Chromium and Tungsten Pentacarbonyl Groups as Reactivity and Selectivity Auxiliaries in [3 + 2] Cycloaddition of Alkynyl Fischer Carbene Complexes with *N*-Alkyl Nitrones

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Alkynyl Fischer carbene complexes were found to undergo chemoselective, regioselective, and rate-enhanced 1,3-dipolar cycloaddition with nitrones to give 2,3-dihydroisoxazole carbene complexes in excellent yields. These alkynyl complexes can serve as synthons for substituted propiolate esters since the metal pentacarbonyl group of the cycloadducts can be easily oxidatively removed with DMSO. The tungsten carbene complex **4b** reacted with 3 different series of *N*-alkyl nitrones: *N-tert*-butyl **2a–f**, *N*-methyl **1a–h** and *N*-benzyl **3** to give cycloadducts **6a–f**, **7a–h**, and **8–9**, respectively, while the chromium carbene complex **4a** reacted only with *N-tert*-butyl nitrones **2a–g** to give isolable cycloadducts **5a–g**. The structure of *N*-methyl cycloadduct **7d** has been established by a single-crystal X-ray analysis. The reactivity of *N*-alkyl nitrones toward carbene complexes was in the order: *N*-Me > *N*-Bn > *N*-^{t}Bu. In addition, our results showed that the rate of cycloaddition reaction increased as the electron donating ability of para-substituent in *N-tert*-butyl nitrone **2a–f** increased.

Introduction

The [3 + 2] cycloaddition reactions of 1,3-dipoles have been intensely investigated in the last two decades,[1] and their importance in natural product synthesis has been thoroughly established.[2] α,β-Unsaturated Fischer carbene complexes have recently been found to undergo rapid and highly regioselective [4 + 2][3] and [2 + 2][4] cycloaddition reactions with a variety of dienes and alkenes, respectively. However, there are only a few examples of [3 + 2] cycloaddition of Fischer carbene complexes with 1,3-dipoles. It has been shown that the reaction of phenylethynylcarbene complexes with CH_2N_2 leads to competing reactions involving the formation of pyrazolylcarbene and *N*-pyrazolyl complexes in an overall low yield.[5] However, with the same 1,3-dipole containing a TMS group, Me_3SiCHN_2, phenylethynylcarbene complexes give high yields of pyrazolylcarbene complexes in a highly regioselective and rate enhancing manner compared to the analogues of organic esters with the carbene fragments replaced by an oxygen atom.[6] Kalinin *et al.* found that another 1,3-dipole, α,*N*-diphenyl nitrone, undergoes [3 + 2] cycloaddition with trimethylsilylethynyl carbene complexes. However, instead of yielding the desired isoxazoline carbene complexes, rearranged products of oxazoline carbene complexes resulted in low to moderate yields (accompanied with ca. 30% of unreacted carbene complexes).[7] Recently, we reported our preliminary success with the chemoselective and regioselective 1,3-dipolar cycloaddition of alkynyl Fischer carbene complexes with α-phenyl *N-tert*-butyl nitrone (PBN) to give essentially a quantitative yield of 2,3-dihydroisoxazole carbene complexes at room temperature.[8] We now describe our full report on the [3 + 2] cycloadditions of alkynyl Fischer carbene complexes with *N*-alkyl nitrones.

Preparation of Nitrones

N-Alkyl nitrones were conveniently prepared by two reported methods. The first method employs the condensation of alkylhydroxylamine with aldehydes,[9] and the second method takes advantage of the oxidation of secondary amines by hydrogen peroxide in the presence of a catalytic amount of sodium tungstate.[10] A series of α-phenyl *N*-methyl **1a–h** (X-PMN) (Table 1) and α-phenyl *N-tert*-butyl nitrones **2a–f** (X-PBN) (Table 2) were prepared by the condensation of aldehydes with the corresponding hydroxylamines in refluxing CH_2Cl_2 in a suspension of anhydrous $MgSO_4$ according to the procedure of Torssell and Zeuthen.[9] For the preparation of *N*-methyl nitrones, $NaHCO_3$ was added to neutralize the commerically available methylhydroxylamine hydrochloride to generate MeNHOH. In the preparation of *N-tert*-butyl nitrones, the reaction required refluxing under

