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Synthesis of 1,3-dienyl complexes of ruthenium(II) by facile hydroruthenation/dehydration of propargylic alcohols

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Abstract

Reaction of [RuClH(CO)(PPh_3)$_2$(BSD)] (BSD = 2,1,3-benzoselenadiazole) with the propargylic alcohols HC≡C–CR_2OH (CR_2 = CMe_2 or *cyclo*-C_6H_{10}) leads to the σ-vinyl derivatives [RuCl(CH=CH-CR_2OH)(CO)(PPh_3)$_2$(BSD)] whereas the same alcohols when treated with [RuClH(CO)(PPh_3)$_3$] followed by BSD yield (*via* [RuCl(CH=CHCR_2OH)(CO)(PPh_3)$_{2,3}$]), the dehydrated σ-dienyl compounds [RuCl{CH=CHC(=CH_2)Me}(CO)(PPh_3)$_2$(BSD)], and [RuCl{CH=CHC_6H_9}(CO)(PPh_3)$_2$(BSD)]. The last complex is also the product of the reaction of [RuClH(CO)(PPh_3)$_2$(BSD)] with 1-ethynyl cyclohexene. Dehydration of the vinylic alcohol complexes is also induced by trifluoroacetic anhydride.

The complexes [RuCl(CH=CHR)(CO)(PPh_3)$_2$(BSD)] (BSD = 2,1,3-benzoselenadiazole) can be readily synthesized *via* the reactions of [RuClH(CO)(PPh_3)$_3$] with simple terminal alkynes (HC≡CR) followed by treatment with BSD [1]. Alternatively the BSD-hydride complex [RuClH(CO)(PPh_3)$_2$(BSD)] [2] can be treated with simple alkynes to give [RuCl(CH=CHR)(CO)(PPh_3)$_2$(BSD)], which apparently suggests that the sequence of addition of alkyne and BSD to the ruthenium hydride complex [RuClH(CO)(PPh_3)$_3$] is unimportant (Scheme 1). Working on this assumption we have investigated the reactions of the hydrido complexes [RuClH(CO)(PPh_3)$_2$(L)] (L = PPh_3, BSD) with propargylic alcohols, and found that the assumption is not generally true.

Treatment of [RuClH(CO)(PPh_3)$_2$(BSD)] with an excess of 3,3-dimethyl prop-1-yn-3-ol in tetrahydrofuran (reflux, 3 min) provides the orange complex [RuCl(CH=CHCMe_2OH)(CO)(PPh_3)$_2$(BSD)], which was isolated by dilution of the reaction mixture with methanol. A similar orange complex [RuCl{CH=CHC(OH)$(CH_2)_5$}(CO)(PPh_3)$_2$(BSD)] is obtained from 1-ethynyl cyclohexan-1-ol. The spectroscopic data (Table 1) for these complexes are consistent with the formulations shown, but prolonged storage (1 week) of solutions of the former in deuterochloroform

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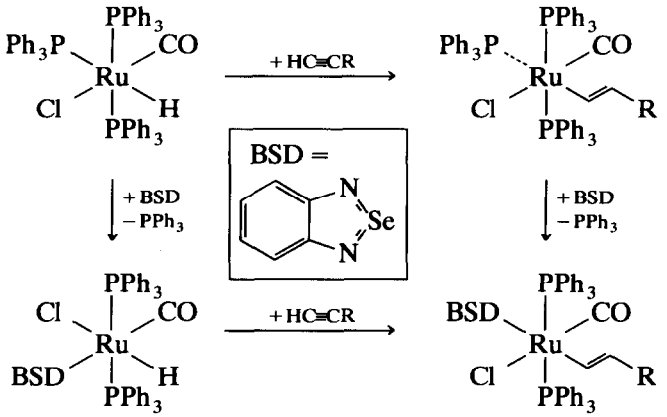


Scheme 1. Hydroruthenation of simple terminal alkynes: R = H, C_4H_9, Ph, C_6H_4Me-4.

resulted in clean formation of a second compound which nevertheless retained a resonance in the region typical of the α-proton of complexes [RuCl(CH_α=CHR)(CO)(PPh_3)$_2$(BSD)] while not showing the signal due to the CMe_2 group, this being replaced by resonances at δ 4.25 (1 H), 4.13 (1 H) and 1.56 (3 H) ppm.

