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## *Communications*

# Reaction of Terminal Alkynes with Hydrazines To Give Nitriles, Catalyzed by $TpRuCl(PPh_3)_2$: Novel Catalytic Transformation Involving a Vinylidene Ruthenium Intermediate

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*Summary: The reaction of terminal alkynes with hydrazines in the presence of $TpRuCl(PPh_3)_2$ (Tp = tris(pyrazolyl)borate) as a catalyst gave nitriles. This reaction involves the intermolecular attack of nitrogen nucleophiles at the α-carbon atom of (vinylidene)metal intermediates which are generated from terminal alkynes.*

Transition-metal vinylidene complexes have a metallaallene structure, which is quite unique.[1] Interestingly and importantly, these unique structures are readily prepared from terminal alkynes under mild reaction conditions and are known to serve as key intermediates in some catalytic reactions.[2] For example, terminal alkynes react with oxygen nucleophiles such as carbamates,[3] carboxylic acids,[4] allyl alcohols,[5] and water[6] catalyzed by ruthenium complexes to yield alkenyl carbamates, alkenyl esters, $\beta,\gamma$-unsaturated ketones, and aldehydes, respectively. Catalytic intramolecular cyclizations of homopropargyl alcohols give 2,3-dihydrofurans,[7] or $\gamma$-lactones[8] in the presence of oxidants. The $W(CO)_5(thf)$ complex catalyzes the endo-cyclization of $\omega$-alkynyl enol silyl ethers.[9] These reactions involve a nucleophilic attack on the α-carbon atom of the (vinylidene)metal species in the catalytic cycles. Whereas a considerable number of reactions of terminal alkynes with oxygen nucleophiles are currently known, to the best of our knowledge, only one example of a

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[1] For general reviews, see: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (c) McDonald, F. E. *Chem. Eur. J.* **1999**, *5*, 3103.

[2] For reviews on catalytic reactions of terminal alkynes via (vinylidene)metal complexes, see: (a) Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1997**, 507. (b) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311.

[3] (a) Dixneuf, P. H.; Lécolier, S. *Tetrahedron Lett.* **1986**, *27*, 6333. (b) Mahé, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1989**, *54*, 1523.

[4] (a) Doucet, H.; Höfer, J.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1993**, 850. (b) Doucet, H.; Martin-Vaca, B.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1995**, *60*, 7247. (c) Doucet, H.; Höfer, J.; Derrin, N.; Bruneau, C.; Dixneuf, P. H. *Bull. Soc. Chim. Fr.* **1996**, *133*, 939. (d) Doucet, H.; Derrin, N.; Kabouche, Z.; Bruneau, C.; Dixneuf, P. H. *J. Organomet. Chem.* **1997**, *551*, 151. (e) Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Mereiter, K.; Schmid, R.; Kirchner, R. *Organometallics* **1996**, *15*, 3998.

[5] (a) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809. (b) Trost, B. M.; Flygare, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 5476. (c) Trost, B. M.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5579. (d) Nishibayashi, Y.; Takei, I.; Hidai, M. *Organometallics* **1997**, *16*, 3091. (e) Trost, B. M.; Vidal, B.; Thommen, M. *Chem. Eur. J.* **1999**, *5*, 1055.

[6] (a) Tokunaga, M.; Wakatsuki, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 2867. (b) Grotjahn, D. B.; Incarvito, C. D.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 3884.

[7] McDonald, F, E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363.

[8] Trost, B. M.; Rhee, Y. H. *J. Am. Chem. Soc.* **1999**, *121*, 11680.

[9] (a) Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928. (b) Miura, M.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 518.

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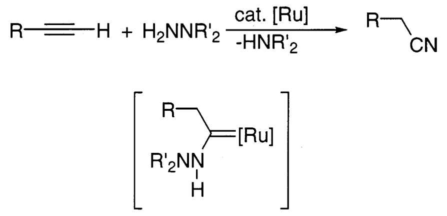
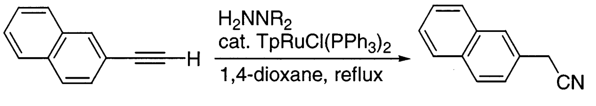
**Scheme 1**



nitrogen nucleophile has been reported.[10] We wish to report here an unprecedented type of ruthenium-catalyzed reaction that enables the conversion of terminal alkynes to nitriles via the use of hydrazines. This reaction represents the first example of a catalytic reaction involving the intermolecular attack of a nitrogen nucleophile on a (vinylidene)metal intermediate (Scheme 1).