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(1) Padwa, A. *1,3 Dipolar Cycloaddition Chemistry*; Wiley-Interscience: New York; 1984, Vols. 1 and 2.
(2) Desimoni, G.; Tacconi, G.; Barco, A.; Pollini, G. P.; Eds. *Natural Products Synthesis Through Pericyclic Reactions*; American Chemical Society: Washington, DC, 1983.
(3) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726. (b) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565. (c) Dotz, K. H.; Kuhn, W. *J. Organomet. Chem.* **1985**, *286*, C23. (d) Wulff, W. D.; Tang, P. C.; Chan, K. S. McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813. (e) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc.* **1991**, *113*, 7418. (f) Bao, J.; Dragisich, V.; Wenglowsky, S.; Wulff, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 9873.
(4) (a) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1988**, *110*, 8727. (b) Camps, F.; Moreto, J. M.; Ricart, S.; Vinas, J. M.; Molins, E.; Miravitlles, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1560. (c) Faron, K. L.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 6419. (d) Camps, F.; Llebaria, M. G.; Moreto, J. M.; Ricart, S.; Vinas, J. M. *Tetrahedron Lett.* **1990**, *31*, 2479. (e) de Meijere, A.; Wessjohann, L. *Synlett.* **1990**, 20. (f) Merlic, C. A.; Xu. D. *J. Am. Chem. Soc.* **1991**, *113*, 7418. (g) Pipoh, R.; van Eldik, R.; Wulff, W. D.; Wang, S. L. B. *Organometallics* **1992**, *11*, 490.
(5) Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G. *J. Organomet. Chem.* **1973**, *57*, C9.
(6) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5229.
(7) Kalinin, V. N.; Shilova, O. S.; Kovredov, A. I.; Petrovskii, P. V.; Batsanov, A. S.; Struchkov, Y. T. *Organomet. Chem. USSR* **1989**, *2* (3), 268.
(8) Chan, K. S. , *J. Chem. Soc. Perkin Trans. 1* **1991**, 2602.
(9) Torssell, K.; Zeuthen, O. *Acta Chem. Scand., Ser. B* **1978**, *B32*, 118.
(10) Murahashi, S. I.; Shiota, T.; Imada, Y. *Org. Synth.* **1991**, *70*, 265.

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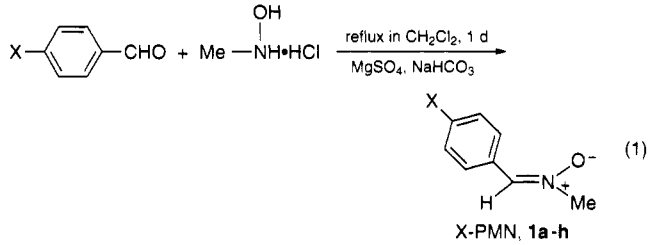
Table 1. Preparation of Substituted PMN 1a–h (X-PMN) (eq 1)

X-PMN	yield (%)
1a NMe_2-PMN	87
1b OMe-PMN	80
1c Me-PMN	87
1d H-PMN	85
1e Br-PMN	70
1f Cl-PMN	73
1g CN-PMN	90
1h NO_2-PMN	90

Table 2. Preparation of Substituted PBN 2a–c, 2e–f (X-PBN) (eq 2)

X-PBN	solvent	rxn time (d)	rxn temp	yield (%)
2a Me_2N-PBN	CH_2Cl_2	4	reflux	47
2b MeO-PBN	CH_2ClCH_2Cl	1	reflux	63
2c Me-PBN	CH_2Cl_2	1	reflux	90
2e Br-PBN	CH_2Cl_2	6	rt	61
2f Cl-PBN	CH_2Cl_2	1	reflux	75

nitrogen in order to avoid undesired aerobic oxidation of *N-tert*-butylhydroxylamine (preparaed by the reduction of 2-methyl-2-nitropropane with aluminum amalgam)[11] to the nitroso compound. The yields of *N*-methyl nitrones **1** (73–90%) were generally higher than those of *N-tert*-butyl nitrones **2** (47–90%), likely due to less bulky methyl group in facilitating the condensation. Alternatively, the



