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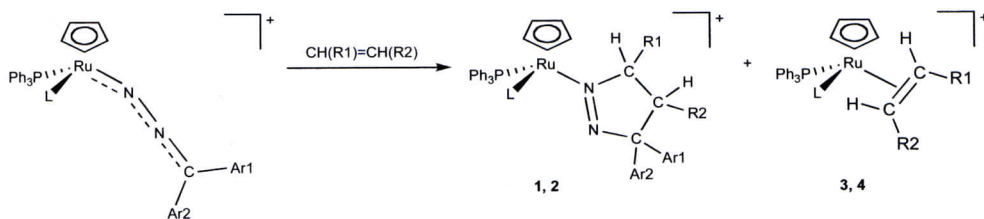
Cyclization of coordinated diazoalkane to alkene and alkyne to afford 3*H*-pyrazole derivatives

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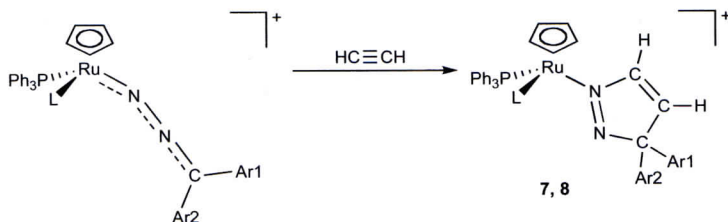
Diazoalkane complexes $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{N}_2\text{CAr}_1\text{Ar}_2)(\text{PPh}_3)\text{L}$ react with ethylene under mild conditions (1 atm, RT) to give not only small amounts of ethylene complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-CH}_2=\text{CH}_2)(\text{PPh}_3)\text{L}]\text{BPh}_4$ (**3**, **4**), but also the novel derivatives $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\eta^1\text{-N}=\text{NC}(\text{Ar}_1\text{Ar}_2)\text{CH}_2\text{CH}_2\}(\text{PPh}_3)\text{L}]\text{BPh}_4$ (**1**, **2**). The reaction proceeds with (3+2) cycloaddition of ethene to the coordinated diazoalkane, giving dihydro-3*H*-pyrazole derivatives **1**, **2**. Activated alkenes $\text{R}_1\text{CH}=\text{CHR}_2$ also react with diazoalkane complexes, leading to the corresponding dihydro-3*H*-pyrazole derivatives.



L = P(OMe)₃, P(OEt)₃; Ar₁ = Ph, Ar₂ = *p*-tolyl; Ar₁Ar₂ = C₁₂H₆; R₁ = H, R₂ = CN; R₁ = R₂ = CN; R₁R₂ = OC–O–CO; R₁R₂ = C₆H₆

Instead, treatment of diazoalkane complexes with propylene under pressure (7 atm, RT) gives exclusively substitution of the diazoalkane, with formation of the propylene complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-CH}_3\text{CH}=\text{CH}_2)(\text{PPh}_3)\text{L}]\text{BPh}_4$ (**5**, **6**).

Dipolar (3+2) cycloaddition of coordinated diazoalkane to ethyne $\text{HC}\equiv\text{CH}$ under mild conditions was also observed, yielding the 3*H*-pyrazole derivatives $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\eta^1\text{-N}=\text{NC}(\text{Ar}_1\text{Ar}_2)\text{CH}=\text{CH}\}(\text{PPh}_3)\text{L}]\text{BPh}_4$ (**7**, **8**).



All the complexes were characterized spectroscopically and by X-ray crystal structure determination of compounds **1**, **5** and **7**.