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Facile O−H Bond Activation in Alcohols by [Cp*RuCl(^{i}Pr$_2$PSX)] (X = Pyridyl, Quinolyl): a Route to Ruthenium(IV) Hydrido(alkoxo) Derivatives

Manuel Jiménez-Tenorio,* M. Carmen Puerta,* and Pedro Valerga

Departamento de Ciencia de Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

Supporting Information

ABSTRACT: The complexes [Cp*RuCl(^{i}Pr$_2$PSX)] (X = pyridyl, quinolyl) react directly with alcohols ROH (R = Me, Et, ^{i}Pr, ^{n}Pr) and NaBPh$_4$, affording the novel cationic hydrido(alkoxo) derivatives [Cp*RuH(OR)(^{i}Pr$_2$PSX)][BPh$_4$]. These ruthenium(IV) compounds result from the formal oxidative addition of the alcohol to the 16-electron fragment {[Cp*Ru(^{i}Pr$_2$PSX)]$^+$}, generated in situ upon chloride dissociation. The hydrido(alkoxo) complexes are reversibly deprotonated by a strong base such as KOBu^t, yielding the neutral alkoxides [Cp*Ru(OR)(^{i}Pr$_2$PSX)], which are remarkably stable toward β elimination and do not generate the corresponding hydrides. The hydrido(alkoxo) complexes undergo a slow electron-transfer process, releasing H_2 and generating the dinuclear ruthenium(III) complex [{Cp*Ru(κ^2-*N*,*S*-μ-*S*-SC$_5$H$_4$N)}$_2$][BPh$_4$]$_2$. In this species, the Ru−Ru separation is very short and consistent with what is expected for a Ru≡Ru triple bond.

Hydrido(alkoxo) complexes of transition metals produced by OH bond activation are known to be involved in various metal-mediated catalytic transformations.[1] Very recently, Milstein and co-workers have demonstrated the involvement of hydrido(alkoxo) complexes of ruthenium in the environmentally benign dehydrogenative coupling of alcohols to esters with liberation of H_2 under neutral conditions.[2] This and other related processes are catalyzed by pyridine-based PNP and PNN pincer complexes of ruthenium and are possible through remarkable metal−ligand cooperation.[3] Ruthenium catalysts capable of oxidizing alcohols to ketones also feature OH activation, and the OH bond activation in the alcohol by the metal complex remains one of the key steps in such a process.[4]

We have recently reported the preparation of the half-sandwich complex [Cp*RuCl(^{i}Pr$_2$PSPy)] (**1**).[5] We now show that this complex and the related derivative [Cp*RuCl(^{i}Pr$_2$PSQuin)] (**2**; prepared by the reaction of [{Cp*RuCl}$_4$] with ^{i}Pr$_2$PSQuin in petroleum ether) react directly with alcohols ROH (R = Me, ^{i}Pr, ^{n}Pr) and NaBPh$_4$ over a period of 6−12 h at room temperature, affording the corresponding cationic hydrido(alkoxo) derivatives [Cp*RuH(OR)(^{i}Pr$_2$PSX)][BPh$_4$] [X = Py and R = Me (**3a**), ^{i}Pr (**3b**); X = Quin and R = Me (**4a**), ^{i}Pr (**4b**), ^{n}Pr (**4c**)]. These ruthenium(IV) compounds result formally from the oxidative addition of the alcohol to the 16-electron fragment {[Cp*Ru(^{i}Pr$_2$PSX)]$^+$}, generated in situ upon chloride dissociation. Although monomeric hydrido(hydroxo) or hydrido(aryloxido) complexes of ruthenium have been isolated as result of the oxidative addition of either water[6] or *p*-cresol[7] to ruthenium(0) complexes, this is the first case in which the formal oxidative addition of alcohols to a ruthenium(II) complex has been observed. Other hydrido(alkoxo) complexes of ruthenium(II) have been obtained or postulated as intermediate products in hydrogen-transfer reactions to ketones.[4,8] In our case, the hydrido(alkoxo) derivatives **3a**, **3b**, and **4a**−**4c** were characterized by NMR spectroscopy. These complexes exhibit one outlying methyl resonance of one of the phosphine isopropyl substituents in the range 0.3−0.6 ppm, whereas the other methyl groups resonate around 1.1 ppm. This upfield shift is most likely attributed to ring magnetic current effects from pyridine or quinoline groups rather than to an unlikely agostic interaction. We have previously noted a similar upfield shift affecting phosphine isopropyl substituents in the case of TpRu complexes, also attributable to ring-current effects.[9] The hydrido ligand appears in the ^{1}H NMR spectrum of complexes **3a**, **3b**, and **4a**−**4c** as one high-field doublet in the range −6 to −8 ppm in all cases. The values of the coupling constants $^2J_{HP}$ for the hydride resonance are between 27 and 31 Hz. These values for $^2J_{HP}$ compare well with those found in transoid dihydride complexes of ruthenium, which exhibit cisoid arrangement of the hydride and phosphine atoms as determined by X-ray crystallography, i.e., $^2J_{HP}$ = 28.4 Hz in [Cp*RuH$_2$(PPh^{i}Pr$_2$)$_2$][BAr′$_4$] [Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$)][10] or $^2J_{HP}$ = 24 Hz in [Cp*RuH$_2$(dippae)][BPh$_4$] [dippae = 1,2-bis(diisopropylphosphinoamino)ethane].[11] In the trihydride complexes [Cp*RuH$_3$(^{i}Pr$_2$PCH$_2$X) (X = pyridyl, quinolyl),[12] the values of $^2J_{HP}$ between H and P in cisoid positions are 31 Hz but are ca. 0 Hz for H and P in transoid positions. These data suggest that the hydride and the phosphorus atom in complexes **3a**, **3b**, and **4a**−**4c** are most likely in mutually cisoid positions. Consistent with this, NOE NMR experiments performed on solutions of **3a** and **3b** with irradiation of the hydride signals revealed no through-space interaction with OCH$_3$ or OCH(CH$_3$)$_2$ groups. Reciprocally, irradiation of the OCH$_3$ (**3a**) or OCH(CH$_3$)$_2$ (**3b**) resonances did not reveal through-space interactions with the hydride. If the hydride and