(1)

X-PMN, **1a-h**

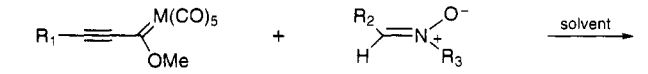
(2)

X-PBN, **2a-c**, **2e-f**

nonsubstituted *N-tert*-butyl nitrone **2d** and *N*-benzyl nitrone **3** (PBnN) were prepared by slow addition of aqueous hydrogen peroxide into a methanolic solution of *tert*-butylbenzylamine and dibenzylamine respectively in the presence of sodium tungstate at 0 °C.[10]

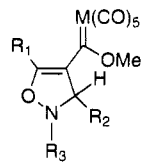
Cycloadditions of Carbene Complexes with Nitrones

When pyridine *N*-oxide was reacted with complex **4a**, instead of undergoing [3 + 2] cycloaddition at the carbon–carbon triple bond, undesired oxidative cleavage of chromium–carbon double bond was observed to give methyl 2-phenylethynyl carboxylate (**12**).[8] However, when a more reactive nitrone PBN **2d** was treated with carbene complexes of chromium **4a** and tungsten **4b**, it underwent chemoselective cycloadditions at the carbon–carbon triple bond to give the dihydroisoxazole carbene complexes **5d** and **6d** in excellent yields (Table 3, entries 4 and 16). Besides, the yield of the cycloadduct **5d** remained practically the same when **4a** was reacted with either 1 or 2 equiv of H-PBN **2d** (Table 3, entries 4 and 5). Double cycloaddition and oxidative cleavage were, therefore, insignificant.[8]



4a: R_1 = Ph, M = Cr
4b: R_1 = Ph, M = W
4c: R_1 = *p*-Me-C_6H_6, M = Cr
4d: R_1 = *p*-Me-C_6H_6, M = W

1: R_2 = *p*-X-C_6H_6, R_3 = Me
2: R_2 = *p*-X-C_6H_6, R_3 = ^{t}Bu
3: R_2 = Ph, R_3 = Bn

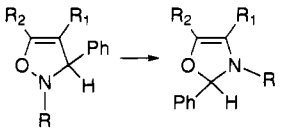


(3)

5: R_1 = Ph, M = Cr, R_2 = *p*-X-C_6H_6, R_3 = ^{t}Bu
6: R_1 = Ph, M = W, R_2 = *p*-X-C_6H_6, R_3 = ^{t}Bu
7: R_1 = Ph, M = W, R_2 = *p*-X-C_6H_6, R_3 = Me
8: R_1 = Ph, M = Cr, R_2 = Ph, R_3 = Bn
9: R_1 = Ph, M = W, R_2 = Ph, R_3 = Bn
10: R_1 = *p*-Me-C_6H_6, M = Cr, R_2 = Ph, R_3 = ^{t}Bu
11: R_1 = *p*-Me-C_6H_6, M = W, R_2 = Ph, R_3 = ^{t}Bu

Furthermore, the cycloadditions were highly regioselective since only one regioisomer was observed and the regioselectivity was at least over 20 to 1 based on ^{1}H NMR analysis. The regiochemistry of the cycloadducts was secured by NOE experiments. Upon irradiation of the methoxy protons, NOE enhancements were observed at the methine protons [% NOE: Cr complex **5d** = 2.0, W complex **6d** = 0.8]. Other carbene complex cycloadducts were therefore assigned to have the same regiochemistry.[8]

The above NOE experiment not only determined the regiochemistry of the *N-tert*-butyl cycloadduct **5d** but also ruled out the possibility of the isoxazoline–oxazoline rearrangement. Cycloadduct **5d** had been heated at 40 °C in benezene-d_6 for 2 days; however, no obvious change of the NMR spectrum was observed. Futher heating at elevated temperature of 80 °C for 2 more days induced decomposition and no rearranged product was found. Indeed, the *N*-phenylisoxazoline is known to rearrange thermally at 80 °C to oxazoline readily.[12] A higher



