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REDUCTIVE ELIMINATION OF A Ru(IV) ALKYL COMPLEX PROMOTED BY NEUTRAL LIGANDS

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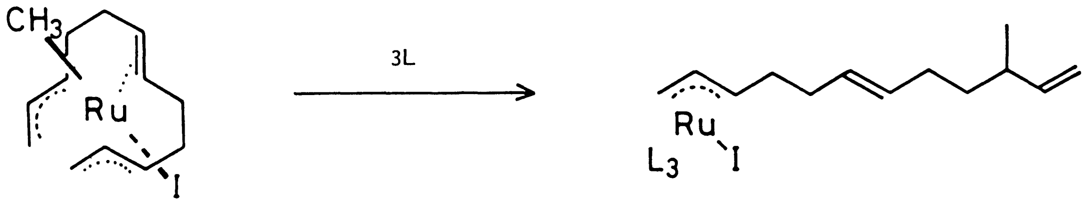
Treatment of Ru(CH_3)I(1-3:6-7:10-12-η-$C_{12}H_{18}$) with CO, ^{t}BuNC, or phosphites facilitates reductive coupling of the methyl group and the π-allyl moiety to give Ru(II) complexes, RuIL_3(1-3-η-$C_{13}H_{21}$) [L=CO, ^{t}BuNC, P$(OR)_3$]. Addition of one equivalent of ^{t}BuNC leads to selctive formation of Ru(^{t}BuNC)I(1-3:6-7:11-12-η-$C_{13}H_{21}$).

Transition metal catalyzed carbon-carbon bond forming reactions generally involve reductive elimination, in which organic substrates are liberated from the metal center, as a key step to complete the catalytic cycle.1) For the elucidation of the reductive elimination, behavior of transition metal alkyl complexes have been studied, showing that the reaction is promoted or accelerated thermally, by irradiation, or by contact with oxidants.1) Recent systematic scrutiny on nickel and palladium dialkyl complexes by Yamamoto et al.2) revealed that coordination of additional neutral ligands such as electron deficient olefins,3) CO,4) and phosphines5) critically facilitates the reductive elimination, providing important information on the mechanism of the Grignard coupling reaction.6)

In a preceding paper, we described the first preparation of Ru(IV) methyl complexes, Ru$(CH_3)_2$(1-3:6-7:10-12-η-$C_{12}H_{18}$) (**1**) and Ru(CH_3)I(1-3:6-7:10-12-η-$C_{12}H_{18}$) (**2**), which are thought to have the methyl group and the π-allyl moiety in cis-orientation.7) Reductive elimination of these complexes, namely coupling between the methyl group and the π-allyl moiety, is a clue to open a redox system between Ru(II) and Ru(IV) involving carbon-carbon bond formation.8) In this paper, we wish to report that the smooth reductive elimination of **2** took place by coordination of neutral ligands, giving the complexes of the type, RuL_3I(1-3-η-$C_{13}H_{21}$) (**3**).



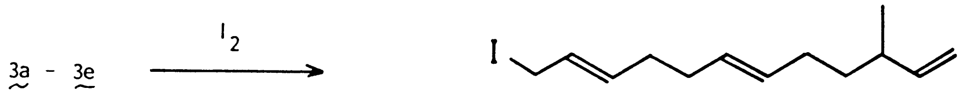
2 **3**

L=CO, ^{t}BuNC, P$(OCH_3)_3$, P$(OCH_2)_3CCH_2CH_3$, P$(O^iPr)_3$, P$(OPh)_3$

Exposure of a CH_2Cl_2 solution of **2** to an atmospheric pressure of CO resulted in a rapid up-take of CO (ca. 3 equiv. to **2**). After concentration of the solution and successive chromatographic purification of the residue (Al_2O_3, hexane), a stable ruthenium complex was obtained. This showed typical ν_{CO} absorptions at 2010, 2042, and 2096 cm^{-1} in IR spectrum. ^1H-NMR studies of this complex indicated disappearance of a singlet arising from Ru-CH_3 (δ -0.5 ppm) in **2** and emergence of a doublet at 1.05 ppm. Proton signals from one set of the π-allyl groups, where two sets of π-allyl group are involved in **2**, were also replaced by the protons attached to an uncordinated terminal olefin and an allylic carbon.[9] These results indicate that the Ru-CH_3 of **2** was migrated on the substituted terminus of the π-allyl moiety, as a result of coordination of CO. Thus, this complex can be assigned to **3a**, with which other signals in ^1H- as well as ^{13}C-NMR spectra are consistent.[9]

Similar migration of the methyl group was observed in the reaction of **2** with three-fold excess of ^tBuNC, $P(OCH_3)_3$, $P(OCH_2)_3CCH_2CH_3$, $P(O^iPr)_3$, and $P(OPh)_3$. As shown in Table 1, the reaction proceeded in $CDCl_3$ at room temperature under an inert gas atmosphere to give the Ru(II) complexes, **3b**, **3c**, **3d**, **3e**, and **3f**, respectively. We also attempted the reaction with other neutral ligands, such as PPh_3, $P(CH_3)_2Ph$, $P(^nBu)_3$, maleic anhydride, methyl acrylate, and dimethyl acetylenedicarboxylate, but the reductive migration of the Ru-CH_3 did not occur.

In the above examples, ^1H-NMR studies of the products **3a** - **3f** indicate the methyl group exclusively coupled with the substituted terminus of the π-allyl moiety. In order to confirm this regioselectivity, oxidative decomposition of **3a** - **3e** was carried out. In $CDCl_3$, treatment of **3a** - **3e** with I_2 gave 1-iodo-10-methyl-2,6,11-dodecatriene (**4**). (Table 1) The fact that a regioisomeric product, 1-iodo-2,6,10-tridecatriene, was not detectable supports the exclusively high regioselectivity in the reductive migration of the methyl group.



