Journal of Organometallic Chemistry, 430 (1992) C60–C63
Elsevier Sequoia S.A., Lausanne
JOM 22715PC

Preliminary communication

Half-way coordination state of a butadienyl group on ruthenium. η^3-Allylic bonding with η^1-character or *vice versa*

Yasuo Wakatsuki [a], Hiroshi Yamazaki [a], Yooichiroh Maruyama [b]
and Isao Shimizu [b]

[a] *The Institute of Physical and Chemical Research, Wako-shi, Saitama 351-01 (Japan)*
[b] *Department of Applied Chemistry, School of Science and Engineering, Waseda University, 3-4-1 Ookubo, Shinjyuku-ku, Tokyo 169 (Japan)*

(Received January 24, 1992)

Abstract

The butadienyl complexes formed by the reaction of *trans*-(R^1)CH=CHC≡CR^2 (R^1, R^2 = SiMe$_3$, ^{t}Bu, Me, Et) with RuCl(CO)H(PPh$_3$)$_3$ exhibit unique structures: instead of taking the 18-electron configuration of the metal by conventional η^3-coordination of the butadienyl ligand, they shift significantly to the 16-electron η^1-coordination state.

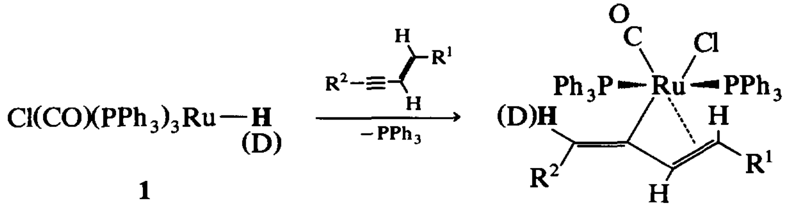
Allyl ligands in transition metal complexes take the η^3-coordination mode when two adjacent coordination sites are available. This applies to the known butadienyl ligands: Bruce *et al.* [1] and Nesmeyanov *et al.* [2] have prepared W, Fe, and Ru complexes with highly substituted η^3-butadienyl ligands whilst Drew *et al.* [3], Brisdon *et al.* [4], and Green *et al.* [5] have reported Mo complexes with mono- and non-substituted butadienyl groups, respectively. X-ray crystallographic analyses carried out for most of these complexes have revealed that the bonding mode of the butadienyl moiety can be viewed as that of η^3-allyl group, one terminal carbon of which is involved in an *exo*-allylic double bond.

Here we report a novel bonding mode of butadienyl groups whose allylic moiety can be regarded as coordinating to the metal *via* neither a distinct η^3-nor η^1-manner, but intermediate of the two.

The reaction of excess *trans*-(R^1)CH=CHC≡CR^2 (R^1, R^2 = SiMe$_3$, ^{t}Bu, Me, Et) with RuCl(CO)H(PPh$_3$)$_3$ (**1**) takes place in THF smoothly at room temperature to give orange yellow crystals (**2a–d**) of the composition RuCl(CO)(H ·

Correspondence to: Dr. Y. Wakatsuki, The Institute of Physical and Chemical Research, Wako-shi, Saitama 351-01, Japan.

$R^1CHCHC_2R^2)(PPh_3)_2$ in almost quantitative yields. In ^1H NMR spectra the three protons of the dienyls show resonances at the olefinic region [6*].



