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Preliminary communication

A VERSATILE ROUTE TO (η^5-C_5R_5)RuL_2X FROM ALLYLMETHYLRUTHENIUM COMPLEXES

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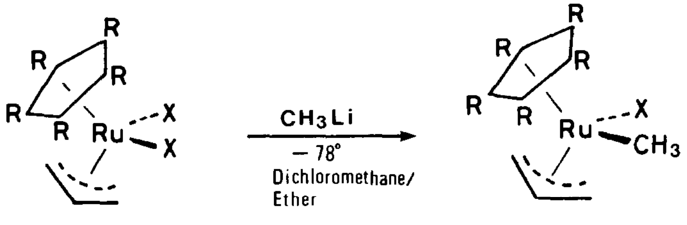
Summary

Divalent ruthenium complexes, (η^5-C_5R_5)RuL_2X (R = H, CH_3; X = Br, Cl), are formed by thermal decomposition of (η^5-C_5R_5)$Ru(CH_3)X$(η^3-C_3H_5) in the presence of several neutral ligands.

The organoruthenium complexes, (η^5-C_5R_5)RuL_2X (**1**), are an attractive starting point for organometallic and catalytic studies of ruthenium(II) [1]. Despite their potential reactivity, the variety of auxiliary ligands, L, has been limited to CO [2], several phosphines [3], and phosphites [4] by the known methods. Thus, versatile preparation of **1** is one of the problems for their extensive studies. Recently, Grubbs [5] and Suzuki [6] reported a short route to (η^5-C_5Me_5)RuL_2X from a ruthenium(III) precursor, in which several phosphines or dienes are introduced as L. This procedure, however, cannot be applied to the preparation of simple cyclopentadienyl complexes. During our studies on the reactions of alkylruthenium(IV) complexes, we have been aware of facile reductive elimination of the alkyl or η^3-allyl ligands induced by the action of several neutral ligands with the formation of ruthenium(II) complexes [7,8]. We describe here the extension of this reductive elimination of alkyl ligands from alkylallyl complexes to the general preparation of **1**.

The starting alkylruthenium(IV) complexes, (η^5-C_5R_5)$Ru(CH_3)X$(η^3-C_3H_5) (**2**), are successfully prepared by methylation of (η^5-C_5R_5)RuX_2(η^3-C_3H_5) (**3**) [7] (Scheme 1). Typically, a CH_2Cl_2 solution of **3a** was treated with an ethereal solution of CH_3Li (1.1 equiv.) at —78°C for 0.5 h under nitrogen. After aqueous work-up and successive chromatographic purification (alumina, hexane/ether), **2a** was isolated as air- and thermally-stable yellow crystals (yields 70—90%; 70—80°C (dec.); ^1H NMR ($CDCl_3$): δ (ppm) 0.73 (s, 3H, Ru—CH_3), 1.60 (s, 15H, C_5Me_5), 1.37 (d, 1H), 1.83 (d, 1H), 2.85 (dd, 1H), 3.45 (ddd, 1H), 4.15 (m, 1H) (η^3-allyls); ^{13}C NMR ($CDCl_3$): δ (ppm) 7.9 (q, Ru—CH_3), 9.1 (q, C_5Me_5), 58.1 (t), 62.6 (t), 95.4 (d) (η^3-allyls), 99.5 (s) (C_5Me_5); Anal. Found: C, 45.31; H, 5.96. $C_{14}H_{23}BrBu$ calcd.: C, 45.16; H, 6.23%.) The reactivity toward methylation yielding 2c was decreasing in the order Ru—Br > Ru—Cl.



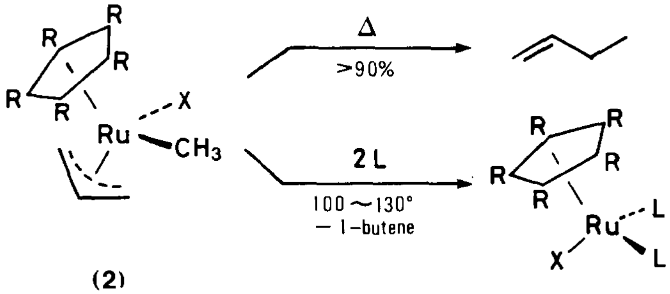
(3)

(2)

70~90%

SCHEME 1: 2a; 3a; R = CH_3, X = Br;
2b; 3b; R = H; X = Br;
2c; 3c; R = H; X = Cl.

Thermal decomposition of 2 either in solution or in the solid state resulted in selective formation of 1-butene (>90%) and dark brown insoluble materials. The butene formation is considered to produce 14-electron species, "(C_5R_5)RuX", and hence, trapping of this intermediate by several ligands should result in formation of 1 (Scheme 2). In fact, successful preparation of 1 was achieved by heating a decane solution of 2 at 100—130°C in the presence of CO, t-BuNC, phosphites, dienes, or phosphines. The results are summarized in Table 1.



(2)

(1)

SCHEME 2

In a typical example, a solution of 2b (23.1 mg, 0.077 mmol) and t-BuNC (8.5 μl, 0.168 mmol) in n-decane (1.5 ml) was heated at 100°C for 5 min under nitrogen. The cooled mixture was moved onto a short alumina column, and eluted by hexane to remove the solvent. A yellow fraction obtained by an ethereal eluent was collected, and the solution was dried in vacuo to give 1h as yellow crystals (27 mg, 92% yield); ^{1}H NMR ($CDCl_3$): δ (ppm) 1.50 (s,

TABLE 1

PREPARATION OF $(\eta^5\text{-}C_5R_5)RuL_2X$ [a]

Entry	Starting complex	Temperature (°C)	Time (min)	Ligand (L_2)	Product/ yield (%)
1	**2a**	130	40	2CO	**1a**/88
2	**2a**	130	10	2t-BuNC	**1b**/75
3	**2a**	130	15	2P(OR)$_3$ [b]	**1c**/80
4	**2a**	100	40	COD [c]	**1d**/95
5	**2a**	130	5	NBD [d]	**1e**/97
6	**2a**	130	5	dppe [e]	**1f**/97
7	**2b**	100	30	2CO	**1g**/67
8	**2b**	100	5	2tBuNC	**1h**/92
9	**2b**	100	5	2P(OR)$_3$	**1i**/78
10	**2b**	100	5	COD	**1j**/88
11	**2b**	100	5	NBD	**1k**/88
12	**2b**	100	5	dppe	**1l**/70
13	**2b**	100	5	2PPh$_3$	**1m**/98
14	**2c**	120	30	dppe	**1n**/55
15	**2c**	120	30	2PPh$_3$	**1o**/44
16	**2c**	100	5	COD	**1p**/74

[a] All reactions were carried out in n-decane under nitrogen or CO. For procedures see text. [b] $P(OR)_3$ = $P(OCH_2)_3CCH_2CH_3$. [c] COD = 1,5-cyclooctadiene. [d] NBD = norbornadiene. [e] dppe = 1,2-bis(diphenylphosphino)ethane.

t-Bu), 3.80 (s, C_5H_5); IR (nujol) 2095, 2135 cm^{-1}. In the preparation of the diene complexes, **1d**, **1e**, **1j**, **1k**, or **1p**, efficient trapping of the coordinatively unsaturated ruthenium(II) species required 10—100 molar excess of dienes.

This reaction offers an extremely versatile route to **1**. Isonitrile complexes (**1b** and **1h**), phosphite complexes (**1c** and **1i**), and diene complexes (**1j**, **1k**, and **1p**) are prepared for the first time by this method and their chemical properties are now under investigation.

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