Facile Routes to Ru(η^3-Allyl)(NO)(PPh_3)$_2$ Complexes via Hydrometallation of RuH(NO)(PPh_3)$_3$ to 1,3-Butadienes and Allenes

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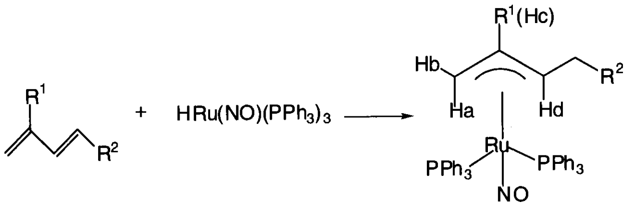
Hydrometallation of RuH(NO)(PPh_3)$_3$ to 1,3-butadienes and allenes proceeded regio- and stereoselectively to give η^3-allyl ruthenium complexes as a sole complex in good yields. The structure of the complex was unambiguously determined by X-ray analysis.

η^3-Allyl transition-metal complexes have been recognized as versatile reagents in both stoichiometric and catalytic organic reactions. In contrast to well utilized η^3-allyl complexes such as palladium[1] and molybdenum[2] complexes, η^3-allyl ruthenium complexes have not been enough developed in their preparation and application to the organic synthesis.[3] One of the interesting η^3-allyl complexes is that having nitrosyl ligand because the allyl and nitrosyl ligands can change in bonding mode from 3e$^-$ to 1e$^-$ donors as a means of generating coordinative unsaturation.[4] With respect to such complexes, only one complex, Ru(η^3-CH_2CHCH_2)(NO)(PPh_3)$_2$, was reported to be prepared by the reaction of tetraallyltin with Ru(Cl)(NO)(PPh_3)$_2$.[5] Effective routes to the preparation of η^3-allylnitrosylruthenium complexes promote further investigation into the structural features of the complexes as well as their chemical reactions. We report here a convenient synthesis of Ru{η^3-(substituted allyl)}(NO)(PPh_3)$_2$ complexes through hydrometallation of RuH(NO)(PPh_3)$_3$ to 1,3-butadienes and allenes. Hydrometallation of hydridometal complexes to 1,3-butadienes and allenes is useful method to prepare the η^3-allyl transition-metal complexes.[6]



1a-c

1a: R^1=H, R^2=H, **1b** :R^1=CH_3, R^2=H, **1c**: R^1=H, R^2=CH_3

Scheme 1.

RuH(NO)(PPh_3)$_3$ complex was synthesized by the literature methods.[7] To a solution of CH_2Cl_2 (15 mL) containing RuH(NO)(PPh_3)$_3$ (1.5 mmol) a mixture of 1,3-butadiene (1.3 mmol) and CH_2Cl_2 (5 mL) was slowly added at 15 °C and the resulting mixture was stirred for 5 h at room temperature. Column chromatography of the reaction mixture using CH_2Cl_2 as eluent gave η^3-allyl ruthenium complex **1a** as red brown solids.[8] Other solvents such as benzene, toluene, and THF were also utilized for the η^3-allyl ruthenium complex-forming reaction. But, ethanol, acetonitrile, and chloroform are ineffective solvents for the reaction because of insolubility or decomposition of RuH(NO)(PPh_3)$_3$. Similar treatment of RuH(NO)(PPh_3)$_3$ with 2-methyl-1,3-butadiene and 1,3-pentadiene gave the corresponding η^3-allyl ruthenium complexes **1b** and **1c**, respectively

Table 1. Formation of η^3-allyl complexes and their ^{1}H NMR spectral data

			Chemical shift (δ), coupling constant (Hz)				
1	Yield/%[a]	mp/°C	Ha	Hb	Hc	Hd	Others (R)
1a	90	106-107 (dec)	0.12 (dd, J=8.5, J_{PH}=17)	2.00 (dd, J=6.1, J_{PH}=12)	5.12-5.22 (m)	2.41-2.53 (m)	2.02-2.12 (m, CH_3)
1b	53	45-48 (dec)	0.11 (d, J_{PH}=17)	2.20 (d, J_{PH}=12)	–	2.06-2.15 (m)	2.02, (m, CH_3) 2.22 (d, J=1.8, CH_3)
1c	63	121-123 (dec)	0.23 (dd, J=8.6, J_{PH}=18)	2.00 (dd, J=6.4, J_{PH}=12)	5.11-5.21 (m)	2.21-2.35 (m)	2.40-2.60, (m, CH_2) 1.22 (m, CH_3)
1d	65	101-103 (dec)	0.29 (dd, J=7.9, J_{PH}=18)	2.07 (dd, J=6.1, J_{PH}=12)	5.61-5.71 (m)	3.15-3.24 (m)	7.30-7.52 (m, Ph)
1e	35[b]	–[c]	0.57 (dd, J=8.9, J_{PH}=19)	2.10 (dd, J=6.1, J_{PH}=13)	6.23-6.33 (m)	2.90-2.99 (m)	1.35 (t, J=7.0, CH_3) 4.43 (q, J=7.0, CH_2)

[a] Isolated yields. [b] Determined by ^{1}H NMR spectroscopy. [c] Reliable data was not obtained because of contamination with the polymer.