(4)

temperature of about 160 °C is needed for organic *N*-methylisoxazoline (Table 4).[12] These results are consistent with the findings that the rearrangement occurs readily in the *N*-phenyl cycloadduct carbene complex[7] but not in the *N*-alkyl cycloadduct complexes **5**–**7**. The reason of this rearrangement, however, is not clearly known.[12]

Single crystal of the *N*-methylisoxazoline cycloadduct **7d** was grown from ethanol and its structure was determined by X-ray diffraction (Figure 1),[13] which further consolidated the fact that the *N*-alkyl cycloadduct did not undergo isoxazoline–oxazoline rearrangement at room temperature.

(11) Calder, A.; Forrester, A. R.; Hepburn, S. P. *Org. Synth.* **1972**, *52*, 77.

(12) Freeman, J. P. *Chem. Rev.* **1983**, *83*, 241.

(13) X-ray data has been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, cmanridge Crystallographic DataCentre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Table 3. Cycloaddition of Alkynyl Fischer Carbene Complexes with Nitrones (eq 3)

entry	complex	nitrone	temp	time	solvent	adduct	yield (%)
1	**4a**	**2a** NMe_2-PBN	rt	15 min	THF	**5a**	94
2	**4a**	**2b** MeO-PBN	rt	30 min	THF	**5b**	90
3	**4a**	**2c** Me-PBN	rt	40 min	THF	**5c**	98
4	**4a**	**2d** H-PBN	rt	3 h	THF	**5d**	95
5	**4a**	**2d** H-PBN (2 equiv)	rt	3 h	THF	**5d**	82
6	**4a**	**2d** H-PBN	rt	3 h	hexane	**5d**	92
7	**4a**	**2d** H-PBN	rt	1 h	acetone	**5d**	90
8	**4a**	**2d** H-PBN	rt	1 h	nitromethane	**5d**	87
9	**4a**	**2d** H-PBN	rt	1 h	acetonitrile	**5d**	88
10	**4a**	**2e** Br-PBN	rt	5 h	THF	**5e**	94
11	**4a**	**2f** Cl-PBN	rt	5 h	THF	**5f**	99
12	**4a**	**2g** NO_2-PBN	rt	4 d	THF	**5g**	42
13	**4b**	**2a** NMe_2-PBN	rt	5 min	THF	**6a**	92
14	**4b**	**2b** MeO-PBN	rt	15 min	THF	**6b**	95
15	**4b**	**2c** Me-PBN	rt	40 min	THF	**6c**	95
16	**4b**	**2d** H-PBN	rt	3 h	THF	**6d**	92
17	**4b**	**2e** Br-PBN	rt	5 h	THF	**6e**	99
18	**4b**	**2f** Cl-PBN	rt	5 h	THF	**6f**	96
19	**4c**	**2d** H-PBN	rt	3.5 h	THF	**10**	88
20	**4d**	**2d** H-PBN	rt	1 h	THF	**11**	98
21	**4b**	**1a** NMe_2-PMN	rt	5 min	THF	**7a**	50
22	**4b**	**1b** MeO-PMN	rt	5 min	THF	**7b**	65
23	**4b**	**1c** Me-PMN	rt	5 min	THF	**7c**	85
24	**4b**	**1d** H-PMN	rt	5 min	THF	**7d**	86
25	**4b**	**1e** Br-PMN	rt	5 min	THF	**7e**	97
26	**4b**	**1f** Cl-PMN	rt	5 min	THF	**7f**	75
27	**4b**	**1g** CN-PMN	rt	1 h	THF	**7g**	91
28	**4b**	**1h** NO_2-PMN	rt	5 h[a]	THF	**7h**	90
29	**4a**	**3** PBnN	rt	10 min	THF	**8**	73
30	**4b**	**3** PBnN	rt	10 min	THF	**9**	92

[a] NO_2-PMN was less soluble in THF compare with other PMN, and higher dilution (7-fold dilution) was used to ensure complete dissolution.

