JOC Article

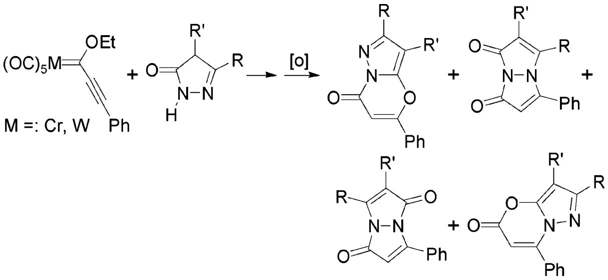
Tautomerism-Dependent Ring Construction of *N*-Heterocyclic Compounds from the Reactions of 1-Alkynyl Fischer Carbene Complexes and Substituted Pyrazolinones

Zhaoyan Zheng,[†] Zhengkun Yu,*[,†,‡] Ning Luo,[†] and Xiuwen Han[§]

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, P. R. China, State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. China, and State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, P. R. China

zkyu@dicp.ac.cn

Received August 19, 2006



Four types of *N*-heterocyclic ring systems were successfully constructed from the reactions of 1-alkynyl Fischer carbene complexes $(OC)_5M{=}C(OEt)C{\equiv}CPh$ (**1**) (M = Cr, W) and substituted pyrazolinones (**2**). Reactions of **1** with 3-methyl-2-pyrazolin-5-one (**2a**), 3-*n*-propyl-2-pyrazolin-5-one (**2b**), 3,4-dimethyl-2-pyrazolin-5-one (**2c**), 3,4-trimethylene-2-pyrazolin-5-one (**2d**), or 3,4-tetramethylene-2-pyrazolin-5-one (**2e**) generated three kinds of Fischer aminocarbene complexes (**3**−**5**), and reactions of **1** with phenyl-substituted pyrazolinones, i.e., 3-phenyl-2-pyrazolin-5-one (**2f**) and its tautomer 3-phenyl-3-pyrazolin-5-one (**2g**), gave Fischer alkoxycarbene complexes (**6**) as the major products and aminocarbene complexes of types **3**−**5** as the minor products. Multiple tautomerism of pyrazolinones is attributed to the versatile formation of *N*-heterocyclic Fischer carbene complexes. Oxidative demetalation of complexes **3**−**6** with pyridine *N*-oxide or *m*-chloroperoxybenzoic acid efficiently afforded organic carbonyl products, and thus, strongly fluorescent *syn*-mixed-bimanes were prepared. The present findings constitute an alternative new method to synthesize mixed bimanes and other novel *N*-heterocyclic compounds.

Introduction

Ring construction has been paid much attention in organic synthesis. Although a variety of success has been achieved over the decades,[1] a lot of effort is still contributed to develop novel synthetic methods and new building blocks for this purpose. Organometallic compounds are usually considered as potential building blocks for rings that cannot be readily constructed by conventional methods.[2] Fischer carbene complexes of group six have been found very useful as reagents or building blocks in organic synthesis.[3] Cyclopropanation,[4] Dötz benzannulation,[3g] and Hegedus reactions[5] of Fischer carbene complexes have been extensively investigated for preparation of carbocyclic compounds. *N*-Heterocyclic compounds have also been synthesized via the reactions of Fischer carbene complexes with N−H- and C═N-containing reagents, from which elaborate combinations of N−H and C═N moieties in an organic reagent may lead to

---

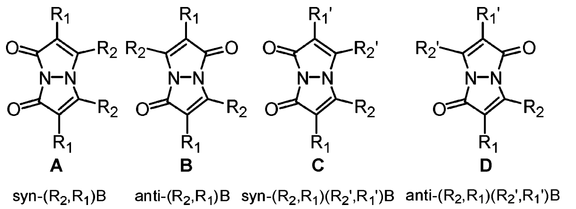
[*] To whom correspondence should be addressed. Fax: +86-411-8437-9227.
[†] Dalian Institute of Chemical Physics, Chinese Academy of Sciences.
[‡] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.
[§] State Key Laboratory of Catalysis, Dialian Institute of Chemical Physics, Chinese Academy of Sciences.

(1) (a) Negishi, E. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, U.K., 1991; Vol. 5, p 1163. (b) Corey, E. J.; Cheng, X. *The Logic of Chemical Synthesis*; Wiley-Interscience: New York, 1989.

(2) (a) Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49.

