Inorg. Chem. **2008**, *47*, 8598−8600

Inorganic Chemistry
Communication

Formation of a Coordinated 2-Aminoethylidene Ligand and Its Rearrangement by Deprotonation into a Phosphinoallyl Ligand Containing a Pyrrolidin-2-yl Ring

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Received July 11, 2008

The activation of 1,1-diphenyl-2-propyn-1-ol by the metallic fragment $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(dippae)}]^+$ {dippae = 1,2-bis[(diisopropylphosphanyl)amino]ethane}, followed by dehydration, produces a cationic complex that, by deprotonation and rearrangement, leads to a neutral complex with a phosphinoallyl ligand containing a pyrrolidin-2-yl ring.

It is well-known that propargyl alcohol activation by means of organometallic complexes yields allenylidene compounds.[1] Ruthenium allenylidene complexes show versatile chemical behavior in relation to the unsaturated character of the carbon chain.[2] They exhibit electrophilic reactivity at the α- and γ-carbon atoms;[3] thus, ruthenium allenylidene complexes are excellent substrates for C−C and C−heteroatom coupling by cycloaddition reactions.[4,5] The β-carbon shows nucleophilic character.[6−8] The allenylidene reactivity greatly depends on the electron richness of the in situ generated 16-electron species but is also a function of the propargyl alcohol substituents.[9] During the last years, we have studied the reactivity of several half-sandwich ruthenium complexes toward 1-alkynes and propargyl alcohols, and we have reported the irreversible rearrangement of half-sandwich ruthenium hydridoalkynyl complexes to their vinylidene isomers.[10] In the course of our studies on the activation of 1,1-diphenyl-2-propyn-1-ol by $[\text{Cp*RuCl(L}_2)]$ [Cp* = C_5Me_5, $\text{L}_2 = 2\text{PEt}_3$[11] or 1,2-bis(diisopropylphosphino)ethane (dippe)[12]], we have described the sequence of species involved.[13] In both cases, the $\eta^5\text{-C}_5\text{Me}_5$ ligand plays a key role in the isolation of the intermediate species, which finally leads to stable allenylidene compounds.[11−13] Very recently, we have reported chloride abstraction from complexes [Cp*RuCl(*R*,*R*-dippach)] {*R*,*R*-dippach = (*R*,*R*)-1,2-bis[(diisopropylphosphanyl)amino]cyclohexane} and [Cp*RuCl(dippae)] {dippae = 1,2-bis[(diisopropylphosphanyl)amino]ethane} under dinitrogen or argon. The reaction carried out under argon yields the expected 16-electron complex $[\text{Cp*Ru(dippae)}]^+$, but in the case of *R*,*R*-dippach, a complex

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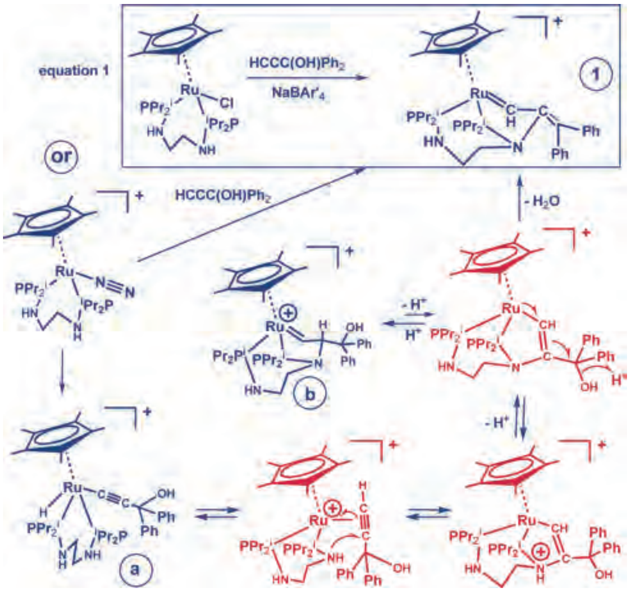
Scheme 1

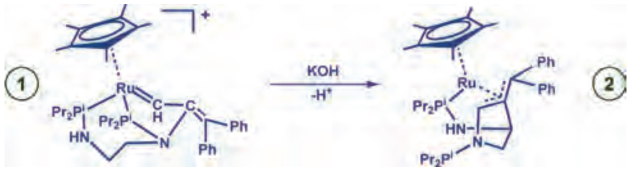


$[Cp^*Ru\{\kappa^3\text{-}P,P',N\text{-}\eta^2\text{-}P,N(R,R\text{-dippach})\}]^+$ was obtained, showing a novel terdentate coordination mode of this ligand.[14]

