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Cycloaddition of Coordinated Diazoalkanes to Ethene To Yield 3*H*-Pyrazole Derivatives

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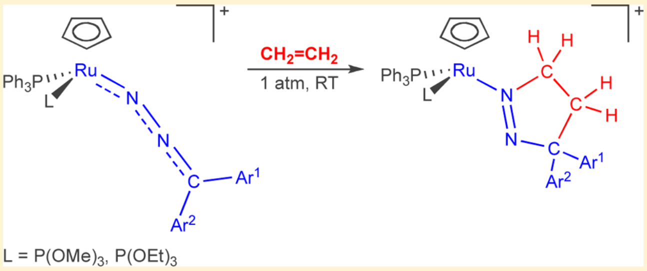
Supporting Information

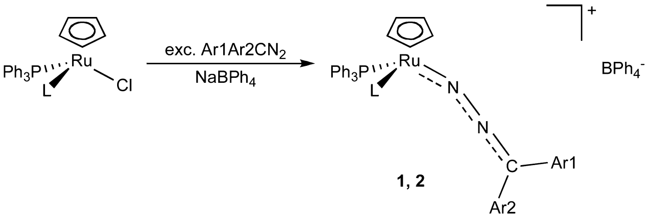
ABSTRACT: Diazoalkane complexes $[Ru(\eta^5\text{-}C_5H_5)(N_2CAr1Ar2)(PPh_3)L]BPh_4$ (**1**, **2**; Ar1 = Ph, Ar2 = *p*-tolyl; Ar1Ar2 = $C_{12}H_8$; L = $P(OMe)_3$, $P(OEt)_3$) were prepared by allowing compounds $RuCl(\eta^5\text{-}C_5H_5)(PPh_3)L$ to react with diazoalkane in ethanol. Treatment of complexes **1** and **2** with ethylene under mild conditions (1 atm, room temperature) led not only to the ethylene complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_2{=}CH_2)(PPh_3)L]BPh_4$ (**5**, **6**) but also to dipolar (3 + 2) cycloaddition, affording the 3*H*-pyrazole derivatives $[Ru(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}\overline{N{=}NC(Ar1Ar2)CH_2CH_2}\}(PPh_3)L]BPh_4$ (**3**, **4**). The propylene complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_3CH{=}CH_2)(PPh_3)L]BPh_4$ (**7**, **8**) were also prepared. The compounds were characterized by spectroscopy and by X-ray crystal structure determinations of **2a**, **3b**, and **7**.



Dipolar (3 + 2) cycloaddition of diazoalkane to alkene is an important reaction which has been extensively studied, for both fundamental and synthetic reasons.[1,2] However, despite numerous studies, no example of cycloaddition of coordinated diazoalkane[3,4] has ever been reported. We describe here the synthesis of new diazoalkane complexes of ruthenium, which undergo unprecedented (3 + 2) cycloaddition of the metal-bonded diazoalkane to ethylene ($CH_2{=}CH_2$), yielding a 4,5-dihydro-3*H*-pyrazole derivative.

Mixed-ligand half-sandwich complexes[5] $RuCl(\eta^5\text{-}C_5H_5)(PPh_3)L$ (L = $P(OR)_3$) react with an excess of $Ar1Ar2CN_2$ in ethanol in the presence of $NaBPh_4$ to afford the diazoalkane derivatives $[Ru(\eta^5\text{-}C_5H_5)(N_2CAr1Ar2)(PPh_3)L]BPh_4$ (**1**, **2**) in about 70% yields (Scheme 1).

Scheme 1. [a]



[a]L = P(OMe) (**1**), $P(OEt)_3$ (**2**); Ar1 = Ph, Ar2 = *p*-tolyl (**a**), Ar1Ar2 = $C_{12}H_8$ (**b**).

Good analytical data were obtained for compounds **1** and **2**, which are red-orange solids and are very stable in air and in solutions of polar organic solvents, where they behave as 1:1 electrolytes.[6] IR spectra show a medium-intensity band at 1959−1961 cm^{-1}, due 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, similar to that found in the solid state for **2a**, an ORTEP[7] drawing of which is shown in Figure 1.