10.1021/jo061725+ CCC: $33.50

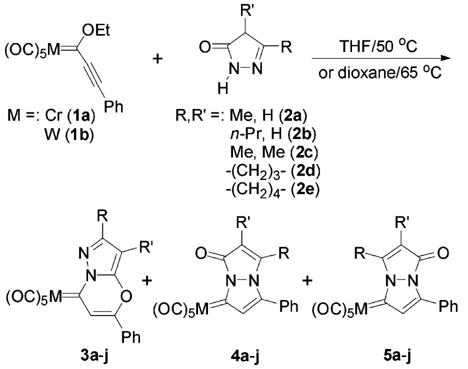
CHART 1. 9,10-Dioxabimanes (Bimanes)



novel Fischer carbene complexes or formation of novel organic products.[6]

1,5-Diazabicyclo[3.3.0]octadienediones (briefly, 9,10-dioxabimanes or “bimanes”) are a class of bicyclic *N*-heterocyclic compounds, as described in Chart 1. The syn compounds are usually strongly fluorescent, but the anti isomers are normally nonfluoroscent and possibly phosphorescent.[7] Bimane derivatives are important labeling agents and have been successfully used as fluorescent probes for protein structural analysis.[8] A four-step synthesis starting from alkylation of a β-ketoester, and then via pyrazolinone, chloropyrazolinone, and dechlorination affords symmetrical bimanes, i.e., the *syn*-bimane (**A**) and its anti isomer (**B**) (Chart 1). However, symmetrical bimanes are usually prepared in low to moderate yields, strongly depending on the properties of the employed β-ketoesters and reaction conditions.[7] Thus, seven steps are necessary for synthesis of mixed (unsymmetrical) bimanes. That is, two different chloropyrazolinones are reacted to give mixed bimanes of types **C** and **D** as well as up to five other possible bimane products, leading the mixed bimane products to be prepared in rather low yields, and isolation/purification of the desired products to be handled with much difficulty.[7c] We recently found that NH-containing pyrazoles and C=N-containing substituted oxazolines react with 1-alkynyl Fischer carbene complexes $(OC)_5M{=}C(OEt)C{\equiv}CPh$ (**1**) (M = Cr, W) to afford Michael addition and consecutive cycloaddition/cyclization products, respectively.[6a,b] Encouraged by these results, the multiple tautomerism of substituted pyrazolinones, and the multiple reactivities of 1-alkynyl Fischer carbene complexes (**1**), we investigated the reactions of **1** and substituted pyrazolinones (**2**) and oxidative demetalation of the newly formed carbene complexes. Herein, we report our findings in this area, which constitutes a new method to synthesize mixed bimanes and construct novel *N*-heterocyclic ring systems.

SCHEME 1. Synthesis of Complexes 3−5



Results and Discussion

Reactions of 1 with Alkyl-Substituted Pyrazolinones (2a−e). The reactions of 1-alkynyl Fischer carbene complexes $(OC)_5M{=}C(OEt)C{\equiv}CPh$ (M = Cr (**1a**), W (**1b**)) with substituted pyrazolinones, i.e., 3-methyl-2-pyrazolin-5-one (**2a**), 3-*n*-propyl-2-pyrazolin-5-one (**2b**), 3,4-dimethyl-2-pyrazolin-5-one (**2c**), 3,4-trimethylene-2- pyrazolin-5-one (**2d**), and 3,4-tetramethylene-2-pyrazolin-5-one (**2e**), were carried out in THF at 50 °C or in dioxane at 65 °C. Diethyl ether, acetonitrile, toluene, hexane, pentane, dichloromethane, and chloroform were tested as the reaction media, but only THF and dioxane were found to be the suitable reaction solvents in which *N*-heterocyclic Fischer carbene complexes were formed in decent yields. The reaction rates varied so much that the starting complexes were completely consumed within 15−60 min by TLC monitoring on silica gel. Three types of new *N*-heterocyclic Fischer carbene complexes with different polarities and colors, i.e., complexes of types **3**, **4**, and **5**, were isolated as the products (Scheme 1). The carbene complex products of tungsten were usually obtained in yields higher than those of their chromium analogues (Table 1). Complexes **3a−j** (5.5−21.5%) were formed as the minor products, and **4a−j** (15.1−43.7%) and their anti isomers **5a−j** (2.4−53.0%) were isolated as the major products. It is noteworthy that complexes **5g**,**h** were not isolated in measurable yields in the cases of using the pyrazolinone **2d** (entries 9 and 10, Table 1). Yields of complexes **4e**,**f** and **5e**,**f** were obviously improved when the reactions were carried out in dioxane at 65 °C in the cases of using **2c** (entries 5−8, Table 1). For example, the reaction of **1a** with **2c** in THF at 50 °C afforded **3e**, **4e**, and **5e** in 5.5%, 15.1%, and 2.4% yields, respectively, and the reaction in dioxane at 65 °C gave the same products in 7.4%,

---

[3] For selected recent reviews, see: (a) Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E. *J. Organomet. Chem.* **2005**, *690*, 539. (b) Barluenga, J.; Santamaria, J.; Tomás, M. *Chem. Rev.* **2004**, *104*, 2259. (c) Herndon, J. W. *Coord. Chem. Rev.* **2003**, *243*, 3. (d) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591. (e) Dötz, K. H.; Jäkel, C.; Haase, W. C. *J. Organomet. Chem.* **2001**, *617/618*, 119. (f) Barluenga, J.; Floréz, J.; Fañanás, F. J. *J. Organomet. Chem.* **2001**, *624*, 5. (g) de Meijere, A.; Schirmer, H.; Duetsch, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3964. (h) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257. (i) Barluenga, J.; Fañanás, F. J. *Tetrahedron* **2000**, *56*, 4597. (j) Aumann, R. *Eur. J. Org. Chem.* **2000**, 17.