Table 4. Isoxazoline–Oxazoline Rearrangement (eq 4)[12]

R	R_1	R_2	conditions
CH_3	CO_2CH_3	Ph	isoxazoline heated in boiling mesitylene (160 °C)
Ph	CO_2CH_3	Ph	obtained directly from cycloaddition reactions in boiling EtOAc (77 °C); no isoxazoline isolated
Ph	H	CO_2CH_3	obtained directly from cycloaddition reactions in boiling benzene (80 °C); no isoxazoline isolated
Ph	$C(OMe)=W(CO)_5$	TMS	obtained directly from cycloaddition reaction in CH_2Cl_2 at rt; no isoxazoline isolated[7]

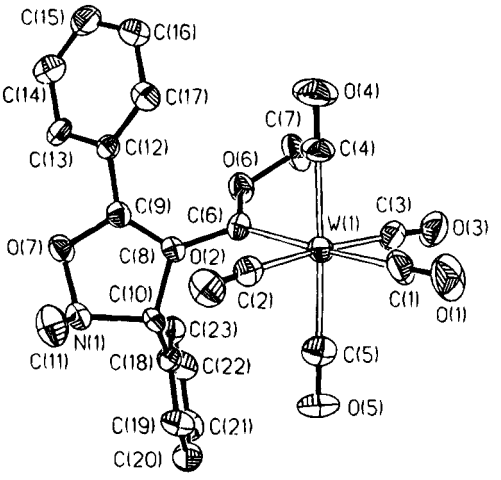
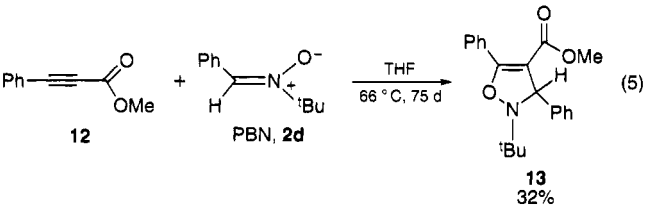


Figure 1. ORTEP diagram of PMN **7d**.

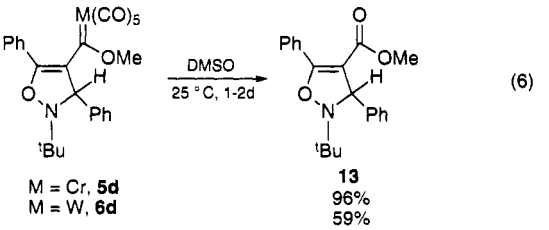
The cycloadditions of chromium carbene complex **4a** with PBN **2a–f** (Table 3, entries 1–4, 10–11) only took 15 min to 5 h to complete at room temperature and gave cycloadducts **5a–f** with excellent yields of above 90%. The reaction of H-PBN **2d** with the closest organic analogue of complex **4a** or **4b**, methyl 2-phenylethynyl carboxylate (**12**) took 75 days at refluxing THF (65 °C) to give ester **13** in only 32% together with unreacted ester (5%) (eq 5).[14]

The rate enhancement of the metal pentacarbonyl moiety over the oxygen atom was estimated to be about



(5)

10^4. It was observed that the metal effect in carbene complexes is not very large. Both the yields and reaction times of the cycloadditions of tungsten carbene complex **4b** with PBN **2a–f** were similar to those of chromium complex **4a** (Table 3, entries 1–4, 10–11, 13–18). The cycloadduct complexes **5d** and **6d** were easily oxidatively demetalated by DMSO to yield the ester **13** (eq 6).[8]



(6)

Apart from PBN, less sterically bulky nitrones such as *N*-benzyl (PBnN) **3** and *N*-methyl nitrone (PMN) **1a–h**

(14) Chan, W. K., Undergraduate Thesis. Department of Chemistry, The Chinese University of Hong Kong, 1991.