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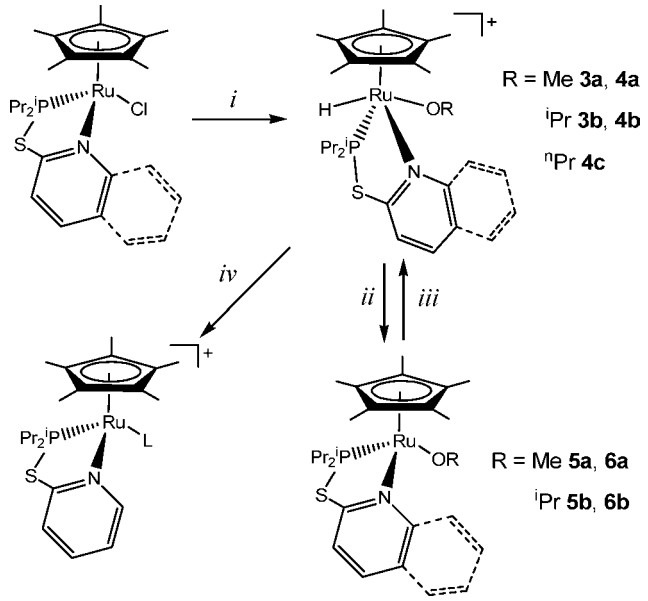
alkoxide moieties were arranged in a cisoid manner, a through-space interaction between the hydride and alkoxide groups should be observed, but this is not the case. The $^{13}C\{^1H\}$ NMR resonances for the oxygen-bound carbon atom of the alkoxide ligands show coupling with phosphorus ($^3J_{CP}$ = 12−15 Hz). Likewise, the protons attached to these carbon atoms also display coupling to phosphorus, in addition to coupling with other hydrogen atoms eventually present in the alkoxide moieties. These spectral data are consistent with a four-legged piano-stool structure, with a transoid arrangement of hydride and alkoxide ligands. This description is particularly relevant because a "classic" oxidative addition of the alcohol would produce complexes with hydride and alkoxide in mutually cisoid positions. With a transoid stereochemistry, we should consider an abnormal oxidative addition mechanism, which might be related to the one recently proposed by Brookhart and co-workers[13] for the formation of a *trans*-iridium(III) dihydride via proton-catalyzed hydrogenation. This possibility is currently under study.