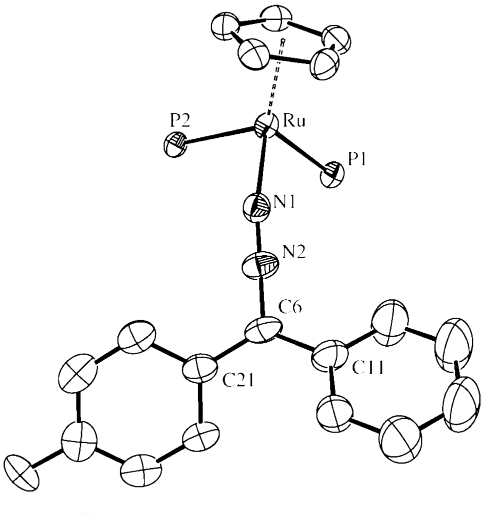


Figure 1. ORTEP[7] view of the cation of **2a** drawn at the 30% probability level. Hydrogen atoms, ethoxy groups at P1, and phenyl rings at P2 are omitted for clarity.

The cation of **2a** consists of a ruthenium atom coordinated by a Cp group, a PPh_3, a $P(OEt)_3$ ligand, and a *p*-tolylphenylmethylenediazo

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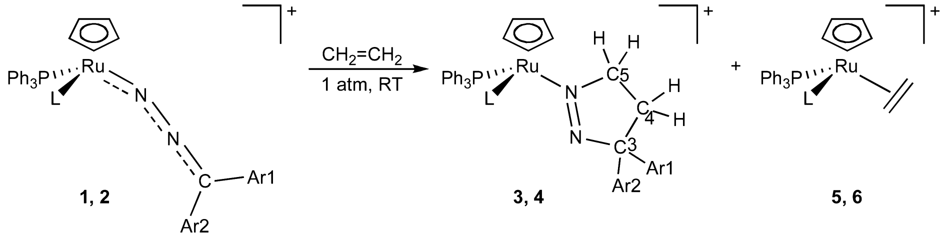
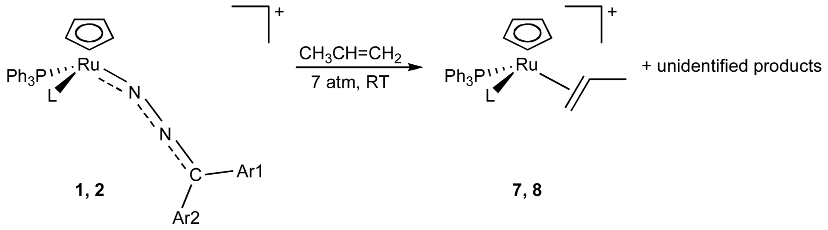
Scheme 2. [a]



[a]L = P(OMe) (**3**, **5**), P(OEt)$_3$ (**4**, **6**); Ar1 = Ph, Ar2 = *p*-tolyl (**a**), Ar1Ar2 = $C_{12}H_8$ (**b**).

Scheme 3. [a]



[a]L = P(OMe) (**7**), P(OEt)$_3$ (**8**).

ligand, bound to the Ru center via the terminal nitrogen atom. Coordination of the last ligand is expected to be linear but, in **2a**, some bending is found, especially in the N−N−Ru angle, 156.0(5)°, rather than in the N−N−C angle, 173.9(6)°. It is noteworthy that these values are large enough for us to propose a linear coordination to ruthenium in this compound, and similar features have previously been reported in the literature: i.e., values of 158.3(3) and 170.1(3)°, respectively, for a diazofluorene compound.[8] It is also remarkable that, when aryldiazenide ligands are used, only the N−N−C(aryl) part is slightly bent.[9]

More information about the nature of this ligand is provided by the short N(1)−N(2) bond distance, 1.147(6) Å, which may be viewed as being between a N−N double and triple bond. It is only slightly longer than that found in the aforementioned diazofluorene compound[8] and similar to those found in other aryldiazenide ruthenium(II) complexes.[9] The N(2)−C(6) bond distance, 1.299(8) Å, is also short enough to be considered as a double bond.[10] Angles around C(6) are close to 120° (from 116.3(6) to 126.1(6)°) and have a sum of 359.9°, thus confirming the sp^2 character of this atom.

