Facile Insertion of Terminal Acetylenes into the $Ru^{II}-NR_2$ Bond of a 14-Valence-Electron Complex

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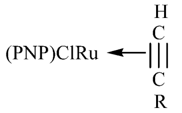
Summary: The reaction of alkynes $RC{\equiv}CH$ ($R = H$, Ph) with (PNP)RuCl, where PNP is $({}^tBu_2PCH_2SiMe_2)_2N$, occurs rapidly below 23 °C to give first an η^2-alkyne adduct and then a final product with a vinylidene group, $C{=}CHR$, inserted into the N−Ru bond. Characterization included X-ray diffraction ($R = Ph$) and DFT calculations to probe mechanistic aspects of the reaction.

The molecule $[({}^tBu_2PCH_2SiMe_2)_2N]RuCl$, (PNP)RuCl, is of interest because of its low coordination number (4), its planar structure, and its triplet ground state for the d^6 configuration of Ru(II).[1] Its high degree of unsaturation, a 14-valence-electron configuration, could give it special chemical reactivity, since it would appear to be suited for simple addition of 4-electron-donor ligands. Among those, we have chosen to explore terminal alkynes as a compact way to deliver 4 electrons (**A**). This offers as additional possible products the vinylidene **B** and, given the reducing power of the metal due to the π-donor amide ligand in PNP, the oxidative addition product **C**. The pioneering studies of the Fryzuk group[2] and others[3] have shown the potential for H migration from a metal to the lone pair present on the amide nitrogen, which thus makes **D** another product for consideration. Overlaid on all of the above is the question[4] of possible “spin forbiddenness” of the reaction: will the change from triplet reactant to singlet product detectably retard the rate of reaction? Here we show (1) facile (time of mixing at −60 °C) binding of RCCH by (PNP)RuCl, (2) facile rearrangement to a diamagnetic product of H migration to form a vinylidene group, (3) near-thermoneutral insertion of the vinylidene into the Ru−amide bond vs retention of a terminal vinylidene on Ru, and (4) DFT calculations which reveal that proton transfer from acetylene to amide N provides a viable intermediate for vinylidene formation. The formation of an N−C(vinyl) bond here is contrasted with earlier stoichiometric and catalytic examples, the latter involving electron-poor metal centers.



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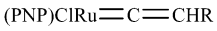

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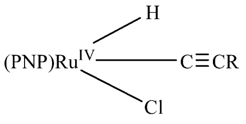

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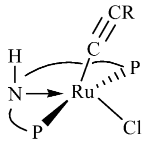

D

When yellow (PNP)RuCl in d_8-toluene is combined with excess HCCH at −196 °C and ^1H and $^{31}P\{^1H\}$ NMR spectra are recorded in 20 °C increments beginning at −60 °C, the spectra can be summarized by eq 1 (showing $\delta(^{31}P)$). Conversion to **1** is complete at −60 °C and is visible by a color change to deep purple-red. The signals of **2** grow only above −40 °C, but at −20 °C, some reversion from **1** to (PNP)RuCl is evident, due to the changing equilibrium constant *K*. At +20 °C, all (PNP)RuCl has been consumed and **2** is the dominant product, forming a green solution. Both species **1** and **2** have only mirror symmetry: two equivalent P atoms, two types of ^{t}Bu groups, and two types of SiMe groups. Species **2** has inequivalent acetylene-derived hydrogens (5.1 and 4.7 ppm). Species **1** has a two-proton ^1H NMR signal at −40 °C, but this broadens in apparent decoalescence at −60 °C. Species **2** shows $^{13}C\{^1H\}$ NMR signals at 168.3 (C_α) and 99.4 (C_β) ppm for the acetylene-derived carbons, neither of which is sufficiently positive to establish an $Ru{=}C{=}CH_2$ structure.[5,6]

$$(PNP)RuCl + HC{\equiv}CH \underset{K}{\overset{fast}{\rightleftharpoons}} \mathbf{1}\ (26.0\ ppm) \xrightarrow{slower} \mathbf{2}\ (50.0\ ppm) \quad (1)$$

Equimolar (PNP)RuCl and PhC≡CH react[7] in benzene at 22 °C with an immediate color change to red and complete consumption of (PNP)RuCl to form $\mathbf{2^{Ph}}$. A strong $^{31}P\{^1H\}$ NMR singlet at 50.8 ppm (cf. eq 1) is accompanied by a weaker peak (4:1 intensity ratio) at 46.4 ppm. The ^1H NMR of the more populated species

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10.1021/om049435b CCC: $27.50

