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Reactivity of a 1-Azavinylidene Ligand with Diphenylacetylene on a Ruthenium Carbonyl Cluster. A Remarkable Alkyne Insertion into a Metal−Nitrogen Bond

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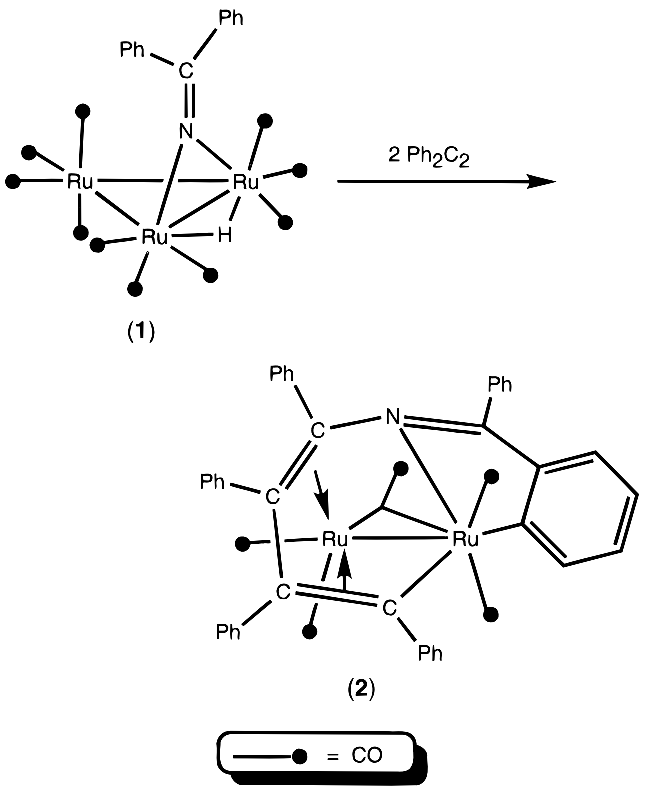
Summary: The insertion of diphenylcetylene into a ruthenium−nitrogen bond is a key step in the preparation of the binuclear derivative ***2****. This is the first example of insertion of a little electrophilic alkyne into a metal−nitrogen bond.*

The interest in the synthesis and reactivity of late-transition-metal amido complexes has grown considerably in the last few years. This research activity has been prompted by the relative scarcity of such compounds[1−4] and by their potential use in nitrogen−carbon bond-forming reactions.[5,6] However, to date, the insertion of unsaturated molecules into the metal−nitrogen bonds of amido complexes has only been achieved with CO or highly electrophilic substrates (i.e. CO_2, COS, PhNCO, $CH_2{=}CHCN$, etc.),[5] dimethyl acetylenedicarboxylate being the only alkyne that has been inserted into such bonds.[6]

Scheme 1



Recently, we have described the synthesis and carbonyl substitution chemistry of $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**),[7] a compound that contains a bridging amido ligand derived from benzophenone imine, which can be regarded as a 1-azavinylidene ligand.[8] We now report that cluster **1** reacts with diphenylacetylene in 1,2-dichloroethane at reflux temperature to give, after a chromatographic workup, the binuclear derivative $[Ru_2\{\mu\text{-}PhC{=}CPhCPh{=}CPhNPh(C_6H_4)\}(\mu\text{-}CO)(CO)_4]$ (**2**) (Scheme 1),[9] a remarkable compound containing a novel ligand which results from the insertion of two diphenylacetylene molecules, the first into a ruthenium−nitrogen bond and the second into a ruthenium-carbon bond. At least 2 equiv of the alkyne is necessary to consume all compound **1**.

The crystal structure of **2** (Figure 1)[10] confirms the fragmentation of the starting material **1**, the consecutive insertion of two diphenylacetylene molecules, and the ortho metalation of a phenyl ring of the original 1-azavinylidene group. The new bridging ligand contributes eight electrons to the electron count, being attached to Ru(1) through the nitrogen atom, the ortho-metalated phenyl ring, and the terminal carbon atom of the butadienyl fragment and to Ru(2) through the four carbon atoms of the butadienyl fragment. The ligand shell is completed by one semibridging and four terminal carbonyl ligands. This ligand arrangement allows

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(1) For reviews on late-transition-metal amido complexes, see: (a) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1. (b) Bryndza, H. E. *Chem. Rev.* **1988**, *88*, 1163.

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(6) *trans*-$[Ni(mes)(NHPh)(PMe_3)_2]$ (mes = mesityl) reacts with dimethyl acetylenedicarboxylate to give the alkenyl derivative *trans*-$[Ni(mes)\{MeO_2CC{=}C(NHPh)CO_2Me\}(PMe_3)_2]$: Van der Lende, D. D.; Abboud, K. A.; Boncella, J. M. *Inorg. Chem.* **1995**, *34*, 5319.