Diazoalkane complexes $[Ru(\eta^5\text{-}C_5H_5)(N_2CAr1Ar2)(PPh_3)L]BPh_4$ (**1**, **2**) react with ethylene under mild conditions (1 atm, room temperature) to give not only a small amount of the ethylene complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_2{=}CH_2)(PPh_3)L]BPh_4$ (**5**, **6**) but also the novel derivatives $[Ru(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}N{=}NC(Ar1Ar2)CH_2CH_2\}(PPh_3)L]BPh_4$ (**3**, **4**), which contain a 4,5-dihydro-3*H*-pyrazole as a ligand (Scheme 2).

The reaction proceeds with (3 + 2) cycloaddition of the ethene to the coordinated diazoalkane, giving the 3*H*-pyrazole derivatives **3** and **4**, in which the novel heterocycle acts as a ligand. Parallel substitution of the diazoalkane by $CH_2{=}CH_2$ also proceeds to a small extent, yielding ethylene complexes **5** and **6**. The two compounds $[Ru(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}N{=}NC(Ar1Ar2)CH_2CH_2\}(PPh_3)L]BPh_4$ (**3**, **4**) and $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_2{=}CH_2)(PPh_3)L]BPh_4$ (**5**, **6**) were recovered as solids and separated by fractional crystallization in good yield (70−75% for **3** and **4**, 8−10% for **5** and **6**) as yellow-orange crystalline solids. In the mother liquor, free $Ar1Ar2CN_2$ formed as a result of substitution with $CH_2{=}CH_2$ was also detected, indicating that only coordinated diazoalkane undergoes cyclization with ethylene to yield the 3*H*-pyrazole species. Note that the complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_2{=}CH_2)(PPh_3)L]BPh_4$ (**5**, **6**) were also prepared by treating $RuCl(\eta^5\text{-}C_5H_5)(PPh_3)L$ with $CH_2{=}CH_2$ (1 atm) in the presence of $NaBPh_4$.

N-bonded diazoalkanes are reported to give both dinitrogen $[M]{-}N_2$ and carbene $[M]{=}CAr1Ar2$ complexes.[4f] N−N bond cleavage[11] was also observed, as well as reduction of the coordinated $N_2CAr1Ar2$ ligand.[8] However, an example of the cycloaddition reaction has been reported for a C-bonded diazoalkane in $Rh[\eta^1\text{-}C(N_2)SiMe_3][P(OEt)_3]_3$,[12] which afforded the triazole derivative $Rh[CC(SiMe_3)N_2NBu^t](Bu^tNC)_2[P(OEt)_3]$ in the reaction with Bu^tNC. The use of the half-sandwich fragment $Ru(\eta^5\text{-}C_5H_5)(PPh_3)L$ not only allowed the diazoalkanes to be coordinated but also led to the unprecedented dipolar (3 + 2) cycloaddition of coordinated $N_2CAr1Ar2$ to ethene, affording a novel dihydrido 3*H*-pyrazole molecule.

Propylene was also treated with the diazoalkane complexes $[Ru(\eta^5\text{-}C_5H_5)(N_2CAr1Ar2)\text{-}(PPh_3)L]BPh_4$ (**1**, **2**) in CH_2Cl_2 solution, but under mild conditions (1 atm, room temperature), no reaction took place. Under pressure (7 atm, room temperature), substitution of the diazoalkane was observed, with the formation of propylene complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_3CH{=}CH_2)(PPh_3)L]BPh_4$ (**7**, **8**), but no evidence of a cycloaddition reaction was detected (Scheme 3). In fact, in addition to propylene complexes, some other unidentified products did form in the reaction under pressure, but NMR spectra excluded the formation of 3*H*-pyrazole species. Cyclization with propylene is probably very slow and requires more drastic conditions if it is to proceed.

