Stereospecific CO Insertion into the Rhodium−Methyl σ Bond in [(Cp′-P)Rh(CO)(Me)]BF_4 and Deinsertion from [(Cp′-P)Rh(COMe)I]: Experimental Evidence for Methyl Migration

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*Summary: We have shown concrete evidence for migration of an alkyl group in carbonyl insertion and deinsertion steps between the methyl carbonyl rhodium complex [{η^5:η^1-(Ind-P)$_{n=3}$}Rh(CO)Me]BF_4 (**3**) and the acetyl rhodium complex {η^5:η^1-(Ind-P)$_{n=3}$}RhI(COMe) (**1**) by crystallography as well as by ^{1}H NMR spectroscopy.*

The conversion of metal alkyls to metal acyl complexes and its reverse reaction are the fundamental steps in many reactions mediated by transition-metal complexes.[1−4] Many experimental and theoretical approaches to clarify the nature of the reactions have been extensively investigated.[5,6] One of the significant issues in the mechanistic study is the stereochemical course of these steps; alkyl migration to CO vs CO insertion into the metal−alkyl bond.[1,7−17] To date, many examples of alkyl migration to a coordinated CO have been reported, including studies of the octahedral methyl Mn carbonyl complex using ^{13}CO[7] and studies of square-planar Pt or Pd diphosphine complexes using ^{31}P NMR analysis.[8] The stereochemical course in three-legged piano-stool iron complexes such as CpFe(CO)(L)R (L = ligand, R = alkyl group) depends on the solvent, the incoming ligand, and the presence of Lewis acid catalysts.[16,17] The stereochemical course, however, was determined mainly on the basis of the spectroscopic studies. Here we wish to describe concrete evidence for methyl migration on the stereospecific conversion of metal alkyl complexes to metal acyl ones and its reverse reaction, in which the absolute configurations of both the starting material and the product were determined crystallographically.

Recently we have designed and prepared several types of the [Cp′-P]H ligand and disclosed unique characters of their Rh, Ru, and Ir complexes.[18] In the course of our research on oxidative addition of an alkyl halide to the Rh carbonyl complex bearing the Cp′-P ligand, we could synthesize the acyl Rh complexes having a stereogenic center on the metal and determine their structures including the absolute configuration around the central metal. For example, the stereochemistry of the major isomer of the three-legged piano-stool complex {η^5:η^1-(Ind-P)$_{n=3}$}RhI(COMe) (**1**), prepared from the reaction of {η^5:η^1-(Ind-P)$_{n=3}$}RhCO with methyl iodide, was determined to be R^*_{pl},S^*_{Rh} from the X-ray analysis.[18d] From the top view of the ORTEP drawing the acyl group was found to be located under the benzene ring of the indenyl group (Figure 1a). Although the Rh complex {η^5:η^1-(Ind-P)$_{n=2}$}RhI(COMe) (**2**), which had an different length of the chelate chain (ethylene group), was also prepared by a similar method,[18d] the X-ray analysis of the major isomer of **2** showed the S^*_{pl},S^*_{Rh} configuration (Figure 1b), which is the opposite relative configuration

(1) For clear understanding, we define here several terms: "conversion of metal alkyl to metal acyl" means the net process of metal alkyl to metal acyl interconversion, which does not imply any stereochemistry at the metal center; "alkyl migration" or "retro-alkyl migration" means the stereospecific migration of alkyl to CO that leaves a vacant site at the position formerly occupied by the alkyl group or its reverse reaction; "CO insertion" or "retro-CO insertion" means the stereospecific insertion of CO into the metal−alkyl bond that leaves a vacant site at the position formerly occupied by CO or its reverse reaction.

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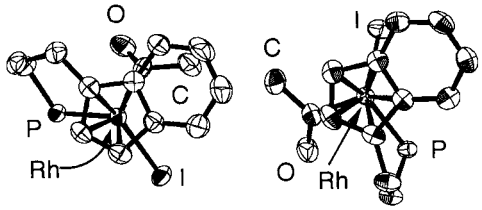
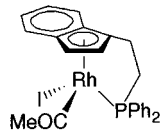


(a) (R^*_{pl},S^*_{Rh})-**1** (b) (S^*_{pl},S^*_{Rh})-**2**

Figure 1.

between the metal-centered chirality and the planar chirality compared to that of **1**-major. The acetyl methyl group of **2**-major is located in the opposite side to the benzene ring of the indenyl group.



