Synthesis of (Vinylallene)rhodium(III) Complex of Planar Structure: Perfect $\pi \rightarrow \sigma$ Conversion of 1,3-Diene System

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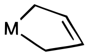
The structures of conjugated diene−transition metal complexes have attracted considerable attention owing to the great diversity of the binding modes. For example, most middle and late transition metal−diene complexes assume the conventional π^2-bonded structures **1**.[1] On the other hand, early transition metals prefer the bent σ^2,π-bonded metallacyclo-3-pentene form **2**.[2] The *s-trans* binding has been also reported.[3] Stereochemical fluxionality of *s-cis* complexes has been often observed and explained by a ring-flipping mechanism.[4] Although implicated as a transitory species in the ring flipping, examples of thermodynamically stable planar σ^2-bonded complexes (**3**) remain few in number[5−7] and are mostly limited to perfluoro-1,3-butadiene[6] and vinyl ketene complexes.[7] Vinylallene is regarded as a conjugated diene with an additional cumulated double bond. However, very little is known about the bonding character of vinylallenes.[8] While studying (vinylallene)rhodium complexes, we found that the binding modes greatly depended on the substitution patterns, probably due to steric reasons.[9] Herein, we report the synthesis of a σ^2-bonded (vinylallene)rhodium complex (**5**) having an essentially planar structure which is determined by X-ray crystallography.

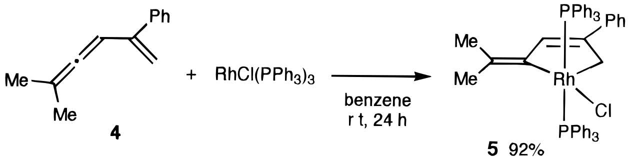
1 π^2-bonded complex

2 bent σ^2,π-bonded complex



3 planar σ^2-bonded complex

Vinylallene (**4**) lacking substituents at the vinylic terminus was treated with $RhCl(PPh_3)_3$ in benzene at room temperature. The vinylallene **4** displaced one molecule of PPh_3 on the rhodium to afford a metallacycle (**5**) as a solid in 92% isolated yield, for which satisfactory analytical data were obtained.[10] Recrystallization from CH_2Cl_2/methanol gave air-stable orange crystals as a methanol solvate.



The solid state structure of **5** was determined by a single-crystal X-ray diffraction study.[11] An ORTEP diagram of the molecule is shown in Figure 1. The most notable feature of the structure is that the five-membered rhodacyclo-3-pentene ring constitutes an almost perfect plane. The maximum deviation from the mean plane is only 0.018 Å. There is no interaction between the C6−C7 double bond and rhodium. The arrangement of the pentacoordinated rhodium atom can be considered as a flat square pyramid or a distorted octahedral geometry with one vacant site over which the C10 methyl group at the allenic terminus hangs. The chlorine atom sits *trans* to the sp² carbon atom (C8) [Cl2−Rh1−C8 = 163.1(2)°], and the two PPh_3 ligands are also *trans*. The C5−C6 and C7−C8 linkages [1.510(5) and 1.452(6) Å, respectively] are longer than that of C6−C7 [1.332(6) Å], reflecting the bond order. The dihedral angle C6−C7−C8−C9 is 179.2°, which infers effective conjugation between the endocyclic (C6−C7) and exocyclic (C8−C9) double bonds.[12] In fact, the C7−C8 distance is significantly shorter than the C5−C6 distance, probably due to the conjugation. This is consistent with the lengthening of the exocyclic C8−C9 double bond [1.362(6) Å] as compared with the corresponding double bond distances in the η^4-bound (vinylallene)rhodium complexes [1.326(6) and 1.321(5) Å] previously reported.[9] The sp² carbon−metal distance (C8−Rh1

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(10) Anal. Calcd for $C_{49}H_{44}ClP_2Rh$: C, 70.64; H, 5.32. Found: C, 70.91; H, 5.48. As frequently observed with pentacoordinate complexes,[14] **5** became stereochemically nonrigid in solution to present complicated NMR spectra. The data for the predominant isomer, which are consistent with the planar crystal structure, are given below: ^1H NMR (C_6D_6, 400 MHz) δ 1.41 (s, 3 H), 1.66 (s, 3 H), 4.25−4.33 (br, 2 H), 5.35 (s, 1 H), 6.80−8.10 (m, 35 H); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz) δ 19.6, 25.7, 31.1 (d, $J_{Rh-C} = 32.8$ Hz), 120−145 (m); $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz) δ 26.5 (d, $J_{Rh-P} = 126.2$ Hz).