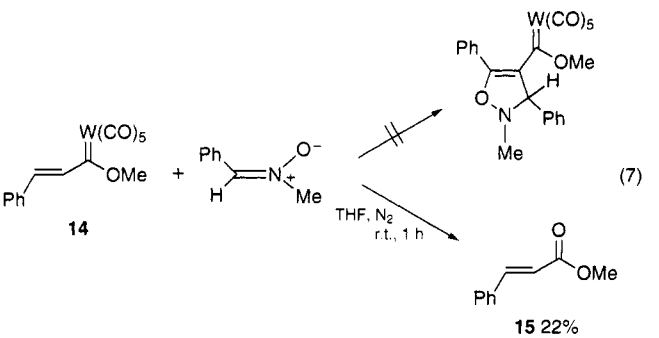
were found to be much more reactive towards alkynyl carbene complexes. Complexes **4a** and **4b** reacted with PBnN **3** to give cycloadducts **8** (73%) and **9** (92%) within 10 min (Table 3, entries 29 and 30). Tungsten carbene complex **4b** reacted with PMN **1a**–**h** to give cycloadducts **7a**–**h** (Table 3, entries 21–28) with yields ranging from 50 to 90%. The reactions for all PMN were completed within 5 min except for CN-PMN **1g** and NO_2-PMN **1h** (Table 3, entries 27–28), with both of them bearing stronger electron-withdrawing groups. Their reactions with tungsten carbene complex **4b** took a longer time of 1 h and 5 h to complete respectively. The cycloadducts **7a**–**h** with stronger electron withdrawing groups on the phenyl ring were found to be relatively stable although they decomposed slowly even when stored at −20 °C for about 1 month. The reaction time of *N*-methyl nitrones with carbene complexes were obviously shorter than that of *N*-*tert*-butyl nitrones. The reactivity of *N*-alkyl nitrones toward carbene complexes was in the following order (Table 3, entries 24, 30, 16): *N*-Me > *N*-Bn > *N*-^{t}-Bu, since, presumably, the more steric crowding in the transition state decreases the rate of reaction. However, chromium carbene complex **4a** reacted with PMN **1d** to give thermally labile cycloadducts. At first, monitored by TLC, the reaction showed a new orange-red spot which turned black in air within several minutes. In order to examine if the transient product was the desired cycloadduct, the reaction was then carried out under nitrogen in a NMR tube in acetone-d_6 and monitored immediately at room temperature. A characteristic peak of methine proton of cycloadduct at δ 5.5 ppm was observed but disappeared after 3 min, which may be probably due to the formation of the unstable desired cycloadduct. The above results showed *N*-methyl tungsten cycloadduct was more stable than chromium cycloadducts presumably owing to the stronger metal carbon double bond.[15]

To gain a better understanding of the cycloaddition reaction, the substituent effect on nitrones was investigated. When carbene complex **4a** (or **4b**) was treated with *para*-substituted PBN **2a**–**g**, the more electron donating nitrone, NMe_2-PBN **2a**, reacted with carbene complex **4a** within 15 min (Table 3, entry 1). However, Cl-PBN **2f** (Table 3, entry 11), took about 5 h to complete the reaction. The above results concluded that the rate of reaction increased as the electron-donating ability of the *para*-substitutent in *N*-*tert*-butyl nitrones **2a**–**f** increased.

Frontier molecular orbital (FMO) theory serves to rationalize the reactivity and regioselectivity of cycloaddition reactions. Our results have indicated that the rate of cycloaddition of carbene complexes with *N*-*tert*-butyl nitrones increases as the electron-donating ability of the *para*-substitutent in *N*-*tert*-butyl nitrone increases. The reaction is likely due to the interaction between the LUMO of carbene complex and the HOMO of nitrone. For electron rich nitrone, higher HOMO energy level is expected and hence smaller HOMO–LUMO energy gap is resulted, consequently, the rate of reaction increases.

In comparison with chromium carbene complex **4a** or **4b**, the more electron rich *p*-methyl-substituted chromium carbene complex **4c** or **4d** is likely to have a higher LUMO energy level and is thus less reactive (3.5 h) to give cycloadducts **10** or **11** respectively (Table 3, entry 19, 4; 20, 16). Indeed, the rate was found to be slightly slower than that of the nonsubstituted carbene complex **4a** or **4b** (3 h) (Table 3, entry 4).