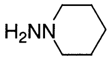
After a number of unsuccessful attempts using various amines such as aniline, allylamine, and aziridine to give complex reaction mixtures, we found that hydrazines, i.e., amines having a leaving group, can participate nicely in a catalytic reaction. A variety of transition-metal complexes were examined. Among these, the $CpRuCl(PPh_3)_2/NH_4PF_6$ system was employed as a catalyst, because it had been known to be a good catalyst in some of the reactions described above.[5a–c,8] The reaction of 2-ethynylnaphthalene (**1a**, 1 mmol) with 1-aminopiperidine (5 mmol) in the presence of $CpRuCl(PPh_3)_2$ (0.1 mmol) and $NH_4PF_6$ (0.2 mmol) at 100 °C in 1,4-dioxane for 3 h gave 2-naphthylacetonitrile (**2a**) in 45% yield (eq 1). $NH_4PF_6$ was added to produce a cationic ruthenium complex. The other ruthenium complexes used and the respective yields were $[Cp^*RuCl_2]_2/NH_4PF_6$ (24%), $[RuCl_2(cod)]_n/NH_4PF_6$ (21%), and $RuCl_2(dmpe)_2/NH_4PF_6$ (5%). The low yields of **2a** were due to dimerization and/or cyclotrimerization of **1a** as byproducts. However, it was found that the $TpRuCl(PPh_3)_2/NH_4PF_6$ (Tp = tris(pyrazolyl)borate[11]) system showed good catalytic activity (74%), and the use of $TpRuCl(PPh_3)_2$[12] alone gave **2a** in a better yield of 83%. Some hydrazines were examined in the $TpRuCl(PPh_3)_2$-catalyzed reactions of **1a**, and the results are summarized in Table 1. The reaction with *N*,*N*-dimethylhydrazine also afforded **2a** in good yield (84%). The yield decreased when an acetyl-substituted hydrazine was used. Reactions with hydrazine or tosylhydrazine gave not only **2a** but also 2-vinylnaphthalene and 2-ethylnaphthalene, which would have been formed by the reduction of **1a** with HN=NH generated by the decomposition of the hydrazines. The use of hydroxyamine methyl ether as a nitrogen source was unsuccessful.



(1)

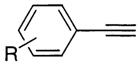
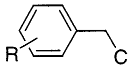
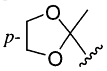
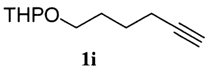
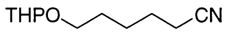
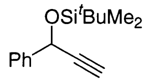
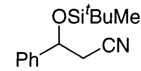
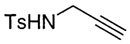
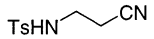
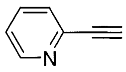
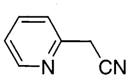
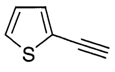
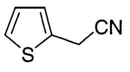
**1a** **2a**

**Table 1. $TpRuCl(PPh_3)_2$-Catalyzed Reactions of 1a with Hydrazines Leading to 2a**[a]

| hydrazine | time | yield[b] |
|---|---|---|
|  | 12 h | 83% |
| $H_2NNMe_2$ | 12 h | 84% |
| $H_2NNHCOMe$ | 24 h | 56% |
| $H_2NNH_2$ | 20 h | 27% |
| $H_2NNHTs$ | 2 h | 51% |
| $H_2NOMe$ | 5 h | trace |

[a] Reaction conditions: **1a** (1 mmol), hydrazine (5 mmol), $TpRuCl(PPh_3)_2$ (0.1 mmol) in 1,4-dioxane (1 mL) under reflux. [b] GC yields.

**Table 2. $TpRuCl(PPh_3)_2$-Catalyzed Reactions of Terminal Alkynes with *N*,*N*-Dimethylhydrazine Leading to Nitriles**[a]

| alkyne | product[b] |
|---|---|
|  |  |
| R = *p*-Me, **1b** | **2b**, 77% (15 h) |
| = *o*-OMe, **1c** | **2c**, 88% (12 h) |
| = *p*-OMe, **1d** | **2d**, 85% (12 h) |
| = *p*-  , **1e** | **2e**, 75% (14 h) |
| = *p*-$NH_2$, **1f** | **2f**, 68% (6 h) |
| = *p*-F, **1g** | **2g**, 49% (12 h) |
| = *p*-CN, **1h** | **2h**, 17% (5 h)[c] |
|  |  |
| **1i** | **2i**, 72% (12 h) |
|  |  |
| **1j** | **2j**, 70% (12 h) |
|  |  |
| **1k** | **2k**, 61% (14 h) |
|  |  |
| **1l** | **2l**, 54% (4 h) |
|  |  |
| **1m** | **2m**, 23% (12 h) |

[a] Reaction coditions: alkyne (1 mmol), *N*,*N*-dimethylhydrazine (5 mmol), $TpRuCl(PPh_3)_2$ (0.1 mmol) in 1,4-dioxane (1 mL) under reflux. [b] Isolated yields based on the starting alkynes. [c] 4-((Dimethylhydrazono)methyl)benzonitrile (42%) was also obtained.