[4] (a) Capriati, V.; Florio, S.; Luisi, R.; Perna, F. M.; Barluenga, J. *J. Org. Chem.* **2005**, *70*, 5852. (b) Florio, S.; Perna, F. M.; Luisi, R.; Barluenga, J.; Rodríguez, F.; Fañanás, F. J. *J. Org. Chem.* **2004**, *69*, 5480.

[5] (a) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105. (b) Hegedus, L. S. *Top. Organomet. Chem.* **2004**, *13*, 157.

[6] For selected recent references on reactions of Fischer carbene complexes with NH/C=N bond-containing compounds, see: (a) Gu, K. C.; Chen, J. Z.; Zheng, Z. Y.; Wu, S. Z.; Wu, X. W.; Han, X. W.; Yu, Z. K. *Polyhedron* **2005**, *24*, 173, and references therein. (b) Chen, J. Z.; Yu, Z. K.; Zheng, Z. Y.; Gu, K. C.; Wu, S. Z.; Zeng, F. L.; Tan, W. Q.; Wu, X. W.; Xiao, W.-J. *Organometallics* **2005**, *24*, 302. (c) Llordes, A.; Sierra, M. A.; Lopez-Alberca, M. P.; Molins, E.; Ricart, S. *J. Organomet. Chem.* **2005**, *690*, 6096. (d) Barluenga, J.; Suárez-Sobrino, A. L.; Tomás, M.; García-Granda, S.; Santiago-García, R. *J. Am. Chem. Soc.* **2001**, *123*, 10494. (e) Barluenga, J.; Tomás, M.; Rubio, E.; López-Pelegrín, J. A.; García-Granda, S.; Priede, M. P. *J. Am. Chem. Soc.* **1999**, *121*, 3065. (f) Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1995**, *14*, 2447.

[7] For selected leading references on preparation and properties of bimanes, see: (a) Kosower, E. M.; Pazhenchevsky, B.; Hershkowitz, E. *J. Am. Chem. Soc.* **1978**, *100*, 6516. (b) Kosower, E. M.; Bernstein, J.; Goldberg, I.; Pazhenchevsky, B.; Goldstein, E. *J. Am. Chem. Soc.* **1979**, *101*, 1620. (c) Kosower, E. M.; Pazhenchevsky, B. *J. Am. Chem. Soc.* **1980**, *102*, 4983. (d) Kosower, E. M.; Pazhenchevsky, B.; Dodiuk, H.; Kanety, H.; Faust, D. *J. Org. Chem.* **1981**, *46*, 1666. (e) Kosower, E. M.; Zbaida, D.; Baud’huin, M.; Marciano, D.; Goldberg, I. *J. Am. Chem. Soc.* **1990**, *112*, 7305. (f) Shalev, D. E.; Chiacchiera, S. M.; Radkowsky, A. E.; Kosower, E. M. *J. Org. Chem.* **1996**, *61*, 1689. (g) Kosower, E. M.; Ben-Shoshan, M. *J. Org. Chem.* **1996**, *61*, 5871.

[8] For selected recent references, see: (a) Sosa-Peinado, A.; Gonzalez-Andrade, M. *Biochemistry* **2005**, *44*, 15083. (b) Mansoor, S. E.; Farrens, D. L. *Biochemistry* **2004**, *43*, 9426. (c) Lee, S.; Rosazza, J. P. N. *Org. Lett.* **2004**, *6*, 365. (d) Radkowsky, A. E.; Kosower, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 4527.

TABLE 1. Reactions of 1 and 2a−e To Form 3a−j, 4a−j, and 5a−j[a]

entry	1	2	M	R, R′	solvent[b,c]	time (min)	products (%)[d]		
1	**1a**	**2a**	Cr	Me, H	THF	30	**3a** (12.0)	**4a** (23.4)	**5a** (35.1)
2	**1b**	**2a**	W	Me, H	THF	30	**3b** (12.7)	**4b** (23.0)	**5b** (46.4)
3	**1a**	**2b**	Cr	*n*-Pr, H	THF	30	**3c** (14.4)	**4c** (16.0)	**5c** (46.7)
4	**1b**	**2b**	W	*n*-Pr, H	THF	30	**3d** (21.5)	**4d** (15.7)	**5d** (53.0)
5	**1a**	**2c**	Cr	Me, Me	THF	20	**3e** (5.5)	**4e** (15.1)	**5e** (2.4)
6	**1a**	**2c**	Cr	Me, Me	dioxane	20	**3e** (7.4)	**4e** (43.7)	**5e** (30.0)
7	**1b**	**2c**	W	Me, Me	THF	20	**3f** (19.8)	**4f** (19.2)	**5f** (37.1)
8	**1b**	**2c**	W	Me, Me	dioxane	30	**3f** (8.4)	**4f** (33.6)	**5f** (44.0)
9	**1a**	**2d**	Cr	$-(CH_2)_3-$	THF	60	**3g** (9.1)	**4g** (24.1)	**5g** (−)[e]
10	**1b**	**2d**	W	$-(CH_2)_3-$	THF	60	**3h** (10.3)	**4h** (33.5)	**5h** (−)[e]
11	**1a**	**2e**	Cr	$-(CH_2)_4-$	THF	15	**3i** (13.3)	**4i** (24.2)	**5i** (7.7)
12	**1b**	**2e**	W	$-(CH_2)_4-$	THF	15	**3j** (18.3)	**4j** (23.3)	**5j** (41.5)