(11) Crystal data: $C_{50}H_{48}ClOP_2Rh$ (**5** + MeOH), MW = 865.2, orthorhombic, space group $P2_12_12_1$; $a = 19.33(1)$, $b = 21.74(1)$, and $c = 10.13(1)$ Å; $U = 4259.9(4)$ Å^3, $Z = 4$, $D_c = 1.349$ g/cm^3, $\mu = 48.90$ cm^{-1}. Intensity data were measured on a Mac Science MXC^3 diffractometer using $\omega - 2\theta$ scan technique with graphite monochromated Cu Kα radiation ($\lambda = 1.54178$ Å), and 3918 unique reflections within $3 \le 2\theta \le 130°$ were collected. No decay correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by a direct method and refined by the full-matrix least-squares to $R = 0.063$ ($R_w = 0.067$) for 3616 reflections [$I > 3.0\sigma(I)$] using a Crystan GM package program. The crystal contains one molecule of **5** and one molecule of MeOH in an asymmetric unit. The non-hydrogen atoms, except those of MeOH, were refined anisotropically. Hydrogen atoms were included in the refinement at the calculated distances (0.96 Å) with isotropic temperature factors calculated from those of the bonded atoms. Specific interaction is absent between rhodium and MeOH, although there are a few of relatively short intermolecular contacts observed ($C_{(MeOH)}$−C11 = 3.99 Å, $O_{(MeOH)}$−C11 = 3.91 Å).

(12) The dihedral angles in the previous η^4-bound (vinylallene)rhodium complexes which correspond to the C6−C7−C8−C9 angle of **5** are 140.6° and 127.8°.[9]

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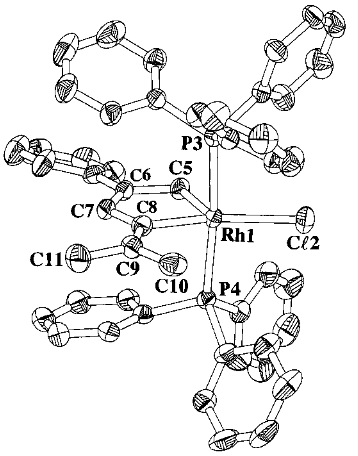
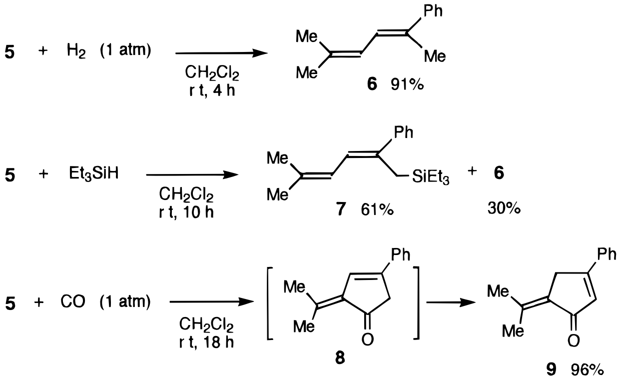


Figure 1. Molecular structure of **5** with the hydrogen atoms and the solvated methanol omitted for clarity (40% probability thermal ellipsoids).

= 2.025(4) Å) is identical with the sp^3 carbon−metal distance (C5−Rh1 = 2.024(4) Å), suggesting little contribution of metal to olefin π^* back-bonding.[13]

The most effective delocalization of the π-electrons of the endo- and exocyclic double bonds can be relevant to the observed preference for the planar structure with the vinylallene ligand **4**. We have found that a vinylallene having a trimethylsilyl group at the vinylic terminus reacts with $RhCl(PPh_3)_3$ to displace two molecules of triphenylphosphine, affording a (η^4-vinylallene)$RhCl(PPh_3)$ complex.[9] In this case, it might be that the steric bulk of the trimethylsilyl group disfavors the coordination of two molecules of bulky triphenylphosphine, instead resulting in participation of the whole conjugated diene system in the bonding to furnish the 16-electron η^4-complex as the most stable form.

Several stoichiometric reactions of **5** were examined. A solution of **5** in CH_2Cl_2 under 1 atm of dihydrogen was stirred at room temperature for 4 h. Hydrogenation proceeded to give diene **6** (91%) with retention of the stereochemistry of the double bond. Hydrosilation took place on treatment of **5** with Et_3SiH to afford dienylsilane (**7**) in 61% isolated yield together with the diene **6** (30%). In the formation of **7**, the triethylsilyl group was regioselectively introduced on the sp^3 carbon (C5) of **5** with the double-bond geometry retained. Like η^4-bound (vinylallene)rhodium complexes, carbonylative [4 + 1] cycloaddition was effected by simply stirring a solution of **5** in CH_2Cl_2 under 1 atm of CO atmosphere. A conjugated cyclopentenone (**9**) was produced in 96% yield, presumably by isomerization of cyclopentenone (**8**) formed initially.



In summary, a planar (vinylallene)rhodium complex is directly synthesized by simple ligand displacement of $RhCl(PPh_3)_3$ with vinylallene, wherein the conjugated diene system binds to rhodium in a purely σ^2-manner. The present study lends direct evidence to the ring flipping of a η^4-complex via a planar metallacyclopentene complex.

Supporting Information Available: Synthetic details, crystal structure determination data, tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **5** (8 pages). See any current masthead page for ordering and Internet access instructions.

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