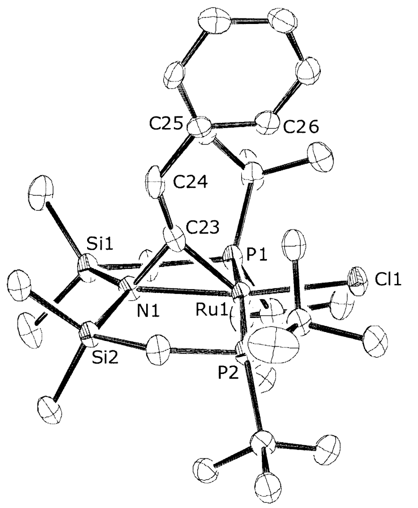

Figure 1. ORTEP view (50% probability ellipsoids) of the non-hydrogen atoms of [($^tBu_2PCH_2SiMe_2)_2NCCHPh$]RuCl, showing selected atom labeling. Unlabeled atoms are carbon. Notable structural parameters (distances in Å and angles in deg): Ru1−C23, 1.903(8); Ru1−N1, 2.270(6); Ru1−Cl1, 2.379(2); C23−C24, 1.347(10); N1−Ru1−Cl1, 168.88(18); C23−C24−C25, 126.7(7); N1−C23−Ru1, 83.9(4).

has, like **2** above, two ^{t}Bu and two SiMe signals. The $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{2^{Ph}}$ shows signals at 170.4 (C_α) and 113.6 (C_β) ppm for the acetylene-derived carbons. A crystal of $\mathbf{2^{Ph}}$, grown from benzene, was shown by X-ray diffraction[8] to have the structure in Figure 1. The structure has an aminovinyl ligand η^2 coordinated to Ru via N and one carbon. This is a product of C−N bond formation, and the C−C π bond in the vinyl group does not donate to Ru, leaving the metal still unsaturated (16 electrons). The hydrogen migration needed to convert an alkyne to a vinylidene has been shown, both experimentally[9] and computationally,[10] to often be a high activation energy process, and the rate observed here at −20 °C is unusually fast. The ^{t}Bu groups anti to C23 do not have agostic interactions with Ru, nor does the ortho C26−H.[11] The three nonmetal atom angles at N1 total 358.9°; therefore, this tertiary amine nitrogen is essentially planar, with its lone pair very poorly oriented to bind to Ru, but the Ru−N distance, 2.270(6) Å, is bonding.

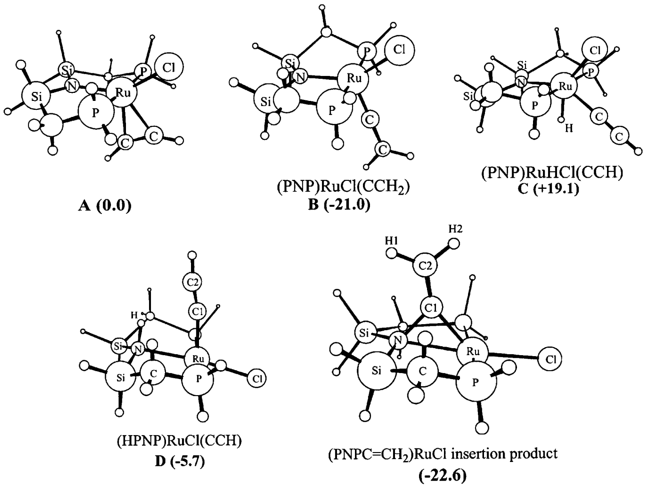

Figure 2. DFT(B3PW91) optimized geometries and energies (E + ZPE, kcal/mol) of isomers of $(H_2PCH_2SiH_2)_2$-$NRuClC_2H_2$.

The results of DFT(B3PW91) calculations[8] of the model [$(H_2PCH_2SiH_2)_2N$]$RuClC_2H_2$ shown in Figure 2 reveal that the vinylidene isomer **B** is more stable than *both* the η^2-acetylene complex **A** (by 21 kcal/mol) and the C−H oxidative addition product **C** (by 40.1 kcal/mol). The (observed) insertion product is calculated to be *only* 1.6 kcal/mol more stable than the vinylidene and has an Ru−N distance of 2.26 Å. The structure of the η^2-acetylene product **A** has HCCH lying in the mirror plane, not perpendicular to it; this product conformation also minimizes steric repulsion between alkyne and the ^{t}Bu groups *during* adduct formation. We propose this as the identity of **1**. The proton-transfer intermediate **D** is indeed a minimum, and the structure shows signs of hydrogen bonding from NH to the alkyne π density,[12] which could be a mechanistic step in the facile conversion (see above) to inserted vinylidene; it would give the observed stereoisomer of phenyl anti to N in $\mathbf{2^{Ph}}$. In contrast, the complex $Ru(NH_2)H(Me_2PC_2H_4PMe_2)_2$ reacts[13] with PhC≡CH by proton transfer to an evidently very Brønsted basic amide nitrogen, to form Ru(CCPh)H-$(Me_2PC_2H_4PMe_2)_2$ and release NH_3.