The complex that we formulate as the σ-dienyl derivative [RuCl{CH=CH–C(=CH_2)CH_3}(CO)(PPh_3)$_2$(BSD)] was the exclusive product of an attempted "one-pot" preparation of [RuCl(CH=CHCMe_2OH)(CO)(PPh_3)$_2$(BSD)]. Thus heating [RuClH(CO)(PPh_3)$_3$] with an excess of HC≡$CCMe_2$OH in tetrahydrofuran (reflux, 5 min) followed by cooling to room temperature and addition of BSD gave [RuCl{CH=CH–C(=CH_2)CH_3}(CO)(PPh_3)$_2$(BSD)] in high yield. A similar result was obtained for 1-ethynyl cyclohexan-1-ol; however, in this case we were able to confirm the formulation of the product unequivocally because the product [RuCl{CH=CHC=CH(CH_2)$_4$}(CO)(PPh_3)$_2$(BSD)] is identical to that obtained from the reaction of [RuClH(CO)(PPh_3)(BSD)] with the readily available 1-ethynyl cyclohexene (Scheme 2). Notably, the cyclohexan-1-ol-1-yl substituted vinyl complexes undergo dehydration significantly more rapidly than do those bearing the CMe_2OH group. This latter reaction is itself of interest because the reaction of [RuClH(CO)(PPh_3)$_3$] with *cis*-1,4-bis(trimethylsilyl)butenyne has been shown to involve hydroruthenation of the alkene group, not the alkyne unit [3].

It is not clear whether these dehydration reactions are acid ($CDCl_3$) or base (BSD) catalysed since, in NMR-tube experiments, either addition of trifluoroacetic anhydride or excess BSD lead to acceleration of the dehydration process. Clearly a more detailed mechanistic study is required, since the presumed base BSD must also ultimately return to the coordination sphere as a ligand. It is noteworthy that π-acids CO and $CNC_6H_3Me_2$-2,6 do not induce appreciable dehydration of [Ru(CH=CHCMe_2OH)Cl(CO)(PPh_3)$_2$] (< 5%) but instead give the compounds [Ru(CH=CHCMe_2OH)Cl(CO)(PPh_3)$_2$(L)] (L = CO, $CNC_6H_3Me_2$-2,6).

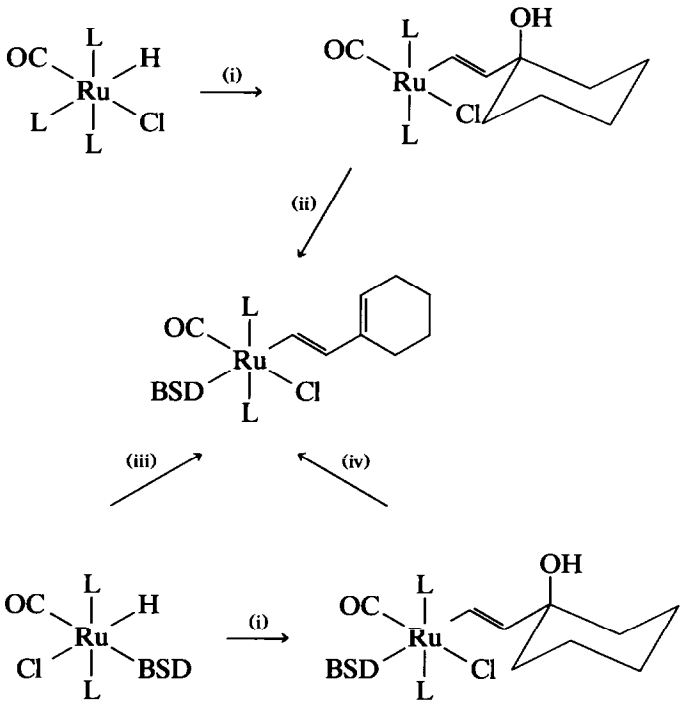
σ-Dienyl complexes have been prepared in related systems. Reaction of [RuClH(CO)(PPh_3)$_3$] with an excess of ethyne gives some uncharacterized impurities assumed to be [RuCl{$(CH{=}CH)_n$H}(CO)(PPh_3)$_m$] (n, m = 2, 3), and with an excess of activated monosubstituted alkynes, e.g. HC≡CCOR (R = Me, OMe, OEt)

