

1,3-Dipolar Cycloadditions of Alkynyl Fischer Carbene Complexes with Nitrones

Kin Shing Chan*

Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China 10964 and
Department of Chemistry, Chinese University of Hong Kong, Shatin, Hong Kong

Phenylethynyl Fischer carbene complexes of chromium **1** and tungsten **2** were found to undergo chemoselective, regioselective and rate-enhanced 1,3-dipolar cycloadditions with phenyl *N*-*t*-butyl nitron **3** at room temp. to give 2,3-dihydroisoxazole carbene complexes **4** and **5** in excellent yields.

As part of the interest in the use of transition metal complexes in organic syntheses,¹ the synthetic utility of Fischer carbene complexes has been well demonstrated,² particularly in tandem cycloadditions and annulations.^{3–5} However, only one example of 1,3-dipolar cycloaddition with diazoalkanes has been reported,⁵ in spite of the fact that such reactions of dipoles with alkynyl complexes might extend the potential of the tandem cycloadditions and annulations. We report our preliminary success with chemoselective and regioselective 1,3-dipolar cycloadditions of alkynyl Fischer carbene complexes with phenyl *N*-*t*-butyl nitron (PBN) to give 2,3-dihydroisoxazole carbene complexes.

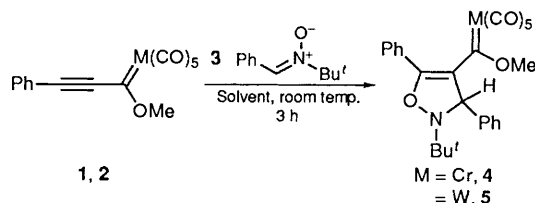
Pyridine *N*-oxide reacted with complex **1** in a non-chemoselective fashion so that instead of undergoing [2 + 3] cycloaddition at the carbon–carbon triple bond, the chromium complex **1** was oxidized to the metal–carbene cleaved product, methyl phenylethynecarboxylate.

The more reactive nitron dipole PBN **3** when treated with the carbene complexes of chromium **1** and tungsten **2**, underwent chemoselective cycloaddition at the carbon–carbon triple bonds to give the dihydroisoxazole carbene complexes **4** and **5** in excellent yields (Table 1): **5**, δ_{H} (250 MHz, [²H₆]acetone) 1.22 (s, 9 H), 4.29 (s, 3 H), 6.03 (s, 1 H), 7.25–7.60 (m, 10 H); δ_{C} (62.5 MHz, CDCl₃) 25.16, 61.68, 67.45, 71.70, 127.79, 128.55, 128.65, 128.90, 129.60, 132.95, 142.85, 160.29, 197.38 (*J*_{w,c} 63.9), 202.12 and 303.04; ν_{max} (neat)/cm⁻¹ 2063 and 1919 (*M*⁺, 645.0931). The characteristic lowfield carbene carbon resonances (Cr = 339.28 ppm, W = 303.04 ppm) confirmed the integrity of the metal–carbene bonds. The yields of the product remained practically the same whether 1 or 2 equiv. of PBN were used and double cycloaddition was, therefore, insignificant. Neither the rate of the cycloadditions nor the yields of products were affected by the change of metal from chromium to tungsten and by a change of solvent from THF to hexanes. The lack of solvent effect suggests that the cycloaddition might be a concerted one.⁶

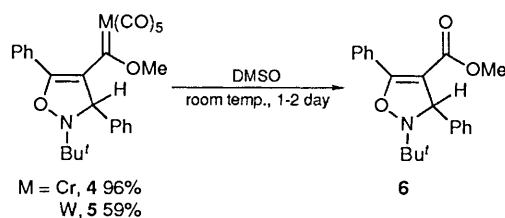
The cycloadditions are very regioselective since only one regioisomer has been observed and the regioselectivity is at least over 20 to 1 based on ¹H NMR analysis. The regiochemistry of the cycloadducts were secured by NOE experiments. Upon irradiation of the methoxy protons, NOE enhancements were observed at the methine protons [% NOE: Cr complex **4** = 2, W complex **5** = 0.8].

The pentacarbonylmetal moieties can serve as reactivity auxiliaries in accelerating the cycloadditions.² Both the complexes **4** and **5** were oxidized smoothly by DMSO at room temperature to yield the ester **6** (1 day, 96%) and (2 days, 59%) respectively (Scheme 1). The cycloaddition–oxidation sequences provide facile preparations of the ester **6**. In contrast, in a preliminary experiment, methyl phenylethynecarboxylate reacted with PBN **3** in refluxing THF (65 °C) over 75 days to

Table 1 Cycloadditions of nitron **3** with alkynyl complexes



M	Equiv. of 3	Solvent	Yield (%)	Compound
Cr 1	1	THF	97	4
Cr 1	1	Hexanes	92	4
Cr 1	2	THF	82	4
W 2	1	THF	94	5



Scheme 1

give the ester **6** (32%) together with unchanged ester (5%);⁷ this proved, therefore, to be an impractical route for the preparation of the ester **6**.

Experimental

Synthesis of the Complex 4.—A solution of the chromium complex **1** (50 mg, 149 μmol) and the nitron **3** (26.4 mg, 149 μmol) in THF (2 ml) was stirred at room temperature for 3 h. The mixture was then evaporated and the residue was flashed chromatographed on silica gel with dichloromethane–hexanes (1:1) to give the red complex **4** (75 mg, 97%), m.p. 85–87 °C (decomp.); δ_{H} (200 MHz, [²H₆]acetone) 1.42 (s, 9 H), 4.30 (s, 3 H), 6.35 (s, 1 H) and 7.67 (s, 10 H); δ_{C} (50 MHz, [²H₆]acetone) 26.57, 63.20, 66.04, 73.91, 129.52, 129.80, 130.32, 130.64, 130.92, 132.89, 218.53, 225.43 and 339.28; ν_{max} (neat)/cm⁻¹ 2058, 1939, 1452, 1234, 1206 and 1132 (Found: C, 60.4; H, 4.15; N, 2.9. C₂₆H₂₃NO₇Cr requires C, 60.82; H, 4.52; N, 2.73).

Acknowledgements

Financial support from the National Science Council (NSC79-0208-M002-53) and NMR assistance from Ms Sien-leng Eng and Shiyan Fan are acknowledged.

References

1 J. P. Collman, L. S. Hegeudus, J. R. Norton and R. G. Finke, *Principles*

* Current address: Department of Chemistry, Chinese University of Hong Kong, Shatin, Hong Kong.

- and Applications of Organotransition Metal Chemistry*, University Science Books, 1987.
- 2 (a) For leading reference, W. D. Wulff, in *Advances in Metal-Organic Chemistry*, ed. L. S. Libeskind, JAI Press Inc., Greenwich, 1989, vol. 1; (b) K. H. Dotz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587.
- 3 K. L. Faron and W. D. Wulff, *J. Am. Chem. Soc.*, 1988, **110**, 8727.
- 4 K. S. Chan and W. D. Wulff, *J. Am. Chem. Soc.*, 1986, **108**, 5229.
- 5 W. D. Wulff, W. E. Bauta, R. W. Kaesler, P. J. Lankford, R. A. Miller, C. K. Murray and D. C. Yang, *J. Am. Chem. Soc.*, 1990, **112**, 3642.
- 6 *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley-Interscience, New York, 1984, vols. 1,2.
- 7 W.-K. Chan, unpublished results.

Paper 1/03280A

Received 2nd July 1991

Accepted 16th July 1991