufficient to characterize the complex as a classical trihydride complex.

Compound **3** was also obtained in 80% isolated yield by the reaction of a cubane-type ruthenium complex {Cp′Ru(μ_3-Cl)}$_4$ with Li[Cp′IrH$_3$] in tetrahydrofuran.

The X-ray diffraction study of **3′** demonstrated a dinuclear structure triply bridged by hydrides.[6] An ORTEP drawing is displayed in Figure 1 along with some of the relevant bond distances and angles.

The dinuclear structure is disordered between two orientations (53:47). The Ru−Ir distance of 2.4858(4) Å is significantly shorter than the sum of the covalent radii (2.69 Å)[7] and also the reported Ru−Ir distance for (η^4-C_8H_{12})Ir(μ-H)$_2$RuH(PPh$_3$)$_3$ (2.623 Å)[2f] and is comparable to the Ru−Ru distance in the related hydride-bridged diruthenium complex **1** (2.463(1) Å).[1b]

The hydride ligands of **3** as well as the methyl group of the Cp′ ligand coordinated to iridium undergo an intermolecular H/D exchange reaction with C_6D_6. The solution of **3** in C_6D_6 was heated in a sealed NMR sample tube at 100 °C, and the H/D exchange reaction was monitored by means of ^{1}H NMR spectroscopy by using cyclopentane as an internal standard. Upon heating for 48 h, three resonance signals assignable to the hydrides of isotopomers Cp′Ru(μ-H)$_3$IrCp′ (**3-*d*$_0$**), Cp′Ru(μ-H)$_2$(μ-D)Ir(Cp′-d_m) (**3-*d*$_1$**), and Cp′Ru(μ-H)(μ-D)$_2$Ir(Cp′-d_n) (**3-*d*$_2$**)[8] appeared at δ −17.37, −17.41, and −17.43, respectively, and a decrease in the integral intensity of the ^{1}H signal for the Cp′ group bound to Ir was observed. Concomitantly the intensity of the signal for the benzene $C_6D_{6-k}H_k$ increased. After heating for an additional 450 h, 91% of the hydride ligands and 54% of the Cp′ methyl hydrogen atoms were converted into a deuterium atom and the molar ratio of the isotopomers **3-*d*$_0$/3-*d*$_1$/3-*d*$_2$/3-*d*$_3$** became 0/3.5/18.5/78.0. Interestingly, the H/D exchange of the bridging hydrides preceded that of the Cp′ methyl hydrogen, and the H/D exchange of the methyl hydrogen exclusively occurred on the Cp′ ligand bound to Ir. The H/D exchange of the bridging hydrides proceeds by way of η^2-coordination of C_6D_6 likely to form a 32-electron intermediate, Cp′Ru(μ-H)$_3$(η^2-C_6D_6)IrCp′,[9] which underwent oxidative addition of the C−D bond, probably at the iridium center, and consecutive reductive elimination of C_6D_5H. The H/D exchange of the Cp′ methyl hydrogen atom proceeds most likely via an η^6-1,2,3,4-tetramethylfulvene or an η^1,η^6-tetramethylcyclopentadienylmethyl intermediate, as proposed for the reversible ring methyl-to-titanium hydrogen shift in Cp′$_2$Ti.[10]

To prove the site-selectivity of the heterobimetallic polyhydride system toward organic substrates, we examined the reactions of **3** with ethylene, diphenylacetylene, and 1-phenylpropyne. The results of the reaction of **3** with these substrates are shown in Scheme 1 together with the X-ray studies of **4** and **7**.[11,12]

The reaction of **3** with ethylene (10 atm) in toluene at 50 °C for 3 days led to the exclusive formation of a new complex, Cp′IrH(μ-η^1,η^2-CH=CH$_2$)$_2$RuCp′ (**4**) together with ethane (δ 0.83) as a result of hydrogenation of ethylene. The new complex **4** was isolated as a red solid in 89% yield after chromatographic purification on alumina and assigned as a dinuclear complex bridged by two σ,π-vinyl ligands on the basis of three ^{1}H NMR signals at δ 2.00 (d, J = 9.2 Hz, 2H), 4.35 (dd, J = 6.7 and 1.8 Hz, 2H), and 8.87 (ddd, J = 9.2, 6.7, and 1.5 Hz, 2H) and two ^{13}C NMR signals at δ 64.1 (J_{CH} = 161.4 and 144.1 Hz, C_β) and 141.8 (J_{CH} = 151.4 Hz, C_α) characteristic of σ,π-vinyl ligand. A notable feature of this reaction is the site-selectivity in which C−H bond cleavage exclusively takes place at the iridium center. The ruthenium center most likely plays the role of a coordination site.