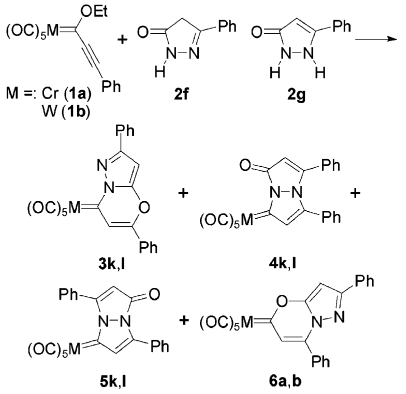
[a] Reaction conditions: **1**, 1.0 mmol; **2**, 1.0 mmol. [b] THF, 3 mL, 50 °C. [c] Dioxane, 6 mL, 65 °C. [d] Isolated yields. [e] Trace amount.

TABLE 2. Reactions of 1 and 2f,g To Form 3k,l−5k,l and 6a,b[a]

entry	1	2	M	solvent	time (min)	products (%)[d]			
1	**1a**	**2f**	Cr	THF	40	**3k** (8.4)	**4k** (13.6)	**5k** (−)[c]	**6a** (13.4)
2	**1a**	**2f**	Cr	dioxane	180	**3k** (9.1)	**4k** (11.9)	**5k** (−)[c]	**6a** (25.9)
3	**1b**	**2f**	W	THF	25	**3l** (8.9)	**4l** (−)[c]	**5l** (4.9)	**6b** (34.2)
4	**1b**	**2f**	W	dioxane	110	**3l** (8.6)	**4l** (9.7)	**5l** (14.1)	**6b** (35.6)
5	**1a**	**2g**	Cr	THF	60	**3k** (8.2)	**4k** (14.7)	**5k** (−)[c]	**6a** (10.3)
6	**1a**	**2g**	Cr	dioxane	180	**3k** (8.6)	**4k** (10.3)	**5k** (−)[c]	**6a** (23.9)
7	**1b**	**2g**	W	THF	25	**3l** (5.2)	**4l** (−)[c]	**5l** (5.9)	**6b** (32.7)
8	**1b**	**2g**	W	dioxane	110	**3l** (7.5)	**4l** (4.0)	**5l** (12.9)	**6b** (36.2)

[a] Conditions: carbene, 1.0 mmol; pyrazolinone, 1.0 mmol; THF, 3 mL/ 50 °C, or dioxane, 6 mL/ 65 °C. [b] Isolated yields. [c] Trace amount.

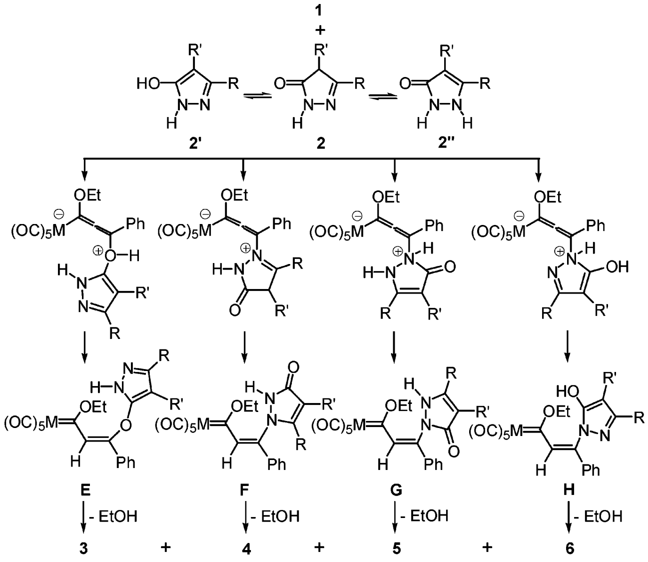
SCHEME 2. Reactions of 1 with 2f or 2g



43.7%, and 30.0% yields, respectively. However, such solvent and temperature effects were not found in the reactions of **1** with pyrazolinones **2a**,**b**,**d**,**e**.