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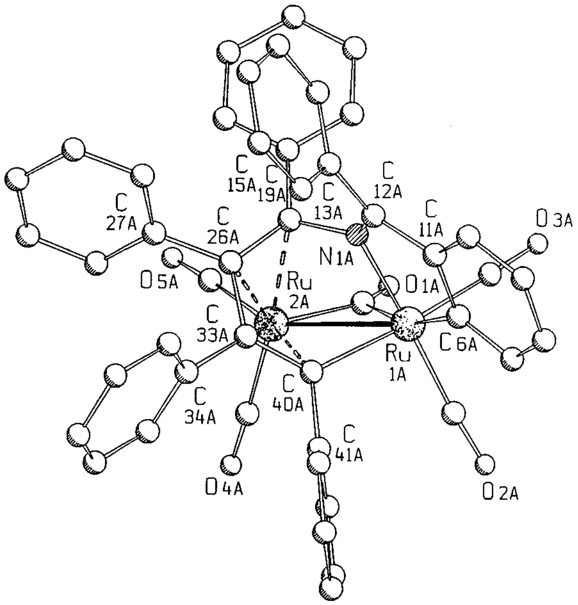

Figure 1. Molecular structure of crystalline **2**. Only one (molecule A) of the two independent molecules found in the asymmetric unit is shown. Selected interatomic distances (Å) and angles (deg): Ru(1)−Ru(2) = 2.764(1), Ru(1)−N(1) = 2.049(3), Ru(1)−C(6) = 2.066(4), Ru(1)−C(40) = 2.141(5), Ru(2)−C(19) = 2.319(4), Ru(2)−C(26) = 2.218(4), Ru(2)−C(33) = 2.316(5), Ru(2)−C(40) = 2.253(4), C(19)−C(26) = 1.420(6), C(26)−C(33) = 1.463(6), C(33)−C(40) = 1.421(6), Ru(1)−C(1) = 2.313(5), Ru(2)−C(1) = 2.001(6); Ru(1)−C(1)−O(1) = 133.6(4), Ru(2)−C(1)−O(1) = 146.9(5).

the assignment of formal oxidation states to the metal atoms: II for Ru(1) and 0 for Ru(2).

Examples of fragmentation of trinuclear edge-bridged hydrido carbonyl clusters upon reactions with alkynes[11] and of ortho metalation of 2,2-diphenyl-1-azavinylidene ligands[7] are known. However, complex **2** represents the first example of insertion of a little electrophilic alkyne into a metal−nitrogen bond and also the first example in which the three processes noted in this paragraph occur together.

Although it is now clear that normal amido complexes have no tendency to insert nonactivated alkynes into their metal−nitrogen bonds,[3a,b,e] the results described herein suggest that this is not the case for 1-azavinylidene complexes. This finding may have important implications for the synthesis of new compounds.

Studies aimed at extending the results described herein to other alkynes and using the obtained products for further carbon−carbon bond formation reactions are in progress in our laboratories. Preliminary experiments indicate that the reactions of **1** with some other alkynes (i.e. 1-phenyl-1-propyne) give products analogous to **2**.

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Supporting Information Available: Tables of crystal and refinement data, bond distances and angles, and positional and thermal parameters for the X-ray structure of compound **2** (14 pages). Ordering information is given on any current masthead page.

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(9) A solution of **1** (200 mg, 0.261 mmol) and Ph_2C_2 (94 mg, 0.549 mmol) in 1,2-dichloroethane (20 mL) was stirred under nitrogen at reflux temperature for 9 h. The solvent was removed under reduced pressure, the residue was dissolved in toluene (2 mL), and this solution was separated by column chromatography (10 × 2 cm) on neutral alumina (activity I). Hexane−toluene (1:1) eluted an orange solution which gave compound **2** after solvent removal and crystallization from dichloromethane−pentane (129 mg, 56%). The elemental analysis (CHN) was correct. IR (toluene): 2045 (s), 2019 (vs), 1984 (s), 1966 (m), 1869 (m) cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, 290 K): 7.6−6.5 (m, 27 H), 5.76 (d, 7.6 Hz, 1 H), 5.04 (d, 7.6 Hz, 1 H) ppm.

(10) (a) Crystal data: $C_{46}H_{29}NO_5Ru_2$, triclinic, $P\bar{1}$, $a = 13.539(4)$ Å, $b = 17.287(8)$ Å, $c = 17.918(5)$ Å, $\alpha = 108.46(3)°$, $\beta = 98.10(2)°$, $\gamma = 101.42(3)°$, $V = 3085(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.066$ g cm^{-3}, $\mu = 1.684$ mm^{-1}, $3 < \theta < 25°$, $\lambda = 0.710\ 69$ Å, $\omega{-}2\theta$ scan mode, $T = 293(2)$ K, R1($I > 2\sigma(I)$) = 0.0372, wR2(all data) = 0.1127. The structure was solved by direct methods[10b] followed by difference Fourier syntheses and subsequent full-matrix least-squares refinement on F^2 using SHELX92.[10c] Two crystallographically independent molecules were found in the asymmetric unit. All non-H atoms were treated anisotropically. H atoms were refined using a riding model. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. (c) Sheldrick, G. M. SHELXL92, Program for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1993.

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