The reactivity of the heteronuclear cluster **3** toward diphenylacetylene is significantly different from that observed for homonuclear cluster **1**. Complex **3** smoothly reacts with diphenylacetylene at ambient temperature

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(6) Complex **3′** crystallized from pentane at 0 °C in the monoclinic system, space group $P2_1/n$ (#14), with a = 7.544(3) Å, b = 15.739(4) Å, c = 18.403(2) Å, β = 90.62(2)°, V = 2185.0(9) Å^3, Z = 4, d(calcd) = 1.765 g/cm^3. The data were collected at 23 °C on a Rigaku AFC-7R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) in the 5° < 2θ < 55° range. The data were processed using the TEXSAN crystal structure analysis package operated on an IRIS Indigo computer. At the early stages of the refinement, the atomic scattering factors were obtained from the standard sources. In the reduction of the data, Lorentz/polarization corrections and empirical absorption corrections based on azimuthal scans were applied to the data. The structure was solved by Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3047 observed reflections (I > 3.00σ(I)) and 218 variable parameters and converged with unweighted and weighted agreement factors of R = 0.037 and R_w = 0.026.

(7) Donahue, J. *The Structure of the Elements*; Wily: New York, 1974.

(8) **3-*d*$_n$**: The subscript ***n*** means the number of deuterium directly bound to the metal centers.

(9) Jones et al. have reported that aromatic C−H bond cleavage by the unsaturated mononuclear rhodium complex proceeded via an intermediate η^2-arene complex; see for example: Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814.

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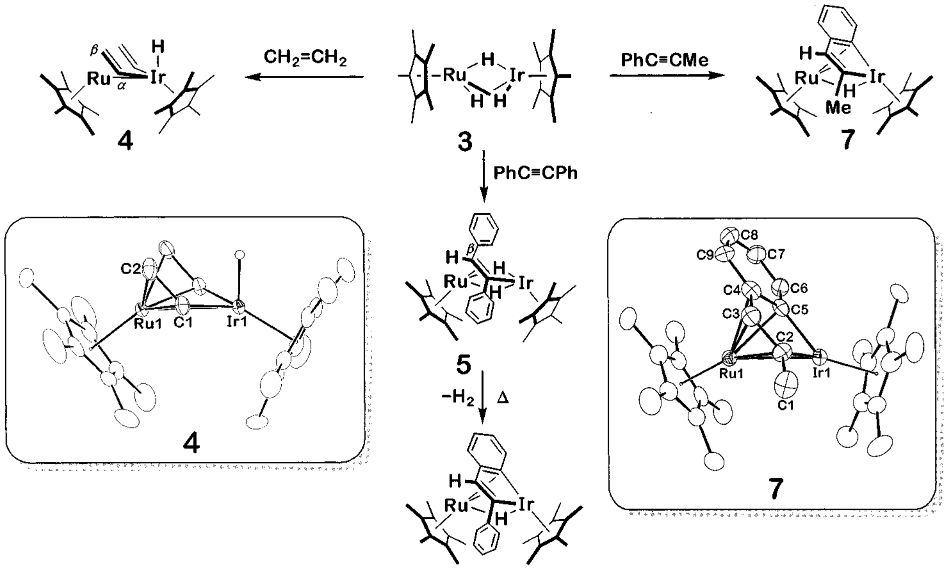
(11) Complex **4** crystallized from toluene in the orthorhombic system, space group *Pnma* (#62), with a = 8.915(2) Å, b = 14.332(1) Å, c = 17.735(2) Å, V = 2265.9(8) Å^3, Z = 4, d(calcd) = 1.814 g/cm^3. Data collection, solution and refinement were carried out as in ref 6. The final cycle of full-matrix least-squares refinement was based on 2300 observed reflections (I > 3.00σ(I)) and 143 variable parameters and converged with unweighted and weighted agreement factors of R = 0.024 and R_w = 0.024.

(12) Complex **7** crystallized from pentane in the monoclinic system, space group $P2_1/n$ (#14), with, a = 8.456(2) Å, b = 19.201(2) Å, c = 16.431(3) Å, β = 97.512(19)°, V = 2644.8(9) Å^3, Z = 4, d(calcd) = 1.710 g/cm^3. Data collection and solution were carried out as in ref 6. The non-hydrogen atoms were refined with full-matrix least-squares on F^2 using the SHELXL-97 program systems. The final cycle of refinement was based on 4562 observed reflections (I > 2.00σ(I)) and 299 variable parameters and converged with unweighted and weighted agreement factors of R = 0.0467 and wR_2 = 0.1210.