Reactions of 1 with Phenyl-Substituted Pyrazolinones (2f,g). Reactions of 3-phenyl-2-pyrazolin-5-one (**2f**) or its tautomer 3-phenyl-3-pyrazolin-5-one (**2g**) with **1** in THF at 50 °C or in dioxane at 65 °C afforded four types of carbene complex products, i.e., **3k**,**l**, **4k**,**l**, **5k**,**l**, and **6a**,**b**, depending on the metal and reaction conditions (Scheme 2, Table 2). It is obvious from the solvent and temperature effects that products were isolated from the reactions in dioxane at 65 °C in yields higher than those from the reactions in THF at 50 °C. Total yields of complexes **3**−**6** obtained from the reactions of phenyl-substituted pyrazolinones with **1** are lower than those for the products from the reactions of alkyl-substituted pyrazolinones with **1** (Scheme 1, Table 1). It should be noted that complexes **4l** and **5k** were not always obtained under the reaction conditions (Table 2). Unexpectedly, although it is not apparent that complexes of type **6** are less sterically hindered than **3k**,**l**, the complexes **6a**,**b** were obtained as the major products in most cases, which might be attributed to some kinetic influences.

SCHEME 3. Proposed Reaction Pathways of 1 and 2



Possible Reaction Pathways of 1 and 2. Formation of *N*-heterocyclic Fischer carbene complexes **3**−**6** is proposed in Scheme 3. Tautomerism of **2** generates at least two active hydrogen-containing tautomers, i.e., 5-hydroxypyrazole (**2′**) and 3-pyrazolin-5-one (**2″**). Michael-type addition of **2** and its tautomers **2′** and **2″** to **1** forms the intermediate species **E**−**H**, which undergoes cyclization to afford complexes **3**−**6** by loss of ethanol. Michael-type addition of NH-containing compounds[6] or OH-compounds[9] to **1** have been well documented. Versatile

---

[9] For selected references, see: (a) Camps, F.; Llebaria, A.; Moretó, J. M.; Ricart, S.; Viñas, J. M.; Ros, J.; Yáñez, R. *J. Organomet. Chem.* **1991**, *401*, C17. (b) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 2051. (c) Aumann, R. *Chem. Ber.* **1992**, *125*, 2773. (d) Aumann, R.; Jasper, B. *Organometallics* **1994**, *13*, 3502.

SCHEME 4. Oxidative Demetalation of 3−6

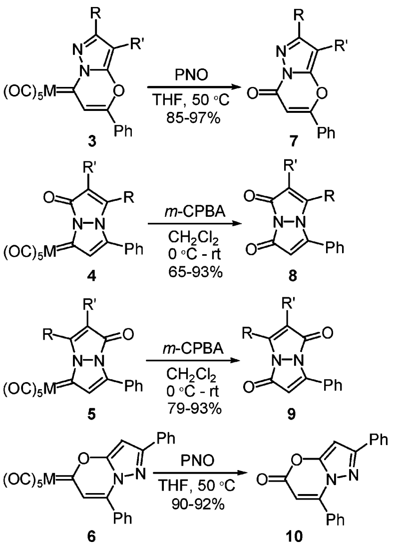


TABLE 3. Oxidative Demetalation of 3a−d, 4a−d, and 5a−d[a,b]

entry	carbene	M	R, R′	time (min)	product (%)[c]
1	**3a**	Cr	Me, H	20	**7a** (88.2)
2	**3b**	W	Me, H	10	**7a** (94.4)
3	**3c**	Cr	*n*-Pr, H	15	**7b** (85.2)
4	**3d**	W	*n*-Pr, H	15	**7b** (90.5)
5	**4a**	Cr	Me, H	60	**8a** (76.4)
6	**4b**	W	Me, H	50	**8a** (85.6)
7	**4c**	Cr	*n*-Pr, H	40	**8b** (73.5)
8	**4d**	W	*n*-Pr, H	60	**8b** (91.7)
9	**5a**	Cr	Me, H	30	**9a** (794)
10	**5b**	W	Me, H	40	**9a** (88.5)
11	**5c**	Cr	*n*-Pr, H	45	**9b** (80.0)
12	**5d**	W	*n*-Pr, H	40	**9b** (92.9)

[a] Complex **3**, 0.3 mmol; PNO, 0.3 mmol; THF, 3 mL; 50 °C. [b] Complex **4** or **5**, 0.3 mmol; *m*-CPBA, 1.2 mmol; CH_2Cl_2, 6 mL; 0 °C to rt. [c] Isolated yields.

TABLE 4. Oxidative Demetalation of 3e−j, 4e−j, and 5e−j[a,b]

entry	carbene	M	R, R′	time (min)	product (%)[c]
1	**3e**	Cr	Me, Me	20	**7c** (91.5)
2	**3f**	W	Me, Me	35	**7c** (97.3)
3	**3g**	Cr	$-(CH_2)_3-$	50	**7d** (86.9)
4	**3h**	W	$-(CH_2)_3-$	25	**7d** (91.3)
5	**3i**	Cr	$-(CH_2)_4-$	30	**7e** (86.8)
6	**3j**	W	$-(CH_2)_4-$	50	**7e** (93.7)
7	**4e**	Cr	Me, Me	40	**8c** (76.2)
8	**4f**	W	Me, Me	30	**8c** (83.4)
9	**4g**	Cr	$-(CH_2)_3-$	30	**8d** (86.2)
10	**4h**	W	$-(CH_2)_3-$	45	**8d** (83.3)
11	**4i**	Cr	$-(CH_2)_4-$	50	**8e** (64.9)
12	**4j**	W	$-(CH_2)_4-$	60	**8e** (76.4)
13	**5e**	Cr	Me, Me	45	**9c** (80.4)
14	**5f**	W	Me, Me	30	**9c** (87.6)
15	**5i**	Cr	$-(CH_2)_4-$	50	**9e** (83.0)
16	**5j**	W	$-(CH_2)_4-$	35	**9e** (85.2)