To futher explore the scope of dipolar cycloaddition of Fischer carbene complexes with nitrones, the dipolar cycloaddition of alkenyl Fischer carbene complex **14** was investigated since complex **14** was widely studied in [4 + 2] cycloaddition with a variety of dienes, for the sake of its great rate acceleration and highly regioselectivity and stereoselectivity.[3] However, the reaction between complex **14** and the 1,3 dipole PMN did not undergo desired [3 + 2] cycloaddition over the carbon–carbon double bond. Instead, **14** was oxidatively cleaved at the tungsten–carbon double bond by PMN to give the corresponding organic ester **15**, methyl cinnamate, in 22% yield (eq 7).



(7)

In order to gain some mechanistic insights of the cycloaddition, carbene complex **4a** was treated with H-PBN **2d** in five different solvents (Table 3, entries 4, 6–9). The reaction rates were 3-fold faster for reactions in solvents with higher dielectric constants: acetone, acetonitrile, and nitromethane than in THF and hexane. However, the small difference in solvent effect indicated that the reaction might likely be a concerted one.[1]

Conclusion

In summary, alkynyl Fischer carbene complexes have been demonstrated to undergo chemoselective and regioselective [3 + 2] cycloaddition with *N*-alkyl nitrones to give 2,3-dihydroisoxazole carbene complexes in excellent yields with rate enhancement of 10^4 over alkynyl organic ester. Further kinetic studies of the cycloaddition is continued in our laboratory.

Experimental Section

Melting points were uncorrected. IR spectra were recorded on a FT-IR spectrophotometer as neat films on KBr plates. ^{1}H NMR spectra were measured either at 60 MHz or at 250 MHz. In all ^{1}H NMR measurements, chemical shifts were referenced to tetramethylsilane. ^{13}C spectra were obtained at 62.9 MHz. Mass spectra were obtained at 20 eV unless otherwise noted. Elemental analyses were performed by the Medac Ltd, Department of Chemistry, Brunel University, U. K. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. THF was distilled from sodium benzophenone ketyl immediately prior to use. *N*-*tert*-Butylhydroxylamine was dried under reduced pressure and stored under nitrogen in a freezer. All cycloadditions were run with the reaction mixture deoxygenated by the freeze-pump-thaw method (−195 to 25 °C, three cycles) in 8×10^{-2} M. Silica gel chromatographic purification were performed under air by flash chromatoraphy[16] with 70–230 mesh silica packed in glass column.

(15) Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905.

(16) Still, W. C. Kahn, M.; Metra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Preparation of Alkynyl Carbene Complex: General Procedure.[6] The preparation of the known [methoxy-(2-phenylethynyl)methylene]pentacarbonylchromium (**4a**)[6] is described as a typical example. A solution of n-butyllithium (1.6 M in hexane, 5.7 mL, 9.1 mmol) was added dropwise to phenylacetylene (1.0 mL, 9.1 mmol) in 10 mL of THF at 0 °C. After 45 min at 0 °C the solution was transferred dropwise *via* cannula to a suspension of chromium hexacarbonyl (2.2 g, 10.0 mmol) in THF (20 mL). After 1 h at rt, methyl triflate (1.3 mL, 11.0 mmol) was slowly added to the reaction mixture at 0 °C. When the addition was complete, the mixture was stirred for another 0.5 h at 0 °C. The reaction was quenched by adding 20 mL of saturated $NaHCO_3$ and stirred for 10 min. The organic layer was separated and the aqueous layer was extracted with ether (3 × 20 mL). The organic solutions were combined, washed with water (30 mL) and brine (30 mL), and dried ($MgSO_4$). After removal of solvents, the crude product was flashed chromatographed on silica gel using hexane as the eluent. A dark purple low melting solid was collected in 74% yield (1.32 g, 3.9 mmol): R_f (hexane) = 0.38; IR (KBr) 1950, 1995, 2070, 2160 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 4.43 (s, 3 H), 7.46–7.55 (m, 5 H).

[Methoxy-(2-phenylethynyl)methylene]pentacarbonyltungsten (4b).[6] The black solid was collected in 41% yield: R_f (hexane) = 0.35; IR (KBr) 1930, 1975, 2075, 2170 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 4.35 (s, 3 H), 7.50–7.57 (m, 5 H).