Scheme 1[a]



[a] $Cp'IrH(\mu$-η^1:η^2-$CH{=}CH_2)_2RuCp'$ (**4**). Selected bond distances (Å) and angles (deg): Ru1−Ir1 = 2.7313(6), Ir1−C1 = 2.029(4), Ru1−C1 = 2.081(4), Ru1−C2 = 2.190(5), C1−C2 = 1.407(7); Ir1−C1−C2 = 122.7(4), Ru1−C1−C2 = 75.0(3), Ru1−C2−C1 66.6(3). $Cp'Ir(\mu$-$H)(\mu$-$MeC{=}CH{-}C_6H_4)RuCp'$ (**7**). Selected bond distances (Å) and angles (deg): Ru1−Ir1 = 2.7401(7), Ir1−C2 = 2.028(9), Ir1−C5 = 2.026(9), Ru1−C2 = 2.261(8), Ru1−C3 = 2.183(10), Ru1−C4 = 2.273(9), Ru1−C5 = 2.319(8), C1−C2 = 1.510(12), C2−C3 = 1.384(13), C3−C4 = 1.417(13), C4−C5 = 1.447(13), C5−C6 = 1.432(12), C6−C7 = 1.370(13), C7−C8 = 1.419(16), C8−C9 = 1.347(15), C9−C4 = 1.428(13); Ir1−C2−C3 = 116.1(7), C2−C3−C4 = 117.0(9), C3−C4−C5 = 111.0(9), C4−C5−Ir1 = 116.8(6).

to produce a σ,π-alkenyl complex, $Cp'Ir(\mu$-σ,π-(Z)-$CPh{=}CHPh)(\mu$-$H)_2RuCp'$ (**5**), while the reaction of **1** with diphenylacetylene resulted in the formation of a dinuclear complex bridged by a perpendicularly coordinated diphenylacetylene, $Cp'Ru(\mu$-η^2:η^2-$PhCCPh)(\mu$-$H)_2$-$RuCp'$.[1a] The stereochemistry of the vinylic moiety in **5** was confirmed to be *Z* by comparison of the ^1H NMR chemical shift for β-H (δ 5.84) with those for protons on C-2 of the iridacycles **6** and **7** (δ 5.89 and 5.65, respectively). The formation of **5** is most likely due to an initial μ-(⊥)-η^2:η^2 coordination of a diphenylacetylene molecule and subsequent *trans*-addition of Ir and a hydride to the carbon−carbon triple bond. In the ^1H NMR spectrum of **5** was observed significant upfield shift (δ 6.76) of one of the *aromatic*-H signals. We tentatively assigned this to the *ortho*-H of a phenyl group on the β-carbon of the vinylic ligand. This upfield shift is probably due to anisotropic shielding by the adjacent metal center.[13] The bridging alkenyl complex **5** was quantitatively converted into a dinuclear benzoiridacyclopentadiene complex **6** upon heating at 80 °C as a result of intramolecular activation of the C(*ortho*)−H bond.

The reaction of **3** with 1-phenylpropyne proceeded more readily at ambient temperature to result in the exclusive formation of the corresponding iridacycle **7**. An intermediary vinylic complex $Cp'Ir(\mu$-σ,π-(Z)-$CMe{=}CHPh)(\mu$-$H)_2RuCp'$ was detected by means of ^1H NMR spectroscopy.

The results of these reactivity studies apparently substantiate the allotment of respective roles, namely, coordination site vs activation site, between the metal centers in the heterobimetallic complex **3**.

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Supporting Information Available: Tables of ^1H and ^{13}C NMR spectra assignments of **3**−**7** and ORTEP diagrams, text describing X-ray procedures, and tables of X-ray data, positional and thermal parameters, and distances and angles for **3′**, **4**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) In the CH-2D NMR, the ^1H signal at δ_H 6.76 correlated to the ^{13}C signal at δ_C 133.8 and the coupling constant between them ($^1J_{CH}$) is 158.9 Hz. The $^1J_{CH}$ value of 158.9 Hz is typical for that between C(sp^2) and H. Therefore, it can be concluded that the upfield shift of the ^1H NMR signal is not due to an agostic interaction.