2a $R^1, R^2 = SiMe_3$

2b $R^1, R^2 = {}^tBu$

2c $R^1 = SiMe_3, R^2 = Me$

2d $R^1 = Et, R^2 = {}^tBu$

X-ray crystal analyses of **2a** and **2d** [7*] proved that *cis*-addition of the Ru–H had occurred across the triple bond of the enyne (Fig. 1(a), (b)). The metal is bound to the inner carbon (C_3) and resides apparently in an ideal geometrical situation to accept conventional η^3-butadienyl coordination. However, in reality the allylic double bond of the dienyl interacts with the metal very weakly only, Ru–C(3), Ru–C(2) and Ru–C(1) distances being 2.044(4), 2.336(5) and 2.627(5) Å in **2a** and 2.041(5), 2.358(5) and 2.661(5) Å in **2d** [8*]. In accordance with this, the C(1)–C(2) bond is shorter than C(2)–C(3), 1.339(8) *vs* 1.445(6) Å in **2a** and 1.354(7) *vs* 1.450(7) Å in **2d**. The dihedral angle between (Ru–Cl–CO and (C(1)–C(2)–C(3)) is 112.7(5)° in both **2a** and **2d**, indicating that the π-lobes are not directly oriented towards the metal center. The existence of an attracting interaction, albeit weak, between Ru and the allylic double bond can be shown by comparing the structures of these butadienyl complexes with that of the related stilbenyl complex $RuCl(CO)\{\eta^1\text{-}C(Ph)CHPh\}(PPh_3)_2$ (**3**) [9] illustrated in Fig. 1(c); (Ru–C(2) distance is as wide as 2.74 Å. This is due to the wider Ru–C(3)–C(2) angle of 102.3° in **3** than those of **2a** (82.1(3)°) and **2d** (83.1(3)°). Furthermore, the angles C(3)–Ru–Cl in **2a** and **2d**, 155.7(1) and 144.4(1)°, are much wider than the corresponding value of 132.7° in **3**, owing to the interaction of Ru with C(1)=C(2) allylic double bond.

The unsubstituted enyne (vinylacetylene) also reacted readily with **1** but gave only oily product which gradually decomposed. Geometry optimization of $RuCl(CO)(H_2C{=}CCHCH_2)(PH_3)_2$ carried out by *ab initio* MO calculations [10*] suggested that its structure (Fig. 1(d)) is similar to those of **2a** and **2d**.

It is noteworthy that η^3-allylic complexes of analogous composition, $RuCl(CO)\{\eta^3\text{-}RC(H)C(R)CHR\}(PPh_3)_2$, have been known to be formed by the reaction of **1** with 1,3-dienes [11]. The metal has a discrete 18-electron configuration and the complexes are fairly stable. In contrast, the immediate consequence of the half-way coordination of **2a–d**, reported here, is their instability: on allowing a benzene solution of **2a** in the presence of an equimolar amount of triphenylphosphine, to stand over 3 days *ca.* 90% of the enyne is freed. The white precipitate formed was

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* Reference number with asterisk indicates a note in the list of references.

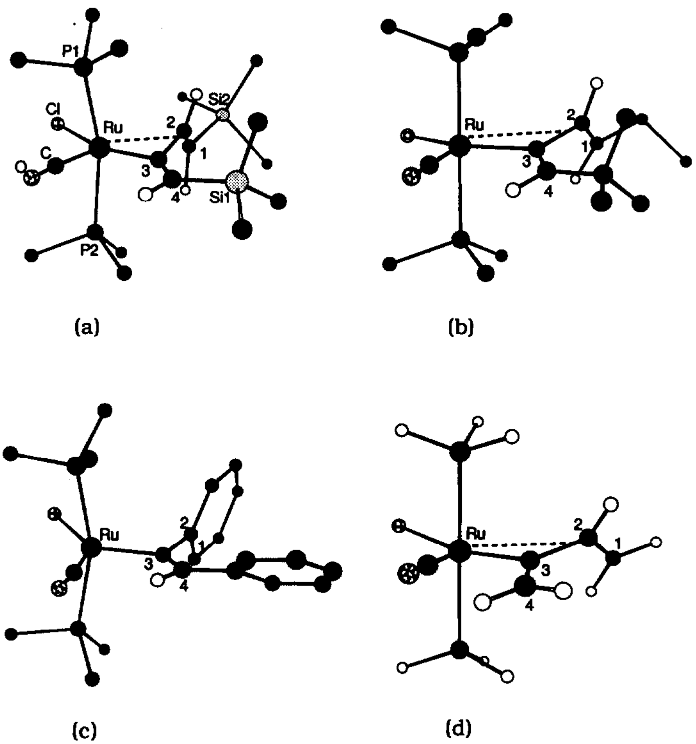

Fig. 1. (a) X-ray structure of complex **2a**. (b) X-ray structure of complex **2d**. (c) X-ray structure of stilbenyl complex [9]. (d) The geometry of unsubstituted butadienyl complex. RuCl(CO)($H_2C{=}CCH{-}CH_2$)$(PH_3)_2$, calculated by *ab initio* MO method. Ru–Cl 2.776, Ru–C2 2.483, Ru–C3 2.051, C1–C2 1.343, C2–C3 1.465, C3–C4 1.320 Å. Ru–C3–C2 88.2, C3–Ru–Cl 163.4°.