The use of the mercaptopyridyl- or mercaptoquinolylphosphine ligands $^iPr_2PSX$ seems crucial for achieving OH activation because this process has not been observed in the case of homologous complexes containing pyridyl- or quinolylphosphines with spacer groups other than S, such as $^iPr_2PNHPy$ or $^iPr_2PCH_2X$ (X = Py, Quin). Thus, no reaction between $[Cp^*RuCl(^iPr_2PCH_2X)]$ and $NaBPh_4$ in MeOH is observed, whereas in the case of $[Cp^*RuCl(^iPr_2PNHPy)]$, the reaction with $NaBPh_4$ in MeOH leads to $[Cp^*RuCl(\kappa^1\text{-}P\text{-}^iPr_2PCH_2Py)(\kappa^2\text{-}P,N\text{-}^iPr_2PCH_2Py)][BPh_4]$.[14] No MeOH activation products have been detected.

The ruthenium(IV) compounds herein described undergo reductive elimination readily. Thus, the hydrido(alkoxo) complexes **3a** and **3b** react with ligands such as CO or MeCN, releasing the alcohol and furnishing the corresponding ruthenium(II) species $[Cp^*Ru(L)(^iPr_2PSPy)][BPh_4]$ (L = CO, MeCN). **3a**, **3b**, **4a**, and **4b** are deprotonated by a strong base such as $KOBu^t$ in tetrahydrofuran (THF), yielding the neutral alkoxides $[Cp^*Ru(OR)(^iPr_2PSX)]$ [X = Py and R = Me (**5a**), ^{i}Pr (**5b**); X = Quin and R = Me (**6a**), ^{i}Pr (**6b**)]. These species are stable toward β elimination and do not generate the corresponding hydrides even when heated at 70 °C in C_6D_6. This observation is not necessarily surprising, given the fact that quantitative studies performed on the mechanism of β-hydrogen elimination from square-planar iridium(I) alkoxide complexes have shown that such species can be quite robust and require hours to decompose at 80−110 °C.[15] The neutral ruthenium(II) alkoxides are unreactive toward the insertion of CS_2 to yield xanthato complexes and toward primary amines such as $PhNH_2$. However, and quite remarkably, they are protonated with HBF_4 in Et_2O at the metal site, regenerating the corresponding cationic hydrido(alkoxide) $[Cp^*RuH(OR)(^iPr_2PSX)]^+$ in the form of a $[BF_4]^-$ salt. These reactions are summarized in Scheme 1.

Attempts made to crystallize any of the hydrido(alkoxo) derivatives from dichloromethane/petroleum ether mixtures were unsuccessful. In all cases, the solutions turned deep green upon standing under dinitrogen or argon. Crystals of the dinuclear ruthenium(III) complex $[\{Cp^*Ru(\kappa^2\text{-}N,S\text{-}\mu\text{-}S\text{-}SC_5H_4N)\}_2][BPh_4]_2$ (**7**) were obtained from the attempted recrystallization of **3b**. An ORTEP view of the cation $[\{Cp^*Ru(\kappa^2\text{-}N,S\text{-}\mu\text{-}S\text{-}SC_5H_4N)\}_2]^{2+}$ is shown in Figure 1, together with selected bond lengths and angles. The thiolate-bridged dinuclear Cp*Ru complex **7** is structurally related to

Scheme 1[a]



[a](i) $NaBPh_4$, ROH (R = Me, ^{i}Pr, ^{n}Pr), 6−12 h; (ii) $KOBu^t$, THF; (iii) $HBF_4{\cdot}OEt_2$, Et_2O, −80 °C; (iv) MeCN or CO/CH_2Cl_2.

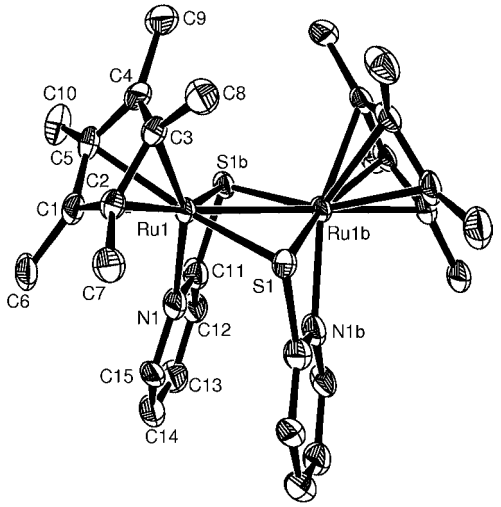


Figure 1. ORTEP drawing (50% thermal ellipsoids) of $[\{Cp^*Ru(SC_5H_4N)\}_2]^{2+}$ in **7**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Ru1−Ru1b 2.4964(10), Ru1−S1 2.4218(13), Ru1−S1b 2.4512(12), Ru1−N1 2.163(4); Ru1−S1−Ru1b 61.63(4), S1−Ru1−S1b 117.18(4), N1−Ru1−S1b 66.52(11).