As shown in Table 2, the reaction is applicable to various terminal alkynes. The reactions of phenylacetylenes substituted with methyl (**1b**), methoxy (**1c**), and acetal (**1d**) groups at the para position gave the corresponding nitriles in good yields. Protection of an aniline nitrogen was not necessary (**2f**). The reaction of 4-(cyanoethynyl)benzene (**1h**) gave not only nitrile **2h** in 17% yield but also 4-((dimethylhydrazono)methyl)benzonitrile in 42% yield. It was confirmed that the hydrazone was formed by direct nucleophilic addition to **1h**, but the hydrazone was not converted into **2h** under the catalytic reaction conditions employed.[13] Functional

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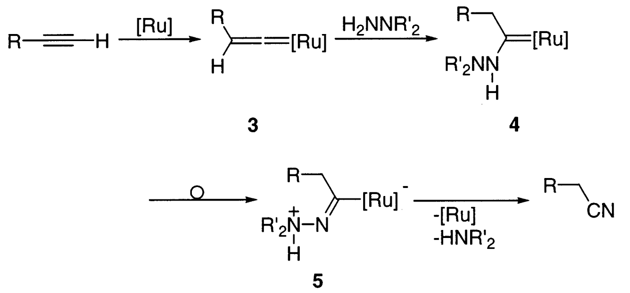
(10) McDonald, F. K.; Chatterjee, A. K. *Tetrahedron Lett.* **1997**, *38*, 7687.

(11) For a review on Tp−transition-metal complexes, see: Trofinenko, S. *Scorpionate-the Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

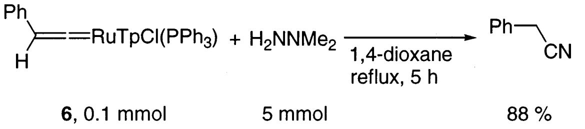
(12) Examples of $TpRuCl(PPh_3)_2$-catalyzed reactions: (a) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275. (b) Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P.; Moreno-Dorado, F. J.; Guerra, F. M.; Massanet, G. M. *Chem. Commun.* **2001**, 2324.

**Scheme 2**



groups such as THP (**1i**), siloxy (**1j**), tosylamide (**1k**), and some heterocycles (**1l** and **1m**) were also compatible with the reaction. The reaction of (triethylsilyl)acetylene resulted in dimerization to give (*Z*)-1,4-bis(triethylsilyl)-butenyne in 76% yield.[12a]

A proposed mechanism for the present reaction is shown in Scheme 2. The formation of the ruthenium–vinylidene complex **3** followed by the nucleophilic attack of hydrazine gives the α-hydrazinocarbene complex **4**. Proton migration in **4** would lead to the zwitterionic complex **5**, and subsequent deamination would give rise to the nitrile. Some precedents in stoichiometric reactions support this reaction mechanism. The conversion of hydrazino(methyl)carbene complexes of Cr, W,[14] and Mn[15] into the corresponding acetonitrile complexes has been reported. The reaction of $[Cp(CO)(PPh_3)Fe{=}C{=}CH_2]^+$ with hydrazines gave the acetonitrile complex $[Cp(CO)(PPh_3)FeNCCH_3]^+$.[16] We also confirmed that the reaction of the benzylidene complex **6** with *N*,*N*-dimethylhydrazine gives phenylacetonitrile in high yield (eq 2).



(2)

In summary, we have reported on a novel, Ru-catalyzed reaction of terminal alkynes with hydrazines to give nitriles. Further studies on catalytic reactions involving the nucleophilic attack of nitrogen compounds on vinylidene intermediates are in progress in our laboratories.

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**Supporting Information Available:** Text giving experimental procedures and compound characterization data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020588D

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(13) (a) *N*,*N*-Dimethylhydrazones were converted into nitriles by oxidation: Stankovic, S.; Espenson, J. H. *Chem. Commun.* **1998**, 1579. (b) Altamura, A.; D'Accolti, L.; Detomaso, A.; Dinoi, A.; Fiorentino, M.; Fusco, C.; Curci, R. *Tetrahedron Lett.* **1998**, *39*, 2009 and references therein.

(14) (a) Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1995**, *14*, 2455. (b) Licandro, E.; Maiorana, S.; Papagni, A.; Perdicchia, D.; Manzotti, R. *Chem. Commun.* **1999**, 925.

(15) Alt, H. G.; Engelhardt, H. E.; Steinlein, E.; Rogers, R. D. *J. Organomet. Chem.* **1987**, *344*, 321.

(16) Barrett, A. G. M.; Carpenter, N. E.; Sabat, M. *J. Organomet. Chem.* **1998**, *352*, C8.