We report now the activation of 1,1-diphenyl-2-propyn-1-ol by the metallic fragment $[Cp^*Ru(dippae)]^+$. In the course of the reaction with [Cp*Ru(dippae)Cl], using $NaBAr'_4$, sodium tetrakis{3,5-bis(trifluoromethyl)phenyl}borate, as a chloride abstractor, a heterocyclic vinylcarbene complex $[Cp^*Ru\{{=}CHC(NHPPr^i_2CHCH_2NHPPr^i_2){=}CPh_2\text{-}\kappa^3\text{-}P,P,C\}]^+$ (**1**) was obtained instead of an allenylidene or an aminocarbene derivative. Ruthenium alkenylalkylidene complexes have already been obtained by the reaction of hydride precursor complexes and propargyl alcohols followed by proton addition to vinylalkenyl derivatives.[15] On the other hand, the addition of a nucleophile to η^2-coordinated alkynes affording vinylruthenium complexes (or more exactly alkenylphosphonio complexes) is less usual.[16] However, as far as we know, heterocyclic vinylalkylidenes bearing an aminic nitrogen atom bonded to the β-carbon atom have not been previously reported. The formation of **1** according to eq 1 in Scheme 1 is remarkable.

The formulation as a alkenylcarbene derivative is consistent with the NMR data. The presence of the carbene moiety Ru=CH is confirmed by the $^{13}C\{^1H\}$ spectrum, which shows the typical low-field resonance of the carbonic carbon nucleus at 289.5 ppm and resonances assignable to C_β and C_γ at 148.5 and 120.5 ppm, respectively. In the ^1H NMR spectrum, the most remarkable features are the downfield resonance (15.3 ppm) of the Ru=CH proton and the corresponding to N−H, which appears at 1.84 ppm. All of these spectroscopic data agree well with those reported for other vinylalkylidene complexes in spite of the fac that they do not have N bonded to C_β.[15] Two doublets at 100.4 and 102.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum indicate the nonequivalence of the two phosphorus atoms.

Scheme 2



In order to establish the sequence of intermediates in the activation of alkynols by the moiety $[Cp^*Ru(dippae)]^+$, we have studied the reaction between the dinitrogen compound $[Cp^*Ru(dippae)(N_2)][BAr'_4]$[14] and 1,1-diphenyl-2-propyn-1-ol in CD_2Cl_2 by monitoring the process by ^1H and $^{31}P\{^1H\}$ NMR at variable temperature.

The formation of **1** can be rationalized as follows: The dissociation of a labile dinitrogen ligand and the C−H activation of the propargyl alcohol should afford **a**, in agreement with a triplet at −7.9 ppm in ^1H and a singlet at 104.78 ppm in $^{31}P\{^1H\}$ NMR spectra at 5 °C. The hydroxyalkynyl hydride **a** is likely in equilibrium with π-alkynol species not detected. Carbene complex **b** is generated from π-alkynol by an intramolecular nuclephilic attack of a nitrogen atom on the π-alkynol ligand. At a temperature of 25 °C in the low-field region of the ^1H spectrum, the most noticeable resonances appear near 16.0 ppm. These signals correspond to carbene species **b** (probably two stereoisomers $\mathbf{b_1}$ and $\mathbf{b_2}$ with the vicinal hydrogen in two different orientations exchange between them). These resonances should appear as multiplets, but they remain unresolved. In the $^{31}P\{^1H\}$ spectra, isomer $\mathbf{b_1}$ shows two doublets at 101.3 and 104.0 ppm ($J_{PP} = 37$ Hz) and isomer $\mathbf{b_2}$ shows two doublets at 98.5 and 100.3 ppm ($J_{PP} = 34$ Hz). After 19 h at room temperature (25 °C), the proton carbenic signals of **b** isomers are very weak and the signal at 15.3 ppm is strongest, indicating the formation of the final carbene complex **1**. In $^{31}P\{^1H\}$ NMR spectra, the presence of **1** is indicated by two doublets at 100.4 and 102.3 ppm ($J_{PP} = 36$ Hz).

Deprotonation of **1** with KOH produces in one step an uncommon rearrangement, leading to a tetrasubstituted trihaptoallyl complex $[Cp^*Ru\{\eta^3\text{-}CHC[(CHCH_2NPPr^i_2)NHPPr^i_2]CPh_2\text{-}\kappa^4\text{-}P,C,C',C''\}]$ (**2**), which is a very unusual transformation that lacks precedent in the literature (Scheme 2).

The reaction leading to neutral compound **2** is relatively fast and takes place in hetereogeneous media. It should involve a sequence of internal rearrangements and C−E couplings. The reaction of **1** with K^tBuO produced in a less clean manner compound **2** with very low yield.

It is not possible to propose mechanistic routes based on our experimental data. Only a description of broken and formed bonds follows: In the final product, a C−N bond is formed over the already existing carbon 1 on the 3,3-diphenylprop-2-enylidene moiety. Carbon 2 results coupled

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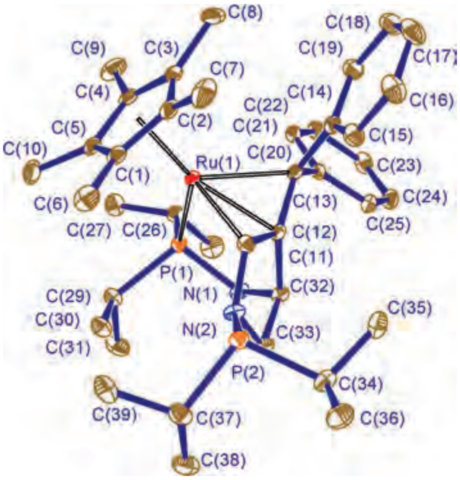


Figure 1. Crystal structure of **2**. The thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms are omitted for clarity.

