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Preliminary communication

IMPROVED PREPARATION OF (η^6-CYCLOHEPTATRIENE)-(η^4-NORBORNADIENE)RUTHENIUM(0) AND ITS REACTION WITH ACETYLENE

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Summary

The complex (η^6-cycloheptatriene)(η^4-norbornadiene)ruthenium(0) is prepared efficiently by organometallic reduction of the readily available dichloro(η^4-norbornadiene)dipyridineruthenium(II) followed by the addition of 1,3,5-cycloheptatriene. The ruthenium(0) complex reacted with acetylene to give (η^6-bicyclo[4.2.1]nona-2,4,7-triene)(η^4-norbornadiene)ruthenium(0) by formal [$\pi 6s+\pi 2s$]-cycloaddition.

Extensive preparative and catalytic experiments of ruthenium(0) complexes, with $Ru_3(CO)_{12}$ in particular, have been studied. Non-carbonylruthenium(0) complexes are another attractive starting point either for formation of several non-carbonylruthenium complexes or homogeneous catalysis; however, relatively limited preparative methods and complexes have been available [1]. In this context, Fischer and Müller reported for the first time (1963) the preparation of several (η^6-cyclic triene)(η^4-cyclic diene)ruthenium complexes by photo-assisted Grignard reduction of insoluble $[RuCl_2(diene)]_n$ in the presence of trienes [2]. Unfortunately, the yields of their preparations were generally poor and the procedures were not convenient for large-scale synthesis. An improved preparation of several (η^6-cyclic triene)(η^4-cyclic diene)ruthenium(0) complexes was reported by Pertici et al. viz. by cleavage of two allylic C—H bonds of cyclic dienes [3]; however, this new method can not be applied to bicyclodienes such as norbornadiene (NBD) because of the absence of proper allylic C—H bonds to be cleaved [4]. In this paper, we describe an efficient modification of Fischer and Müller's preparation of Ru(η^6-1,3,5-cycloheptatriene)(η^4-NBD) (1) from readily available $RuCl_2(\eta^4\text{-NBD})(C_5H_5N)_2$ (2) [3], and a new type of ruthenium-assisted cycloaddition between 1 and acetylene.

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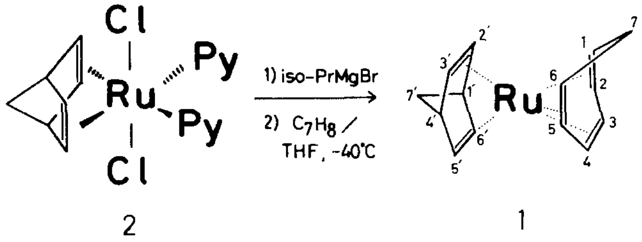
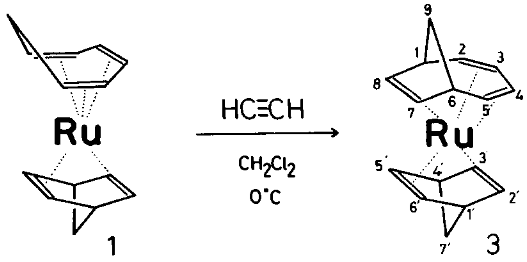
Preparation of 1 was accomplished as follows: to a solution of 2 (339 mg, 0.80 mmol) dissolved in tetrahydrofuran (THF) (8 ml) was added a THF solution of iso-PrMgBr (1 *M* solution, 8 ml) at −78°C. The mixture was stirred at −40°C for 4—5 h under argon. Then 1,3,5-cycloheptatriene (CHT) (10.2 ml, 1.8 mmol) was added, and the resulting solution was stirred at −40°C for another 2 h. Excess methanol was added to the solution to decompose the remaining Grignard reagent, and all volatiles were evaporated in vacuo. Extraction with n-hexane and chromatographic separation of the residue (alumina/n-hexane) followed by recrystallization from n-pentane at −78°C gave yellow crystals of 1, m.p. 43—45°C dec., in 60—80% yield. Alternatively, 1 was also prepared with n-BuLi as a reducing reagent. To a solution of 2 (550 mg, 1.3 mmol) and CHT (0.3 ml, 2.9 mmol) dissolved in THF (10 ml) was added n-BuLi in n-hexane (1.66 *N*, 2.1 ml) at −50°C. The solution was stirred at −50°C for 2 h under argon. Diethyl ether (30 ml) was added to the mixture, and the excess BuLi was decomposed with water (5 ml). The solution was neutralized carefully with aqueous acetic acid (0.1 *N*), and the organic layer was separated and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (alumina, hexane) to give crude 1 (80—90% yield). Recrystallization from n-pentane yield 1 (190 mg, 53%) as yellow crystals. The ^1H NMR spectrum of 1 is identical with reported data [1]. The ^{13}C NMR data of 1 and their off-resonance data were consistent with the structure depicted in Scheme 1: ^{13}C NMR in C_6D_6 (ppm downfield from internal tetramethylsilane); η^6-CHT: C(1) and C(6), 33.81, d; C(2) and C(5), 101.44, d; C(3) and C(4), 93.52, d; C(7), 29.86; t; η^4-NBD: C(1) and C(4), 48.78; d; C(2), C(3), C(5), and C(6), 30.91, d; C(7), 56.02, t.