[a] **3**, 0.2−0.3 mmol; PNO, 0.2−0.3 mmol; THF, 3 mL; 50 °C. [b] **4** or **5**, 0.3 mmol; *m*-CPBA, 1.2 mmol; CH_2Cl_2, 6 mL; 0 °C to rt. [c] Isolated yields.

TABLE 5. Oxidative Demetalation of 3k,l, 4k,l, 5l, and 6a,b[a,b]

entry	carbene	M	time (min)	product (%)[c]
1	**3k**	Cr	10	**7f** (89.0)
2	**3l**	W	15	**7f** (91.3)
3	**4k**	Cr	45	**8f** (87.9)
4	**4l**	W	40	**8f** (85.5)
5	**5l**	W	40	**9f** (77.6)
6	**6a**	Cr	10	**10** (90.2)
7	**6b**	W	30	**10** (92.5)

[a] **3** or **6**, 0.3 mmol; PNO, 0.3 mmol; THF, 3 mL; 50 °C. [b] **4** or **5**, 0.3 mmol; *m*-CPBA, 1.2 mmol; CH_2Cl_2, 6 mL; 0 °C to rt. [c] Isolated yields.

formation of **3**−**6** is presumably attributed to the kinetic and steric influences from the hydroxy oxygen in **2′**, the imine C═N (in **2**), and the amide NH (in **2″**) nitrogen atoms. In the cases of using the phenyl-substituted pyrazolinones **2f**,**g**, N−H addition of their tautomer of type **2′** to **1** generates species **H**, which is further cyclized to form **6**.

Oxidative Demetalation of Complexes 3−6. Oxidation is a useful method to transform Fischer carbene complexes to organic products,[10] but no universal oxidants or procedures have been found to demetalate all kinds of Fischer carbene complexes. Moreover, demetalation of Fischer aminocarbene complexes cannot be easily achieved.[11] Oxidative demetalation of **3**−**6** was carried out with oxidants such as pyridine *N*-oxide (PNO), DMSO, SeO_2, H_2O_2, I_2, or cerric ammonium nitrate (CAN). It was found that complexes **3** and **6** could be efficiently transformed to the *N*-heterocyclic compounds **7** and **10** with PNO in 85−97% and 90−92% yields, respectively (Scheme 4, Tables 3−5). However, complexes **4** and **5** were only efficiently demetalated with *m*-chloroperoxybenzoic acid (*m*-CPBA) under carefully controlled conditions, although *m*-CPBA has been known to oxidatively demetalate a few specific Fischer carbene complexes.[12] By slow addition of *m*-CPBA to a solution of complex **4** or **5** in CH_2Cl_2 at 0 °C and then warming the solution to ambient temperature with stirring, we were able to efficiently demetalate complexes **4** and **5** to the mixed bimanes **8** (65−93%) and **9** (79−93%), respectively. A four-step synthetic route is necessary for the preparation of symmetrical bimanes, i.e., *syn*-bimanes (**A**) and their anti isomers (**B**) (Chart 1) starting from *β*-ketoesters; a seven-step procedure has to be used to make mixed bimanes (unsymmetrical bimanes: **C** and **D**).[7] It is noteworthy that the efficiency to prepare mixed bimanes using our method is much higher than that by means of Kosower's seven-step procedures starting from *β*-ketoesters.[7c]

NMR Spectroscopic Features of Compounds 3−10. For complex **3a**−**l**, the ^{13}C NMR signals of Cr═C appear at 264.6−266.4 ppm and those of C≡O are shown at about 227/217 ppm with a 1:4 intensity, respectively; the W═C and C≡O signals of the corresponding tungsten analogues appear at 238.2−239.4 ppm and about 207/198 ppm, respectively (Table 6). The ^{13}C NMR signals of M═C in **4** and **5** appear upfield about 30−40 ppm from those of **3**. For all the demetalated derivatives **7**−**10**, their NMR spectra feature typical ^1H and ^{13}C NMR signals of organic compounds. The NMR signal assignments of complexes **6a**,**b** and compound **10** were made by comparison with the NMR data of complexes **3k**,**l** and the known complex **11**.[13] Complexes **3k**,**l** and **6a**,**b** are isomers, but they exhibit different NMR

---

(10) (a) Barluenga, J.; Andina, F.; Fernández-Rodríguez, M. A.; García-García, P.; Merino, I.; Aguilar, E. *J. Org. Chem.* **2004**, *69*, 7352. (b) Zheng, Z. Y.; Chen, J. Z.; Yu, Z. K.; Han, X. W. *J. Organomet. Chem.* **2006**, *691*, 3679, and references therein.