Vinylidene insertion into the M−amide (i.e. pyrrole) bond of Fe^{II}(CCHR)(porphyrin)[14] occurs *only* after one-electron oxidation and coordination of a nucleophile to M^{III} in the insertion product obtained. Moreover, since the nitrogen lone pair in the product is involved with the porphyrin π-system, there is no N→M bond. In summary, these precedents illustrate C−N bond formation when the metal is electrophilic. The *analogous* vinylidene insertion into a metal−acetylide bond is thekey C−C bond-forming event in dimerization of

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[7] **Reaction of (PNP^{t}Bu)RuCl with phenylacetylene**: to 10.7 mg (0.171 mmol) of (PNP^{t}Bu)RuCl in C_6D_6 was added 1.88 μL of PhCCH (C_8H_6, 1 equiv). Upon addition of phenylacetylene at 22 °C there was a rapid, distinct color change of the solution from yellow to deep reddish brown. ^1H NMR (400 MHz, C_6D_6): δ 7.4−7.3 (m, *Ph*CCH), 7.2−7.0 (m, *Ph*CCH), 6.9 (m, *Ph*HCCRuN), 6.27 (s, 1H, Ph*H*CCRuN), 2.71 (s, 1H, free PhCC*H*), 1.48 (t, J_{P-H} = 8 Hz, >18H, PCMe_3), 1.37 (t, J_{P-H} = 8 Hz, >18H, PCMe_3), 0.89 (t, J_{P-H} = 3.7 Hz, 2H, SiCH_2P of major isomer), 0.82 (t, J_{P-H} = 3.7 Hz, 2H, SiCH_2P of major isomer), 0.49 (t, J_{P-H} = 2.5 Hz, <2H, SiCH_2P of minor isomer), 0.42 (t, J_{P-H} = 2.5 Hz, 2H, SiCH_2P of minor isomer), 0.40 (s, <6H, Si*Me*, minor isomer), 0.33 (s, <6H, Si*Me*, minor isomer), 0.27 (s, 6H, Si*Me*, major isomer), 0.031 (s, 6H, SiMe, major isomer). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 50.8 (s, major isomer), 46.1 (s, minor isomer). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 170.4 (t, J_{C-P} = 9.2 Hz, PhHC*C*RuN), 139.4 (s, *Ph*HCCRuN), 126.9 (s, *Ph*HCCRuN), 125.2 (s, *Ph*HCCRuN), 124.1 (s, *Ph*HCCRuN), 123.6 (s, *Ph*HCCRuN), 118.3 (s, *Ph*HCCRuN), 113.6 (t, J_{C-P} = 5.3 Hz, PhH*C*CRuN), 37.3 (t, J_{C-P} = 6.8 Hz, P*C*Me_3, minor isomer), 36.5 (t, J_{C-P} = 6.9 Hz, P*C*Me_3, minor isomer), 36.1 (t, J_{C-P} = 5.5 Hz, P*C*Me_3, major isomer), 35.0 (t, J_{C-P} = 5.5 Hz, P*C*Me_3, major isomer), 31.5 (t, J_{C-P} = 2.8 Hz, PCMe_3), 30.3 (t, J_{C-P} = 2.7 Hz, PCMe_3), 29.7 (s), 26.4 (br s), 22.5 (s), 11.0 (s, Si*Me*, minor isomer), 8.8 (s, SiMe, minor isomer), 7.1 (s, SiMe, major isomer), 5.2 (s, Si*Me*, major isomer), 2.53 (t, J_{C-P} = 4 Hz, Si*C*H_2P).

[8] See the Supporting Information.

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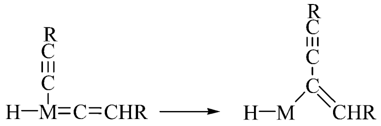
acetylenes to enynes (eq 2).[5,15] Examples of a vinylidene group inserting into an M−phenyl bond of a pincer ligand (eq 3) have been established,[16] and certain examples show some unconventional interaction of the *ipso* carbon with the metal. The difference is that the nitrogen lone pair in a metal amide can confer extra stability to the product. Especially interesting in the aminovinyl isomer is the presence of an N−Ru interaction (**E**), because an M−N bond is absent in these porphyrin precedents (M−N = 2.53−2.64 Å for metals smaller than Ru).[14,17] The transformation observed here has a polarity to the C−N bond formation event completely different from that in studies using very electrophilic zirconium,[18] lanthanide,[19] and actinide[20] metals,[21] where an electron-poor N and a (relatively) unactivated alkyne couple in the slow step (eq 4); there, a vinylidene intermediate is not involved.



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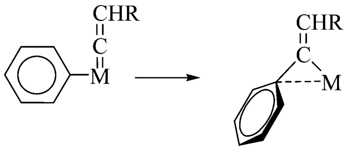

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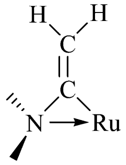

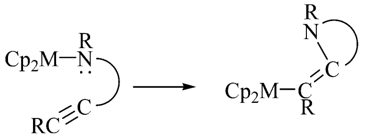

(4)

Finally, any rate reduction due to the "spin forbidden" character of this reaction is not relevant, on the time scale of $\tau_{1/2} > 1$ min at −60 °C.

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Supporting Information Available: Full crystallographic details (CIF file) and tables giving details of the ground-state geometries from DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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