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Hydrolysis of Coordinated Diazoalkanes To Yield Side-On 1,2-Diazene Derivatives

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Supporting Information

ABSTRACT: Diazoalkane complexes [Ru(η^5-C_5Me_5)(N_2CAr1Ar2)(PPh_3){$P(OR)_3$}]BPh_4 [R = Me (**1**), Et (**2**); Ar1 = Ar2 = Ph (**a**); Ar1 = Ph, Ar2 = *p*-tolyl (**b**); Ar1Ar2 = $C_{12}H_8$ (**c**)] were prepared by allowing chloro complexes RuCl(η^5-C_5Me_5)(PPh_3)[$P(OR)_3$] to react with diazoalkane $Ar1Ar2CN_2$ in ethanol. The treatment of compounds **1** and **2** with H_2O afforded 1,2-diazene derivatives [Ru(η^5-C_5Me_5)(η^2-NH═NH)(PPh_3){$P(OR)_3$}]BPh_4 (**3** and **4**) and ketone Ar1Ar2CO. A reaction path involving nucleophilic attack by H_2O on the coordinated diazoalkane is proposed. The complexes were characterized spectroscopically (IR and NMR) and by X-ray crystal structure determination of [Ru(η^5-C_5Me_5)(η^2-NH═NH)(PPh_3){$P(OMe)_3$}]BPh_4 (**3**).

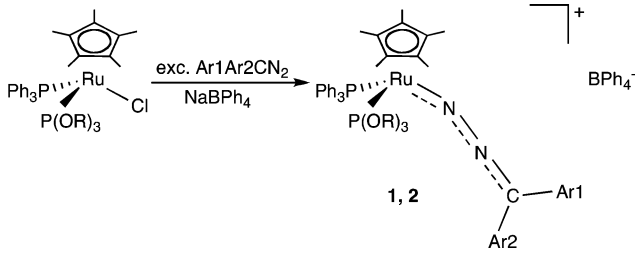
The chemistry of transition-metal complexes containing diazoalkanes $Ar1Ar2CN_2$ as ligands is of long-standing interest[1−3] because of not only the close relationship with N_2 coordination and fixation processes[4] but also the various coordination modes and reactivity of metal-bonded diazoalkane.[1−3,5] Carbene complexes can be obtained[1,2a,f,5] from $Ar1Ar2CN_2$ derivatives after extrusion of N_2, but in some cases, dinitrogen M−N_2 complexes form.[2f,h,i] N−N bond cleavage,[2d] reduction of a coordinated N_2CAr1Ar2 ligand,[2f,h] and 1,3-dipolar cycloaddition[3a,b] with alkene and alkyne were also observed.

As part of our study of diazoalkane complexes, we now report a novel reaction of coordinated $Ar1Ar2CN_2$, which undergoes an unprecedented hydrolysis reaction, yielding 1,2-diazene complexes [M](η^2-NH═NH) and ketone Ar1Ar2CO.

Pentamethylcyclopentadienyl half-sandwich complexes RuCl(η^5-C_5Me_5)(PPh_3)[$P(OR)_3$] react with an excess of diazoalkane $Ar1Ar2CN_2$, in the presence of $NaBPh_4$, to give the diazoalkane derivatives [Ru(η^5-C_5Me_5)(N_2CAr1Ar2)(PPh_3){$P(OR)_3$}]BPh_4 (**1** and **2**) in good yield (Scheme 1).

The complexes are reddish-brown solids stable in air and in a solution of polar organic solvents, where they behave as 1:1 electrolytes.[6] The IR spectra show a medium-intensity band at 1950−1919 cm^{-1}, attributed to $\nu_{C=N=N}$ of the coordinated diazoalkane. This value also suggests an *end-on* η^1-coordination mode for the $Ar1Ar2CN_2$ group,[1] like that found in the comparable cyclopentadienyl derivatives [Ru(η^5-C_5H_5)(N_2CAr1Ar2)(PPh_3){$P(OR)_3$}]BPh_4.[3a] Besides the signals of the ancillary ligands C_5Me_5, PPh_3, and $P(OR)_3$ and the BPh_4^- anion, the ^{1}H NMR spectra of compounds **1** and **2** show the characteristic resonances of the substituents 4-$CH_3C_6H_4$ and $C_{12}H_8$ of the diazoalkane, whereas the ^{31}P NMR spectra are AB multiplets, fitting the proposed formulation for the complexes.