the species extensively studied by Nishibayashi and co-workers, which are particularly relevant in the context of catalytic propargylation reactions of ketones.[16] The structure of the complex cation in **7** is very similar to that of the homologous species $[\{CpRu(\kappa^2\text{-}N,S\text{-}\mu\text{-}S\text{-}SC_5H_4N)\}_2]^{2+}$, reported by Kirchner and co-workers.[17] The Cp* ligands are mutually cisoid, and the SC_5H_4N ligands act simultaneously as chelating and bridging ligands. The most important difference between the cations $[\{(C_5R_5)Ru(SC_5H_4N)\}_2]^{2+}$ (R = H, Me) lies in the separation of the two ruthenium atoms and also in the value of the angle Ru1−S1−Ru1b. In **7**, the Ru1−Ru1b bond length is 2.4964(10) Å, whereas for $[\{CpRu(SC_5H_4N)\}_2]^{2+}$, it is 2.789(1) Å. These values are consistent with a Ru≡Ru triple

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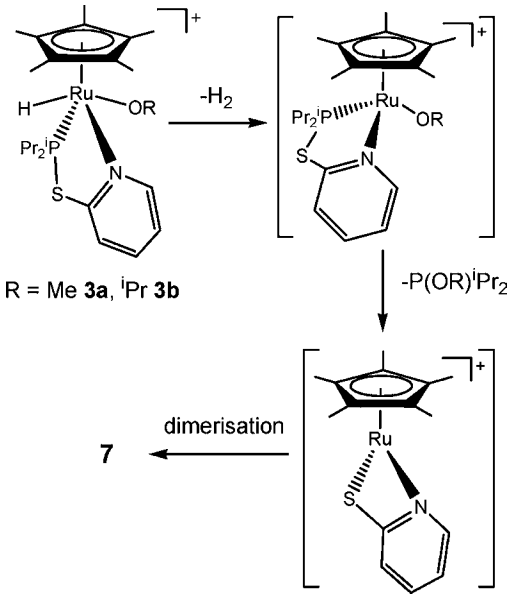
bond[18] and a Ru−Ru single bond, respectively, and with the diamagnetic character of both cations. Also, the Ru1−S1−Ru1b angle in **7** is significantly more acute [61.63(4)°] than that in the Cp analogue [73.9(1)°], suggesting a much stronger Ru−Ru interaction. The contraction in Ru−Ru bond distances upon going from Cp to Cp*, which is a stronger donor, is a most interesting observation. In spite of this, the observed short distance does not necessarily imply multiple bonding. Density functional theory calculations are clearly needed here in order to clarify the status of the metal−metal interactions in this complex.

We can tentatively explain the formation of the dinuclear complex **7** at the expense of the hydrido(alkoxide) complexes **3a** and **3b** by considering an electron transfer from the hydride to the metal, leading to an intermediate ruthenium(III) alkoxide species with concomitant loss of dihydrogen. Migration of the alkoxide group over the P^iPr_2 moiety with subsequent cleavage of the P−S bond would generate $P(OR)^iPr_2$ (R = Me, ^{i}Pr) plus $[(C_5Me_5)Ru(SC_5H_4N)]^+$. Dimerization of the latter yields **7** (Scheme 2).

Scheme 2. Proposed Reaction Sequence for the Formation of 7



We have monitored by NMR a CD_2Cl_2 solution of **3a** over a period of several days. A gradual decrease of the intensity of the signals for **3a** and the appearance of one broad resonance at 4.5 ppm in the ^{1}H NMR spectrum attributable to free H_2 and of one signal at ca. 65 ppm in the $^{31}P\{^1H\}$ NMR that we ascribe to $P(OMe)^iPr_2$ or to a degradation product thereof were observed. These observations support the reaction sequence shown in Scheme 2. From this work, it is clear that half-sandwich ruthenium complexes containing mercaptopyridyl- or mercaptoquinolylphosphine ligands are capable of performing facile OH activation in a number of alcohols, furnishing hydrido(alkoxo) derivatives. We are currently carrying out detailed studies on these systems, in order to understand their unusual reactivity and to expand their applicability to the activation of O−H bonds present in other alcohols as well as in water.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, detailed synthetic procedures, NMR spectral data for the complexes, and experimental details for the X-ray structure analysis of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: manuel.tenorio@uca.es (M.J.-T.), carmen.puerta@uca.es (M.C.P.). Fax: (+34) 956 016288.

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