The new complexes **3**−**8** were characterized by analytical and spectroscopic data and by X-ray crystal structure determinations of $[Ru(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}N{=}NC(C_{12}H_8)CH_2CH_2\}(PPh_3)\{P(OMe)_3\}]BPh_4$ (**3b**) and $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_3CH{=}CH_2)(PPh_3)\{P(OMe)_3\}]BPh_4$ (**7**), the ORTEPs of which are shown in Figures 2 and 3, respectively. The cation of **3b** consists of a ruthenium atom coordinated by a Cp group, a PPh_3, a $P(OMe)_3$, and the new ligand 4′,5′-dihydrospiro[fluorene-9,3′-pyrazole],

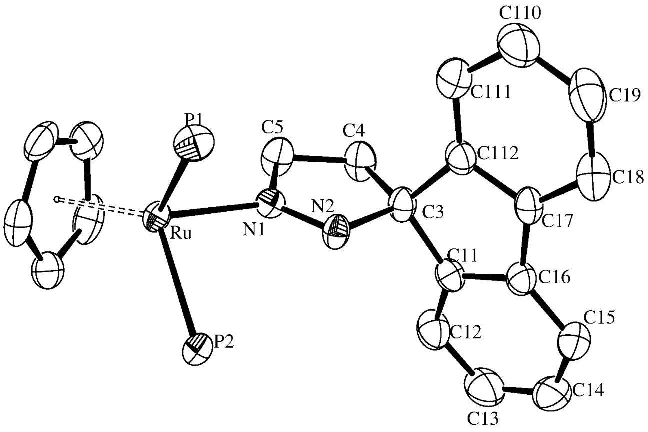


Figure 2. ORTEP[7] view of the cation of **3b** drawn at the 30% probability level. Hydrogen atoms, methoxy groups at P1, and phenyl rings at P2 are omitted for clarity.

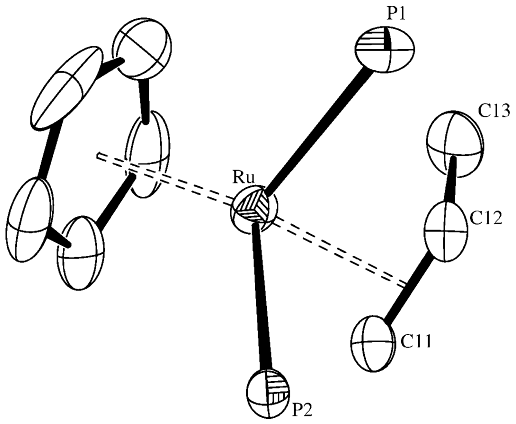


Figure 3. ORTEP[7] view of the cation of **7** drawn at the 20% probability level. Hydrogen atoms, methoxy groups at P1, and phenyl rings at P2 are omitted for clarity.

bound to the Ru center via the nitrogen atom. Cp and the phosphane ligands show their usual behavior.[5]

The most noteworthy parameters of the new ligand 4′,5′-dihydrospiro[fluorene-9,3′-pyrazole] are the N−N bond distance in the 4′,5′-dihydropyrazole ring, 1.241(4) Å, which, although longer than that found in **2a**, corresponds with expected values for a double bond,[10] and the rest of the distances in the ring, from 1.494(5) to 1.533(6) Å, as expected for a single bond. It should be noted that (see the X-ray section in the Supporting Information) the positions of the hydrogen atoms for this ring were found in the density maps. The dihydropyrazole ring (rms deviation of 0.0301 Å) is situated almost perpendicularly to the fluorene plane, forming a dihedral angle of 85.8(2)°.

The cation of **7** consists of a ruthenium atom coordinated by a Cp ligand, a PPh_3, a $P(OMe)_3$ ligand, and a η^2-$CH_2{=}CHCH_3$ ligand. The midpoint of the η^2-coordinated propylene is situated 2.1311(5) Å from the ruthenium atom, in a slightly distorted fashion, with a difference between the two Ru−C bonds of 0.026 Å, the shorter being that of the CH_2.[13] Cp and the phosphane ligands show the usual behavior.[5]

NMR spectra support the proposed formulations for complexes **3**−**8** with geometries in solution like those found in the solid state.