(S^*_{pl},S^*_{Rh})
2-major

Reaction of the acyl complex **1** (70% de, R^*_{pl},S^*_{Rh}:R^*_{pl},R^*_{Rh} = 85:15) with $AgBF_4$ in CH_2Cl_2 at room temperature afforded [{η^5:η^1-(Ind-P)$_{n=3}$}Rh(CO)Me]BF_4 (**3**) quantitatively with 68% de (major:minor = 84:16).[19] Although no intermediates were detected by NMR experiments, the reaction is suggested to proceed via an acyl solvent complex, [{η^5:η^1-(Ind-P)$_{n=3}$}Rh(COMe)-(CH_2Cl_2)][BF_4]. Yellow single crystals of pure **3**-major were obtained by recrystallization of diastereomer mixtures of **3** from CH_2Cl_2 and ether. The ORTEP drawing of **3**-major showed that the stereochemistry was R^*_{pl},R^*_{Rh} and the methyl group is located on the side opposite to the benzene ring of the indenyl group (Figure 2).[20] Both complexes **1** and **3** are configurationally very stable and did not epimerize at all after heating at 60 °C for 24 h in $CDCl_3$.[21] The ratio of the diastereomers was much the same before and after the reaction, indicating that the major isomer of the acyl complex **1** was converted stereospecifically to the major isomer of the cationic complex **3**, and thus, epimerization at the labile intermediate, the acyl solvent complex, could be disregarded. These observations clearly indicated that the conversion from the acyl complex **1** to the cationic complex **3** proceeded by migration of the methyl group to the vacant site obtained after the removal of the iodo ligand (retro-alkyl migration), not by decarbonylation from the acyl group (retro-CO insertion).

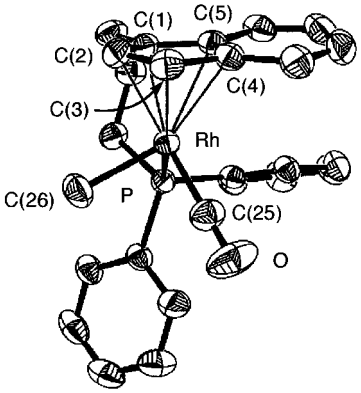
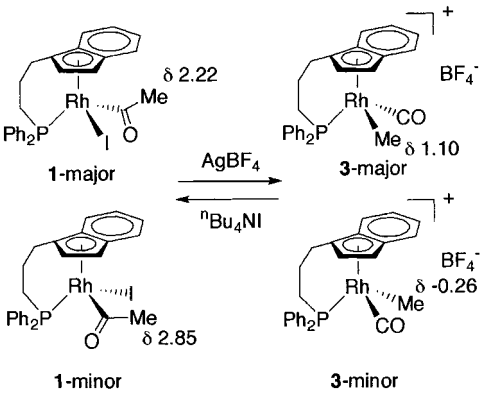


Figure 2. ORTEP drawing of the X-ray crystal structure of the cationic part of **3**-major (R^*_{pl},R^*_{Rh}). Selected interatomic distances (Å) and angles (deg) are as follows: Rh−C(26) = 2.108(3), Rh−C(25) = 1.890(3), Rh−Cp = 1.9213, Rh−P = 2.2987(7), C(25)−O = 1.122(4); C(25)−Rh−C(26) = 86.33(17), C(25)−Rh−P = 97.84(10), C(25)−Rh−Cp = 129.7, C(26)-Rh−Cp = 119.9, P−Rh−Cp = 123.6. Cp is the gravimetric center of the cyclopentadienyl part (C(1) C(2), C(3), C(4), C(5)) of the indenyl group.

Scheme 1



Reaction of the cationic complex **3** (56% de, R^*_{pl},R^*_{Rh}:R^*_{pl},S^*_{Rh} = 78:22)[22] with ^{n}Bu$_4$NI in CH_2Cl_2 at room temperature afforded the starting acyl complex **1** with 52% de (R^*_{pl},S^*_{Rh}:R^*_{pl},R^*_{Rh} = 76:24), indicating that the conversion of the metal alkyl complex **3** to the metal acyl complex **1** is also stereospecific and the methyl group migrates to the Rh−carbonyl bond.