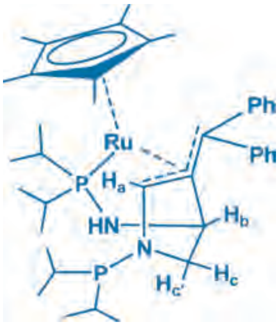
with one carbon from the ethylene chain. Subsequently, a five-membered N-heterocycle is formed and the vicinal Ru−P bond is cleaved.

Crystals suitable for X-ray crystallography were obtained. The single-crystal analysis revealed the unusual structure of this compound (Figure 1).

In this "semisandwich" molecule, the "in situ" formed ligand acts formally as a terdentate chelating ligand, with the allyl moiety occupying two positions of coordination and the phosphorus atom the third one. The bond lengths Ru(1)−P(1) and P(1)−N(1) included in the five-membered chelating ring are 2.2815(6) and 1.689(2) Å, respectively, with the P−N distance being slightly shorter than the analogous distance P(2)−N(2), 1.721(2) Å, found for the noncoordinated phosphorus. The allyl moiety bonds the metal in a trihapto mode, with bond lengths Ru−C being 2.231(2), 2.153(2), and 2.237(2) Å. The distances C(11)−C(12) and C(12)−C(13) are 1.411(3) and 1.449(3) Å, respectively. These structural parameters are similar to those found for the comparable Cp*Ru complexes containing η^3-allyl or η^3-butadienyl entities.[17−19] The allyl carbon atoms C(11) and C(12) form with C(32), C(33), and N(2) a five-membered heterocycle derived of pyrrolidine, which is almost planar. The allyl plane C(11)−C(12)−C(13) and the cyclopentadienyl ring C(1)>C(5) form a dihedral angle of 66.6(2)°. The plane formed by the central atom C(12) in the allyl entity with Ru(1) and P(1) intersects nearly perpendicularly the cyclopentadienyl ring with a dihedral angle equal to 83.09(7)°.

It was confirmed by means of NMR spectroscopy that this solid-state molecular structure is essentially maintained also in solution. In addition to the signals corresponding to the pentamethylcyclopentadienyl ligand and the isopropyl and phenyl groups, some features of interest appear and they will be discussed. In the ^{31}P{^{1}H} NMR spectrum, two singlets at 79.33 and 126.8 ppm correspond to noncoordinated and coordinated phosphorus, respectively. HETCOR and HSQC experiments contributed to explain ^{13}C{^{1}H} and ^{1}H NMR spectra.

Scheme 3



The allylic hydrogen H$_a$ (Scheme 3) exhibits a multiplet at 4.50 ppm (main constant J_{HaP} = 27.5 Hz and some additional coupling with isopropyl group hydrogens). For the cationic ruthenium(IV) complex [Ru(Cp*)Cl(Ph$_2$POMe)(η^3-CH$_2$CMeCH$_2$)][PF$_6$],[20] with 2.01−3.8 ppm for the allylic hydrogens using CD$_2$Cl$_2$ as the solvent, in neutral allyl compounds of ruthenium, the interval is even larger, 1.35−5.79 ppm, although it includes changes by the solvent (C$_6$D$_6$ and CDCl$_3$ were used).[17] H$_b$ originates a doublet at 6.08 ppm ($J_{\mathrm{H_b-H_{c'}}}$ = 8.78 Hz). This coupling constant points out a transoid arrangement for H$_b$ and H$_{c'}$. A doublet at 2.66 ppm ($J_{\mathrm{H_c-H_{c'}}}$ = 11.13 Hz) was assigned to H$_c$ and a multiplet at 3.44 ppm ($J_{\mathrm{H_{c'}-H_c}}$ = 11.13 Hz, $J_{\mathrm{H_{c'}-H_b}}$ = 8.78 Hz) to H$_{c'}$ (the roughly estimated shift for this type of hydrogen is around 3.00 ppm). The carbon related to H$_c$ and H$_{c'}$ appears at 59.8 ppm and the allylic carbon related to H$_a$ at 59.4 ppm. The two other allylic carbons around 60 ppm were not clearly observed. The carbon related to H$_b$ appears at 99.5 ppm.

The formation of complex **2** containing a pyrrolidin-2-yl ring of interest in biochemistry and medicine is facilitated by the flexibility of the ethylene chain in the phosphinoamine ligand dippae.

Acknowledgment. This work was supported by spanish MEC (Project CTQ2007-60137/BQU) and Junta de Andalucía (Grants FQM 188 and FQM 00094). We thank Johnson Matthey plc for generous loans of ruthenium trichloride.

Supporting Information Available: Experimental details (PDF) and X-ray data for complex **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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