(Scheme 1). The η^3-allyl ruthenium complexes thus obtained were purified by recrystallization from the CH_2Cl_2 and hexane solution. The complexes gradually decompose in solution but are stable in pure solids. Yields, melting points and ^1H NMR chemical shifts of the complexes are shown in Table 1. ^1H NMR spectra of the allylic protones clearly indicated that the allyl ligand coordinates to Ru atom in η^3-mode. The bonding mode of the η^3-allyl ligand did not change upon heating the benzene solution containing the η^3-allyl complex **1a** in NMR tube up to 80 °C.

It is noteworthy that the hydrometallation reaction proceeded regio- and stereoselectively to yield the η^3-allyl ruthenium complexes as a sole product. Thus, the attack of the hydrogen occurred on the carbon at 4-position of both 2-methyl-1,3-butadiene and 1,3-pentadiene. In the cases of $CoH(CO)_4$[6a] and $RuH(CO)(PPh_3)_2Cl$,[6c] the attack of the hydrogen is at 1-position of 1,3-pentadiene. The substituents on the η^3-allyl ligands of the η^3-allyl ruthenium complexes formed from the present reaction are situated in *syn*-configuration.

The structure of the η^3-allyl ruthenium complex was unambiguously determined by X-ray analysis as illustrated in Figure 1. The smallest ligand NO is located in *syn-periplanar* conformation to the methyl group on the η^3-allyl ligand. This is similar to that of $Ru(\eta^3\text{-}CH_2CHCH_2)(NO)(PPh_3)_2$.[5]

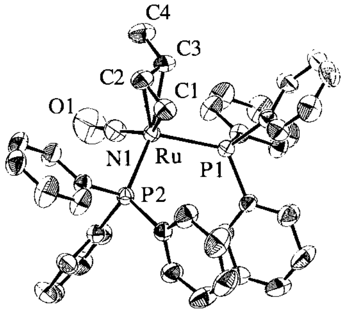
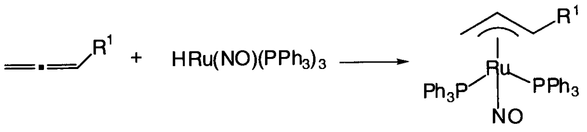


Figure 1. Molecular structure of complex **1a**. Selected bond lengths (Å) and angles (°): C(1)-C(2) 1.420(4), C(2)-C(3) 1.409(4), C(3)-C(4) 1.512(4), Ru-N(1) 1.759(2), N(1)-O(1) 1.169(4), C(1)-C(2)-C(3) 116.9(3), Ru-N(1)-O(1) 175.4(3).



1d: R^1=Ph, **1e** :R^1=CO_2Et, **1f** :R^1=C_5H_{11} **1d-f**

Scheme 2.

The hydrometallation reaction of $RuH(NO)(PPh_3)_3$ was also applied to allenes to give η^3-allyl ruthenium complexes. The reaction of $RuH(NO)(PPh_3)_3$ with phenylallene was carried out under the same conditions to afford η^3-allyl ruthenium complex **1d** in 65% yield as a sole product. The reaction of $RuH(NO)(PPh_3)_3$ with ethoxycarbonylallene and 1,2-octadiene gave a small amount of the corresponding η^3-allyl ruthenium complexes accompanying with large amounts of the polymers from allenes. Properties of the complexes thus obtained are given in Table 1. The hydrometallation reaction restricted to monosubstituted allenes for the preparation of the η^3-allyl ruthenium complex. Thus no η^3-allyl ruthenium complexes were yielded from the reaction of disubstituted allenes such as 1-methyl-1-phenylallene and 1-ethoxycarbonyl-3-phenylallene.

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8 ^{13}C NMR $\{^1H\}$ (67.5 MHz, C_6D_6) of allyl carbons for **1a**: δ 20.8 (d, J_{CP}=2.3 Hz, CH_3), 49.6 (CH_2=), 66.9 (dd, J_{CP}=2.5, 19.4 Hz, =$CHCH_3$), 81.8 (=CH). Anal. Calcd for $C_{40}H_{37}NOPRu{\cdot}C_6H_6$: C, 67.39; H, 5.29; N, 1.71%. Found: C, 66.94; H, 5.25; N, 1.42%. for **1c**: δ 18.5 (d, J_{CP}=3.9 Hz, CH_3), 29.6 (d, J_{CP}=1.7 Hz, CH_2), 49.6 (CH_2=), 66.9 (d, J_{CP}=19.6 Hz, =$CHCH_2$), 80.3 (=CH).