SCHEME 1

The important aspect of this preparation depends on the facile displacement of two pyridine ligands of the ruthenium(II) precursor (2) by CHT. Pyridine has been known to substitute several olefinic ligands [3,4] in several ruthenium(II) complexes [1,5], whereas few pyridineruthenium(0) complexes have been reported indicating that pyridine did not stabilize efficiently the zerovalent Ru moieties. The present preparation of 1 from 3 relies on the large difference in affinity to nitrogen donors between di- and zero-valent states of ruthenium.

The ruthenium(0) complex (1) can be transformed to another ruthenium(0) complex containing two bicyclopolyene ligands. When acetylene gas was passed through a dichloromethane (3 ml) solution of 1 (90 mg) at 0°C for 1—1.5 h, Ru(bicyclo[4.2.1]nona-2,4,7-triene)(η^4-NBD) (3) was isolated as orange crystals in 67% yield after chromatographic separation followed by recrystallization (3): m.p. 92—95°C dec. Found: C, 61.80; H, 5.88. $C_{16}H_{18}Ru$ calcd.: C, 61.72; H, 5.83%.)



SCHEME 2

TABLE 1

NMR SPECTRAL DATA OF 3

Assignment	Chemical shifts (ppm)	
	^{1}H (90 MHz)	^{13}C (22.5 MHz) (Off resonance results)
C(1,6)	3.10 (broad t, J 7 Hz, 2H)	42.0(d)
C(2,5)	1.62 (broad t, J 7 Hz, 2H)	32.7(d)
C(3,4)	5.00 (dd, J 2.5 and 5 Hz, 2H)	88.1(d)
C(7,8)	3.95 (broad s, 2H)	49.9(d)
C(9)	0.8—1.4 (m, 2H)	33.3(t)
C(1',4')	3.25—3.45 (m, 2H)	49.2(d)
C(2',3',5',6')	2.85—2.96 (m, 4H)	31.5(d)
C(7')	1.25 (broad s, 2H)	57.0(t)

[a] Measured in C_6D_6 at 25°C. Chemical shifts were estimated in ppm from internal tetramethylsilane.
[b] Assignments were completed by ^{1}H—^{1}H homo decoupling in ^{1}H NMR and ^{13}C—^{1}H selective decoupling in ^{13}C NMR.

Final assignments of both ^{1}H and ^{13}C NMR data are shown in Table 1.

A similar generation of the bicyclo[4.2.2]decatriene ligand was recently reported by authors from formal [$\pi 6s+\pi 2s$]-cycloaddition of terminal acetylenes to a η^6-cyclooctatriene ligand of ruthenium(0) [6]. The spectroscopic data shown in Table 1 indicate close similarity of the η^6-coordination of bicyclo[4.2.1]nona-2,4,7-triene ligand in 1 to that of bicyclo[4.2.2]deca-2,4,7-triene in Ru(η^6-$C_{10}H_{12}$)(η^4-C_8H_{12}). In particular, the terminal proton signal of the η^4-diene part of the bicyclo[4.2.1]nonatrienes, C(2) and C(5) at δ 1.62 ppm is fairly consistent with the corresponding proton signals in Ru(η^6-$C_{10}H_{12}$)(η^4-C_8H_{12}) [6] (δ 1.63 ppm), Ru(CO)$_3$(η^4-C_4H_6) (δ 1.44 ppm) [7] and Ru(o-quinodimethane)(PMe$_2$Ph)$_3$ (δ 1.90 ppm) [8].

Further studies on the reaction of 1 are under active investigation.

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