Scheme 1[a]

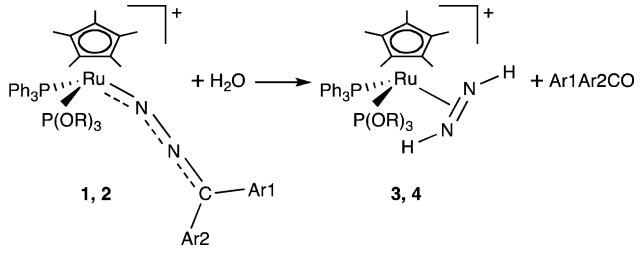


[a]R = Me (**1**), Et (**2**); Ar1 = Ar2 = Ph (**a**); Ar1 = Ph, Ar2 = *p*-tolyl (**b**); Ar1Ar2 = $C_{12}H_8$ (**c**).

At room temperature, diazoalkane complexes **1** and **2** react with H_2O to afford 1,2-diazene derivatives [Ru(η^5-C_5Me_5)(η^2-NH═NH)(PPh_3){$P(OR)_3$}]BPh_4 (**3** and **4**), which were isolated in about quantitative yield and characterized (Scheme 2). The ketone Ar1Ar2CO was also separated from the reaction mixture in about quantitative yield, indicating the stoichiometry shown in Scheme 2 for the hydrolysis reaction.

The formation of diazene complexes **3** and **4** is rather surprising but may be explained as due to the nucleophilic attack of H_2O on the carbon atom of the coordinated diazoalkane, according to the reaction path shown in Scheme 3.

Scheme 2[a]



[a]R = Me (**3**), Et (**4**).

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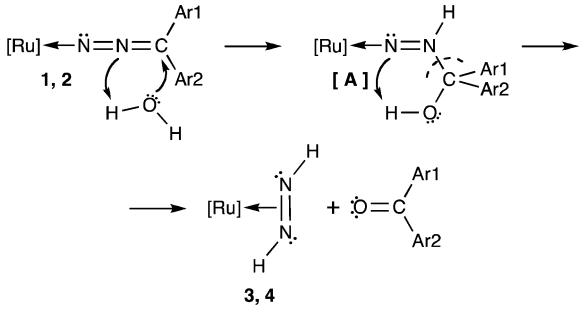
Scheme 3[a]



[a][Ru] = $[Ru(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}]^+$.

H_2O attack, with C−O bond formation, is followed by the shift of one hydrogen atom, giving hydrazido intermediate [**A**]. This species is probably unstable and may give rise to intramolecular hydrogen transfer from the acidic OH group to the hydrazido Nα group with concurrent cleavage of the C sp^3−Nβ bond, affording free ketone Ar1Ar2C═O and the 1,2-diazene molecule, which acts as a π-bonded ligand. The progress of the reaction between complex **1** and H_2O was followed by NMR in an attempt to detect any intermediate such as [**A**]. Unfortunately, as the reaction proceeded, no new species were observed in the spectra, apart from the reagents and the final diazene **3** and ketone Ar1Ar2CO. However, nucleophilic attack at the carbon atom of coordinated diazoalkanes has previously been reported,[7] and this precedent supports the path we propose in Scheme 3.

Free diazomethane and substituted ones are reported to undergo hydrolysis,[8,9] yielding alcohol and N_2. Coordination at our $[Ru(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}]^+$ fragment entails a novel reactivity toward hydrolysis, affording diazene NH═NH and ketone.

1,2-Diazene is a very unstable species[10] that can be stabilized by coordination on a metal center.[11−13] It is a molecule of possible importance to the inorganic and bioinorganic N_2 reduction process[14] and was prepared from oxidation of hydrazine complexes.[11−13] Hydrolysis of a coordinated diazoalkane highlights a new method of synthesizing this important nitrogen dihydride species.

Good analytical data were obtained for diazene complexes $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}NH{=}NH)(PPh_3)\{P(OR)_3\}]BPh_4$ (**3** and **4**), which were isolated as stable yellow solids and characterized by conductivity measurements and IR and NMR spectra.

At room temperature, the ^1H NMR spectra of diazene complexes **3** and **4** show only the characteristic signals of the ancillary ligands C_5Me_5, PPh_3, and $P(OR)_3$. However, the ^{15}N-labeled complexes $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}^{15}NH{=}NH)(PPh_3)\{P(OR)_3\}]BPh_4$ (**3a** and **4a**) were synthesized, and their proton-coupled ^{15}N NMR spectra show a doublet of multiplets at −210.9 (**3a**) and −211.1 (**4a**) ppm, which can be simulated with an NXYAB model (N = ^{15}N; X, Y = ^1H; A, B = ^{31}P; see the Supporting Information, Figure S1) with $^1J_{^{15}N^{H}} = 92.4$ Hz and $^2J_{^{15}N^{H}} = 2.7$ Hz. The spectra collapsed to a single multiplet upon ^1H decoupling, confirming the presence of the NH═NH moiety in the complexes. The ^{31}P NMR spectra are AB multiplets (ABN in the ^{15}N-labeled complex), fitting the proposed formulation for the complexes, and this was further supported by X-ray crystal structure determination of **3**, the ORTEP of which is shown in Figure 1.