confirmed to be the hydride complex **1**. In the cases of **2b** and **2c**, equilibria are reached when *ca.* 30% of the enynes are freed, as monitored by ^{1}H NMR spectroscopy, while **2d** showed only 8% of free enyne [12*]. The initial rate is not affected when excess phosphine is added, suggesting that β-elimination at C(4) is the rate determining step. Therefore this is one of the rare examples for β-elimination of vinylic hydrogens [13].

References and notes

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6 Complex **2a**: m.p. 215–220°C (dec), ^{1}H NMR (C_6D_6): δ 6.36 (broad d, 1H, J(HH) = 18 Hz, H(C_2)), 5.39 (broad d, 1H, J(HH) = 18 Hz, H(C_1)), 4.85 (d, 1H, J(HH) = 1.2 Hz, H(C_4)), 0.16 (s, 9H, $SiMe_3$), −0.02 (s, 9H, $SiMe_3$). The peak at δ 6.36 should appear as dd with J(HH) = 1.2 and 18 Hz but the fine structure was not resolved. The broadness of the peak is likely to originate from very small coupling with phosphines.

Complex **2b**: m.p. 157–159°C (dec), ^{1}H NMR (C_6D_6): δ 5.86 (dd, 1H, J(HH) = 1.8 and 16 Hz, H(C_2)), 5.60 (d, 1H, J(HH) = 16 Hz, H(C_1)), 4.58 (d, 1H, J(HH) = 1.8 Hz, H(C_4)), 0.99 (s, 9H, ^{t}Bu), 0.93 (s, 9H, ^{t}Bu).

Complex **2c**: m.p. 145–148°C (dec), ^{1}H NMR (C_6D_6): δ 6.24 (broad d, 1H, J(HH) ≈ 18 Hz, H(C_2)), 5.59 (d, 1H, J(HH) = 18 Hz, H(C_1)), 3.91 (broad dq, 1H, J(HH) = 1.5 and 6.7 Hz, H(C_4)), 1.46 (broad dd, 3H, J(HH) = 1.2 and 6.7 Hz, Me), 0.15 (s, 9H, $SiMe_3$).

Complex **2d**: m.p. 154–158°C (dec), ^{1}H NMR (C_6D_6): δ 5.48 (broad d, 1H, J(HH) ≈ 14 Hz, H(C_2)), 4.92 (broad s, 1H, H(C_1)), 4.38 (broad s, 1H, H(C_4)), 1.86 (broad s, 2H, CH_2), 0.90 (s, 9H, t-C_4H_9), 0.80 (broad t, 3H, CH_3). Satisfactory C and H analyses were obtained for these complexes.

7 Crystal data for **2a**: $M = 886.6$, monoclinic, space group $P2_1/c$, $a = 18.517(4)$, $b = 11.259(2)$, $c = 22.513(6)$ Å, $\beta = 106.28(2)°$, $U = 4505.2$ Å^3, $Z = 4$, $D_c = 1.31$ g cm^{-3}. $R = 0.047$ for 8383 observed reflections ($F_o > 3.0\sigma F_o$).

Crystal data for **2d**: $M = 910.3$ (contains a CH_2Cl_2 molecule), monoclinic, space group $P2_1/n$, $a = 19.463(4)$, $b = 18.584(3)$, $c = 12.408(2)$ Å, $\beta = 93.07(2)°$, $U = 4481.3$ Å^3, $Z = 4$, $D_c = 1.35$ g cm^{-3}, $R = 0.056$ for 8327 observed reflections ($F_o > 3.0\sigma F_o$). Crystal data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å). The structures were solved by direct methods (MULTAN) and refined by block-diagonal least squares.

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