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An intermediate of the above reductive elimination was obtained as white crystals by treatment of **2** with one equivalent of ^tBuNC in CH_2Cl_2 or $CDCl_3$ at room temperature. Monitoring the reaction by ^1H-NMR shows the decrease of the Ru-CH_3 signal and appearance of a doublet at 1.38 ppm, which indicate the reductive migration of the methyl group from ruthenium to the π-allyl moiety. However, coordinated olefins were not replaced by ^tBuNC under the conditions. Careful assignments based on the ^1H and ^{13}C-NMR spectra including their decoupling data suggest that this complex possesses the structure illustrated as **5**.[10] This finding indicates that in the reaction of **2** with excess CO, ^tBuNC, or phosphites, the

Table 1. Reductive migration of Ru-CH_3 in 2 by neutral ligands and oxidative decomposition of 3 with I_2

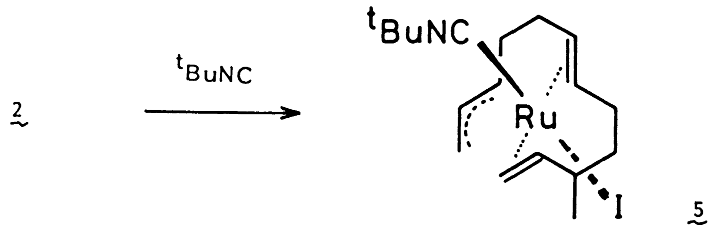
	The reductive migration[a)]			The oxidative decomposition[c)]		
Entry	Ligand	Time/h	Products[b)]	Temp/°C	Time/h	Yield/%
1	CO	1	3a (>90)	45	12	42
2	^{t}BuNC	1	3b (>90)	r.t.	2	66
3	$P(OCH_3)_3$	0.5	3c (>90)	r.t.	12	96
4	$P(OCH_2)_3CCH_2CH_3$	0.5	3d (>90)	45	48	71
5	$P(O^iPr)_3$	0.5	3e (>90)	r.t.	2	76
6	$P(OPh)_3$	0.5	3f (>90)	-	-	-

a) All reactions were carried out in $CDCl_3$ at room temperature under argon atmosphere. In the cases of entry 1, CH_2Cl_2 was used as the solvent and an atmospheric pressure of CO was applied.

b) The yields of the products after chromatographic purification are shown in parentheses.

c) All reactions were carried out in $CDCl_3$ under argon atmosphere. Yields listed are isolated ones.

reductive coupling first takes place by the access of the ligands, followed by the replacement of the coordinated olefinic bond by the excess ligand.



Above results indicate that the neutral ligands such as CO, ^{t}BuNC, and phosphites act as a key ligand to promote the reductive elimination of alkanes from Ru(IV) alkyl complexes. An active investigation on the behavior of other Ru(IV) alkyl complexes aimed at exploring a redox reaction between Ru(II) and Ru(IV) is under study.

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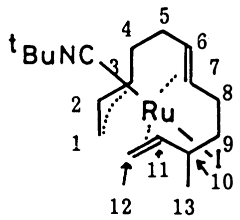
9) Spectral data corresponding to $C_{13}H_{21}$ ligand for **3a** follows: ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.00 (d, J=6.4 Hz, 3H, CH_3), 1.1-1.5, 1.85-2.40 (m, 9H, alkyl), 3.15 (d, J=12.9 Hz, anti proton on the terminal carbon of π-allyl), 3.70 (d, J=7.7 Hz , syn-proton on the terminal carbon of π-allyl), 4.45 (dd, J=7.7, 12.9 Hz, proton on the internal carbon of π-allyl), 4.75 (dd, J= 7.7, 12.9 Hz, proton on the central carbon of π-allyl), 4.82-5.12, 5.56-5.93 (m, 3H, terminal olefinic), 5.40-5.60 (internal olefinic). ^{13}C-NMR ($CDCl_3$, 22.5 MHz) δ 20.1 (q), 30.2 (t), 35.6 (t), 35.7 (t), 36.4 (t), 37.2 (t), 48.0 (d), 81.6 (d), 106.5 (d), 112.7 (d), 128.0 (d), 132.5 (d), 144.5 (d).

10) Spectral data of **5**; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 0.6-1.05 (m, 1H, H10), 1.20 (s, 9H, ^{t}BuNC), 1.38 (d, J= 6.4 Hz, 3H, H13), 1.10-2.00 (m, 4H, H4, H9), 2.10 (d, J= 11.6 Hz, 1H, H1-anti), 2.40-3.05 (m, 4H, H5, H8), 3.16 (d, J= 12.9 Hz, 1H, H12-anti), 3.54 (d, J=6.4 Hz, 1H, H1-syn), 3.85 (d, J=9.0 Hz, 1H, H12-syn), 4.32-4.60 (m, 2H, H3, H11), 4.6-5.5 (m, 2H, H6, H7), 6.04 (dt, J= 6.4, 11.6 Hz, 1H, H2). ^{13}C-NMR ($CDCl_3$, 22.5 MHz) δ 26.7 (q), 31.4 (q), 31.6 (t), 33.9 (t), 36.8 (d), 37.9 (t), 42.0 (t), 44.3 (t), 46.2 (t), 56.8 (s), 86.9 (d), 90.4 (d), 90.7 (d), 94.7 (d), 104.0 (d).



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