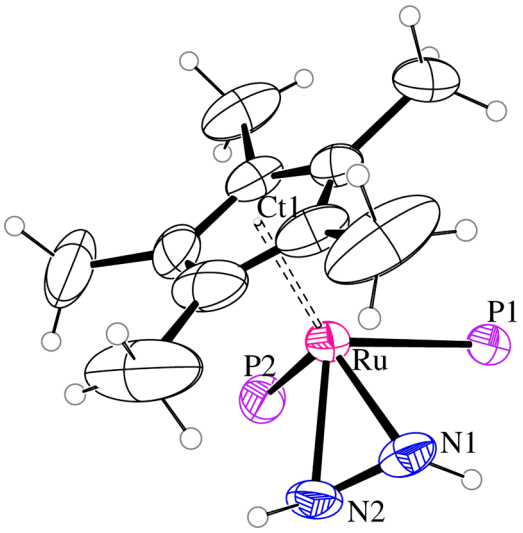


Figure 1. ORTEP[15] view of the cation of **3**. P1 represents a PPh_3 ligand, and P2 represents a $P(OMe)_3$ ligand. Selected bond lengths [Å] and angles [deg]: Ru−CT1, 1.9212(3); Ru−CT2, 1.9160(3); Ru−C1, 2.257(4); Ru−C2, 2.304(3); Ru−C3, 2.295(4); Ru−C4, 2.243(5); Ru−C5, 2.216(4); Ru−C_{av}, 2.263; Ru−N1, 2.030(3); Ru−N2, 2.039(3); Ru−P1, 2.3720(9); Ru−P2, 2.2964(11); N1−N2, 1.367(5); CT1−Ru−N1, 115.77(9); CT1−Ru−N2, 121.95(9); N1−Ru−P2, 116.86(10); N2−Ru−P2, 85.58(12); CT1−Ru−P1, 129.07(2); CT1−Ru−P2, 119.76(3); N1−Ru−P1, 81.14(10); N2−Ru−P1, 101.98(10); P1−Ru−P2, 85.80(4); CT2−Ru−CT1, 120.783(15); CT2−Ru−P1, 91.67(2); CT2−Ru−P2, 101.45(3). CT1 represents the centroid of the Cp ligand and CT2 the middle of the N1−N2 bond.

Compound **3** consists of the tetraphenylborate salt of a ruthenium complex, which crystallizes with a CH_2Cl_2 solvent molecule. Only the cation is shown in Figure 1. The cation complex contains a ruthenium atom in a pseudooctahedral half-sandwich piano-stool structure, coordinated by a η^5-pentamethylcyclopentadienyl ligand (Cp*) having one side-on η^2-diazene (η^2-HNNH) and two phosphine ligands [one PPh_3 and one $P(OMe)_3$] as legs. The Ru−N bond lengths, 2.030(3) and 2.038(3) Å, are shorter than those found in $[Ru(\eta^2\text{-}NH{=}NH)(depe)_2]$, being 2.123(4) and 2.134(3) Å,[13a] and this was attributed to the different trans behavior of Cp* and depe ligands. It is worth noting that, to the best of our knowledge, only two nonbridging side-on diazene ruthenium complexes have been crystallographically described, the aforementioned $[Ru(\eta^2\text{-}NH{=}NH)(depe)_2]$ and the closely related $[Ru(\eta^2\text{-}NH{=}NH)(dmpe)_2]$ complex.[13a] In those compounds, the N−N bond lengths were reported to be 1.414(5) and 1.427(3) Å, respectively; in **3**, this value is now 1.366(5) Å. Both values are shorter than those found in other ruthenium end-on-bound hydrazine complexes (between 1.38 and 1.48 Å), so that they can be considered as multiple bonds. However, these values are longer than those found in other ruthenium diazene complexes reported in the literature (about 1.28 Å),[13a] especially those in the $[Ru(\eta^2\text{-}NH{=}NH)(depe)_2]$ complex. Their authors attributed the lengthening of the N−N bond to back-bonding from filled d orbitals of ruthenium to the antibonding π^* orbitals of the diazene ligand.

Further studies on both hydrolysis and other reactions of metal-bonded diazoalkane derivatives are in progress.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental and spectroscopic details and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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