(11) (a) Perdicchia, D.; Licandro, E.; Maiorana, S.; Vandoni, B.; Baldoli, C. *Org. Lett.* **2002**, *4*, 827. (b) Ezquerra, J.; Pedregal, C.; Merino, I.; Flórez, J.; Barluenga, J.; García-Granda, S.; Llorca, M.-A. *J. Org. Chem.* **1999**, *64*, 6554. (c) Beddoes, R. L.; Painter, J. E.; Quayle, P. *Tetrahedron Lett.* **1996**, *37*, 9385.

(12) (a) Shu, H.-G.; Shiu, L.-H.; Wang, S.-H.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 530. (b) Barluenga, J.; Ballesteros, A.; de la Rúa, R. B.; Santamaría, J.; Rubio, E.; Tomás, M. *J. Am. Chem. Soc.* **2003**, *125*, 1834.

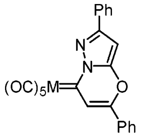
TABLE 6. Selected ^{13}C NMR Chemical Shifts for the Complexes (ppm)

complex	**3a−l**	**4a−l**	**5a−l**	**6a,b**	**11**[13]
δ(Cr═C)	264.6−266.4	232.1−228.0	222.0−225.9	291.5	290.8
δ(Cr−C≡O)	∼227/217	∼225/217	∼222−223/218	∼225/217	∼224/218
δ(W═C)	238.2−239.4	202.6−207.3	201.8−208.4	262.8	263.5
δ(W−C≡O)	∼207/198	∼204−205/198	∼199−202/198	∼205/198	∼204/199

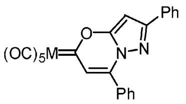
TABLE 7. Absorption and Emission Data for Mixed *syn*-9,10-Dioxabimanes 8 in Dioxane

	absorption		emission	
compound	$\lambda_{1\,\max}$	$\lambda_{2\,\max}$	$\lambda_{\max}$	$\phi_F{}^a$
8a	354	272	412	0.79
8b	357	275	412	0.82
8c	356	268	441	0.12
8d	357	269	436	0.11
8e	357	269	435	0.19
8f	360, 377	276	426	0.42

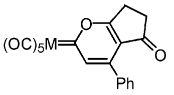
[a] Corrected for refractive index. Referenced to quinine sulfate 0.1 N H_2SO_4, $\phi_F = 0.55$.



3k,**l**



6a,**b**



11[13]

features (Table 6). The ^{13}C signals of M═C carbons at 266.4 (M = Cr) for **3k** and 239.4 (M = W) for **3l** feature typical Fischer aminocarbene complexes; those of M═C carbons at 291.5 (M = Cr) for **6a** and 262.8 (M = W) for **6b** are characteristic of Fischer alkoxycarbene complexes.[13] The corresponding ^{13}C chemical shifts of the M═C and C≡O carbons in **6a**,**b** and **11** are almost the same (Table 6); thus, it is reasonable to conclude that the molecular structures of **6a**,**b** and **11** are similar. Such a conclusion is also supported by the structural determination of **10** (see Supporting Information (SI)).

Fluorescence Spectra. *syn*-9,10-Dioxabimanes **8a** and **8b** exhibit a striking and strong fluorescence in solution. In dioxane, the positions of the fluorescence maxima vary from 412 and 441 nm, accompanied by shoulders at a 10 nm longer wavelength (see SI). The quantum yields of fluorescence of **8a**,**b** and other *syn*-9,10-dioxabimanes, i.e., **8c**−**f**, range between 0.11 and 0.82 (Table 7). In contrast, the fluorescence of the *anti*-9,-10-dioxabimanes **9a**−**f** is very weak, with quantum yields less than 0.002 for maxima between 400 and 500 nm. The measured quantum yields reveal that **8a**,**b** are strongly fluorescent *syn*-mixed-bimanes and **9a**−**f** are *anti*-mixed-bimanes,[7] and the *syn*-bimane molecules of type **8** bearing a 3-substituted alkyl or phenyl and without any substituent on the 4-position can exhibit strong fluorescence maxima; those with 3,4-dialkyl substituents are only bestowed with relatively weak fluorescence maxima (Table 7). These results suggest that coplanarity of the two *N*-heterocyclic rings in the molecules play an important role in fluorescence properties of *syn*-bimanes **8a**−**f**. In addition, **8a**,**b** also demonstrate strong UV absorptions at 254 nm (ϵ = 14 299) for **8a** and 253 nm (ϵ = 14 067) for **8b**, respectively.