From the NMR chemical shift correlations for **1** and **3**, the stereochemical course of metal alkyl to metal acyl interconversion can be also discussed. The ^{1}H NMR signal of the methyl group of **1**-major appears at δ 2.22, while that of **1**-minor appears at δ 2.85. The methyl group of the major isomer is shielded by the ring current of the benzene ring of the indenyl group; that is, the stereochemistry of the major product is R^*_{pl},S^*_{Rh}. In the meantime, the methyl signal of **3**-major in the ^{1}H NMR appeared at δ 1.10 and that of **3**-minor at δ −0.26. The methyl group of **3**-minor, which is clearly affected by the ring-current effect, would be located under the indene ring; that is, the stereochemistry of the minor product is R^*_{pl},S^*_{Rh} and that of the major product is R^*_{pl},R^*_{Rh} (Scheme 1). These arguments reached the same conclusion that the alkyl migration to CO was acceptable.

(19) The ratio of the two diastereomers was determined by ^{31}P NMR before purification; see the Supporting Information.

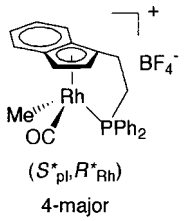
(20) Crystallographic data for **3**-major: $C_{26}H_{25}BF_4OPRh$, (M_r = 574.15), Rigaku AFC-7R (data collection), monoclinic, space group $P2_1/n$ (No. 14), a = 13.2349(15) Å, b = 12.610(3) Å, c = 14.6194(10) Å, β = 91.962(7)°, V = 2438.4(7) Å^3, Z = 4, D_{calcd} = 1.564 Mg/m^3, μ = 0.814 mm^{-1}, T_{max}/T_{min} = 0.9992/0.9227, λ(Mo Kα, 10kW) = 0.71069 Å, F(000) = 1160, 7711 reflections measured at 293(2) K, 7117 unique reflections, R_{int} = 0.0205, $2\theta_{max}$ = 60.0°, solution method SIR97, refinement based on F^2 (SHELXL97-2), R1/wR2($I > 2.0\sigma(I)$, 4525) = 0.0345/0.0725, R1/wR2(all data, 7117) = 0.0801/0.0837, GOF(all data) = 0.996, Δ/σ_{max}-(final cycle) = 0.001, $\Delta\rho$(max/min) = 0.485/−0.349 e Å^{-3}.

(21) The complexes **1**−**4** are all configurationally rigid in solution. We did not observe the fact that the major isomer and the minor isomer interconnected with each other below 60 °C in $CDCl_3$. Cf.: (a) Brunner, H.; Zwack, T. *Organometallics* **2000**, *19*, 2423. (b) Pfeffer, M. *Organometallics* **2000**, *19*, 2427.

(22) The starting complex **3** used in this reaction was obtained after a purification process.

A similar result was observed for the conversion of the metal acyl complex **2** to the metal alkyl complex **4**. The methyl signal of **2**-major in the ^{1}H NMR appeared at δ 3.10 and that of **2**-minor at δ 2.39. The correlation of the NMR data indicated that the acetyl methyl group of **2**-major is located on the side opposite to the benzene ring, which was consistent with the fact that the major isomer of **2** was assigned to be S^*_{pl},S^*_{Rh} from the X-ray analysis (vide supra). Reaction of **2** (34% de, S^*_{pl},S^*_{Rh}: S^*_{pl},R^*_{Rh} = 67:33) with $AgBF_4$ under the same conditions afforded the cationic complex **4** in 36% de (major: minor = 68:32), indicating that this decarbonylation (conversion of the metal acyl **2** to the metal alkyl complex **4**) also proceeded in a stereospecific manner. When the CO deinsertion proceeds via retro-alkyl migration from the metal acyl complex to the metal alkyl complex, just in the same way as that of **1**, the major isomer of the methyl carbonyl complex **4** would be the S^*_{pl},R^*_{Rh} isomer and the minor isomer would be the S^*_{pl},S^*_{Rh} isomer. The methyl signal of **4**-major in the ^{1}H NMR should appear at an upper-field compared to that of **4**-minor. This prediction is consistent with the experimental results: the methyl signal of **4**-major appeared at δ −0.47, and that of **4**-minor was δ 1.20.

In conclusion, we have clearly shown that migration of an alkyl ligand to a coordinated CO is a preferential stereochemical course for conversion of metal alkyl to metal acyl and its reverse reaction on the three-legged piano-stool Rh complex bearing the Cp′-P ligand. Furthermore, in view of the results that the migratory insertion and deinsertion steps can be controlled stereospecifically by the Cp′-P ligands, their Rh complexes having the metal-centered chirality could be applied to stoichiometric or catalytic asymmetric reactions.



(S^*_{pl},R^*_{Rh})
4-major

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Supporting Information Available: Text giving full experimental procedures and spectroscopic and analytical data for all new compounds and tables giving X-ray structural information on **3**-major. This material is available free of charge via the Internet at http://pubs.acs.org.

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