Table 1

Spectroscopic data for the new complexes. [Ru] = 'RuCl(CO)$(PPh_3)_2$'

Complex	IR [a] ν_{max}(CO)	δH_α	δH_β	^{1}H NMR [b]			Other
				$J(H_\alpha H_\beta)$	$J(PH_\alpha)$	$J(PH_\beta)$	
[Ru](CH=CHCMe$_2$OH)(BSD) (orange)	1921 (1927)	7.66	5.49	16.7	2.7	2.0	0.82 (C*Me*$_2$OH)
[Ru](CH=CHC(OH)C$_6$H$_{10}$)(BSD) (orange) [d]	1921 (1927)	7.60	5.51	16.8	2.6	n.r.	0.78, 1.25, 1.42, 1.47, 1.62 [m×5, 10 H, C$_6$*H*$_{10}$]
[Ru](CH=CHC(=CH$_2$)CH$_3$)(BSD) (orange)	1921 (1928)	8.13	5.73	16.6	3.2	n.r.	4.25, 4.13 [AB, *J* (AB) = 2.5, =C*H*$_2$] 1.56 [s, C*H*$_3$]
[Ru](CH=CHC$_6$H$_9$)(BSD) (red) [d]	1915 (1926)	7.77	5.60	16.9	3.5	n.r.	1.47, 1.59, 1.84, 1.98 [m×4, 9 H, C$_6$*H*$_9$]
[Ru](CH=CHCMe$_2$OH)(CO) (colourless)	2037, 1978 (2037, 1975)	7.06	5.21	17.8	3.1	2.2	0.72 (C*Me*$_2$OH)
[Ru](CH=CHCMe$_2$OH)(CNR) (colourless) [c]	1978 (1975)	obs.	5.27	17.8	obs.	2.1	2.05 [s, C$_6$H$_3$*Me*$_2$] 0.73 [s, C*Me*$_2$OH]

[a] Nujol mulls, values in parentheses for dichloromethane solution. [b] Data obtained from saturated solutions in $CDCl_3$ at 25°C and reported relative to internal $SiMe_4$; n.r. = not resolved; resonances due to PPh_3 omitted. [c] R = $C_6H_3Me_2$-2,6, ν(CN) = 2109 (2116) cm^{-1}; obs. = obscured by PPh_3 and BSD resonances. [d] Satisfactory elemental microanalysis not obtained due to co-crystallization with excess BSD (see [1]); unless indicated all other compounds analysed satisfactorily.



Scheme 2. Synthesis of σ-dienyl complexes of ruthenium(II), L = PPh_3. (i) $HC{\equiv}CC_6H_{10}OH$; (ii) BSD; (iii) $HC{\equiv}CC_6H_9$; (iv) $CDCl_3$ (8 days) or $(CF_3CO)_2O$ (2 s). Analogous reactions take place with $HC{\equiv}CCMe_2OH$.

[4], chelated σ-dienyl complexes may be obtained. The cyclopentadienyl complexes $[RuR(PPh_3)_2(\eta\text{-}C_5H_5)]$ (R = H [5], CH_3[6]) also react with activated alkynes to give chelated dienyl complexes. The synthetic route described here has two advantages: (1) a wide range of propargylic alcohols are readily available, and (2) the complexes obtained have labile BSD ligands, which may be replaced under mild conditions, e.g. all the BSD complexes described here react with CO or 2,6-dimethylphenylisonitrile to give $[RuCl(\sigma\text{-vinyl})(CO)(PPh_3)_2(L')]$ (L' = CO, $CNC_6H_3Me_2$-2,6) [1].

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