Complexes $[Ru(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}\overline{N{=}NC(p\text{-tolyl})(Ph)\text{-}CH_2}CH_2\}(PPh_3)L]BPh_4$ (**3a**, **4a**) were obtained as a mixture of two diastereoisomers, owing to the presence of two chiral centers in the molecule: i.e., the ruthenium atom and the C3 atom of the heterocyclic ligand. ^1H, ^{13}C, and ^{31}P NMR spectra confirm the presence of the two diastereoisomers, showing two sets of signals for the nuclei of the ligands (see the Supporting Information). In particular, the ^{31}P NMR spectra of **3a** and **4a** show two AB multiplets, whereas the proton spectra show two singlets for the η^5-C_5H_5 protons and two for the methyl group of the *p*-tolyl substituent at C3 of the 3*H*-pyrazole. In addition, two groups of partially overlapping signals were observed for the H4 and H5 protons of the 3*H*-pyrazole, fitting the proposed formulation for the complexes. The ^{31}P NMR spectra of the related complexes $[Ru(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}\overline{N{=}NC(C_{12}H_8)CH_2CH_2}\}\text{-}(PPh_3)L]BPh_4$ (**3b**, **4b**), which contain only one chiral center, show only one AB quartet, whereas ^1H and ^{13}C spectra support the presence of the heterocyclic ligand. In particular, a triplet at 2.23−2.20 ppm, attributed to methylene protons H4, and two triplets at 4.89−4.84 ppm, attributed to methylene hydrogen atoms H5, were observed in the proton spectra. The ^{13}C spectra of **3b** show two singlets at 30.6 and 88.95 ppm. In an HMQC experiment, the former were correlated with the triplet at 2.23 ppm and the latter with the multiplet near 4.84 ppm and attributed respectively to the C4 and C5 carbon atoms of the 3*H*-pyrazole ligand. The singlet at 98.3 ppm was attributed to C3.

At room temperature, the proton spectra of ethylene complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_2{=}CH_2)(PPh_3)L]BPh_4$ (**5**, **6**) show two multiplets at 2.99−2.71 and 3.01−2.71 ppm, attributed to the protons of the coordinated ethylene. Lowering the sample temperature caused variations in the spectra, but even at −90 °C, ethylene peaks were still broadened, suggesting that rotation of $CH_2{=}CH_2$ still occurred at this temperature. However, the room temperature pattern can be simulated by an ABCDEF model (E, F = ^{31}P) with the parameters reported in the Supporting Information, and the good fit between calculated and experimental spectra strongly supports the proposed attributions. In the ^{13}C NMR spectra, the $CH_2{=}CH_2$ carbon resonances appear as doublets of doublets at 38.25 (**5**) and 38.4 ppm (**6**), whereas the ^{31}P spectra are AB quartets, fitting the proposed formulation for complexes **5** and **6**.

The ^1H NMR spectra of the propylene derivatives $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}CH_3CH{=}CH_2)(PPh_3)L]\text{-}BPh_4$ (**7**, **8**) show two signals for the Cp protons and two for the phosphine protons, due to the presence of two diastereoisomers. At room temperature, two sets of signals are also observed for the propylene hydrogen atoms, which can be simulated with an $ABCD_3EF$ model (E, F = ^{31}P) with the parameters reported in the Supporting Information. The ^{31}P NMR spectra exhibited two AB multiplets, whereas the ^{13}C spectra showed two sets of signals for both carbon atoms of the ancillary ligands and those of the propylene, fitting a geometry like those found in the solid state.

We are extending experimental work to test cyclization with other multiple-bond systems and to study new metal fragments for stoichiometric and catalytic cycloaddition.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and CIF files giving experimental, analytical, and spectroscopic data for new compounds and crystallographic data for compounds **2a**, **3b**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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