Structural Features. The molecular structures of complexes **3h**, **4a**,**j**, **5a**, and organic compounds **7a**, **8a**, and **10** were confirmed by X-ray crystallographical determinations (see SI). Complexes **3** are Fischer aminocarbene complexes and exhibit a bicyclic five-membered pyrazolyl and six-membered oxazinyl core, which is structurally exemplified by the molecular structure of **3h** with a carbene bond (W−C 2.169(8) Å; see SI). Complexes **4** and **5** exhibit molecular structures similar to 1,5-diazabicyclo[3.3.0]octadienediones, i.e., bimanes, and their significant structural difference is that a pentacarbonyl−metal moiety replaces one of the carbonyl oxygens in a bimane molecule, which is exemplified by the molecular structures of **4a**,**j**, and **5a** (see SI). Compound **7a** presents a molecular structure similar to that of **3h**, and the crystallographic data reveals that the corresponding bond distances and angles in **3h** and **7a** are very close. Compound **8a** is a typical syn-mixed-bimane with an average C−O bond distance of 1.216(3) Å (1.2190(19) Å and 1.212(2) Å).[7] The molecular structure of **10** suggests that its precursors, i.e., **6a**,**b**, are Fischer alkoxycarbene complexes (see SI).

Conclusion

In summary, novel *N*-heterocyclic rings were successfully constructed from the reactions of substituted pyrazolinones and 1-alkynyl Fischer carbene complexes via multiple tautomerism of the substituted pyrazolinones. Efficient oxidative demetalation of the newly formed *N*-heterocyclic Fischer carbene complexes with pyridine *N*-oxide (PNO) or *m*-chloroperoxybenzoic acid (*m*-CPBA) afforded strongly fluorescent syn-mixed-bimanes and other novel *N*-heterocyclic compounds. The present method provides an alternative synthetic route to mixed bimanes.

Experimental Section

Synthesis of *N*-Heterocyclic Fischer Carbene Complexes 3, 4, and 5. General Procedure. 1-Alkynylcarbene complex **1** (1.0 mmol) was reacted with substituted pyrazolinone **2** (1.0 mmol) in 3 mL of THF at 50 °C in a 5 mL screwtop vessel with stirring or under other stated conditions. The reaction was monitored by TLC analysis on silica gel. After **1** was completely consumed, all the volatiles were removed under reduced pressure. The resultant mixture was subjected to flash silica gel column chromatography to successively afford the products **3**−**6**.

Oxidative Demetalation of Fischer Carbene Complexes 3 and 6 with Pyridine *N*-Oxide (PNO). A Typical Procedure. Carbene complex **3a** (121 mg, 0.3 mmol) was reacted with pyridine *N*-oxide (29 mg, 0.3 mmol) in 3 mL of THF at 50 °C in a 5 mL screwtop vessel with stirring. **3a** was completely consumed within 20 min by TLC analysis. All the volatiles were removed under reduced pressure. The resultant residue was subjected to flash silica gel column chromatography with petroleum ether (30−60 °C)/diethyl ether (v/v, 1/1) as the eluent to afford the corresponding product **7a** as a white solid (60 mg, 88.2%). In a fashion similar to the oxidation of **3a**, the carbene complex **3b** (160 mg, 0.3 mmol) was oxidized with PNO (29 mg, 0.3 mmol) to afford 64 mg of the product **7a** in 94.4% yield.

Oxidative Demetalation of Carbene Complexes 4 and 5 with *m*-Chloroperoxybenzoic Acid (*m*-CPBA). A Typical Procedure. A pre-cooled-to-0 °C solution of *m*-CPBA (77% purity, 269 mg, 1.2 mmol) in 3 mL of CH_2Cl_2 was added dropwise to a solution of

---

[13] Aumann, R.; Fröhlich, R.; Kotila, S. *Organometallics* **1996**, *15*, 4842.

complex **4a** (121 mg, 0.3 mmol) in 3 mL of CH_2Cl_2 at 0 °C over a period of 2 min. After the addition was complete, the ice−water bath was removed and the reaction mixture was allowed to warm to room temperature and further stirred until the starting complex was consumed by TLC analysis. The resultant mixture was diluted with CH_2Cl_2, filtered through a short pad of celite, and then concentrated under reduced pressure. Purification by flash silica gel column chromatography with dichloromethane/diethyl ether (v/v, 10:1) afforded the oxidatively demetalated product **8a** as a white solid (52 mg, 76.4%). Oxidation of complex **4b** (160 mg, 0.3 mmol) with *m*-CPBA (269 mg, 1.2 mmol) also afforded **8a** (58 mg, 85.6%). In a fashion similar to the oxidative demetalation of **4a**,**b**, complexes **4c**−**l** and **5a**−**l** were transformed to their corresponding organic products **8b**−**f**, and **9a**−**f**, respectively.

Acknowledgment. We are grateful to the Hundred Talented Program Funding of the Chinese Academy of Sciences for financial support of this research.

Supporting Information Available: Experimental details, analytical data, copies of NMR and fluorescence spectra, and X-ray crystallographic files for **3h**, **4a**,**j**, **5a**, **6a**, **7a**, and **10**, also in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JO061725+