[Methoxy-[2-(4-methylphenyl)ethynyl]methylene]-pentacarbonylchromium (4c). The dark purple solid was collected in 45% yield: R_f (hexane) = 0.29; mp 107–108 °C dec; IR (neat) 1933, 1979, 2058, 2149 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.40 (s, 3 H), 4.39 (s, 3 H), 7.24 (d, 2 H, J = 7.6 Hz), 7.47 (d, 2 H, J = 7.9 Hz); ^{13}C NMR (acetone-d_6, 62.9 MHz) 22.27, 67.73, 93.92, 118.88, 131.23, 134.28, 138.94, 144.85, 217.73, 226.71, 316.05; mass spectrum (70 eV) m/z (rel intensity) 350 (M^+, 7), 294 (M^+ – 2CO, 50), 266 (25), 238 (23), 210 (69). Anal. Calcd for $C_{16}H_{10}CrO_6$: C, 54.86; H, 2.86. Found: C, 54.91; H, 2.86.

[Methoxy-[2-(4-methylphenyl)ethynyl]methylene]-pentacarbonyltungsten (4d). The dark solid was collected in 25% yield: R_f (hexane) = 0.21; mp 107–108 °C dec; IR (neat) 1882, 1914, 1940, 1983, 2146 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.40 (s, 3 H), 4.34 (s, 3 H), 7.26 (d, 2 H, J = 7.5 Hz), 7.53 (d, 2 H, J = 7.5 Hz); ^{13}C NMR (acetone-d_6, 62.9 MHz) 21.12, 66.69, 97.67, 117.71, 130.15, 133.29, 143,80, 197.57 ($J_{W,C}$ = 128.9 Hz), 205.09, 287.29; mass spectrum (70 eV) m/z (rel intensity) 482 (M^+, 47), 426 (M^+ – 2CO, 59), 396 (77), 370 (76), 342 (100). Anal. Calcd for $C_{16}H_{10}O_6W$: C, 39.86; H, 2.09. Found: C, 39.86; H, 2.07.

[Methoxy-(2-phenylethenyl)methylene]pentacarbonyltungsten (14). The procedure was according to the literature.[6] The back solid was collected in 17% yield: R_f (hexane) = 0.41; IR (KBr) 1575, 1595, 1925, 1990, 2070 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 4.64 (s, 3 H), 7.21 (d, 1 H, J = 15.5 Hz), 7.30–7.62 (m, 5 H), 7.89 (d, 1 H, J = 15.5 Hz).

Preparation of Methyl 2-Phenylethynecarboxylate (12).[17] A solution of *n*-butyllithium (1.6 M in hexane, 18.8 mL, 30 mmol) was added to phenylacetylene (3.2 mL, 30 mmol) in 20 mL of THF at −78 °C. After 1 h at rt, methyl chloroformate (2.3 mL, 30 mmol) was slowly added to the solution at −78 °C. When the addition was complete, the mixture was stirred for another 1 h at rt. The resulting solution was then extracted with ether (30 mL), and the ethereal extract was dried ($MgSO_4$). After removal of solvents, the crude mixture was chromatographed on silica gel column using hexane/CH_2Cl_2 (3:1) as the eluent to give a pale yellow liquid (3.1g, 65%) upon removal of solvents: IR (neat) 1435, 1445, 1495, 1715, 2240 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.78 (s, 3 H), 7.23–7.63 (m, 5 H).

Preparation of *N*-Methyl Nitrones. The nitrones were prepared by condensation of the appropriate aldehyde (10 mmol) with *N*-methylhydroxylamine hydrochloride (10 mmol) in 40 mL of CH_2Cl_2 containing suspended anhydrous $MgSO_4$ (2.0 g) and $NaHCO_3$ (1.1 g) in refluxing CH_2Cl_2 for 24 h, according to the procedure of Torssell and Zeuthen.[9] After filtration and removal of solvents, the crude product was purified by flash chromatography on silica gel. The yields are tabulated on Table 1.

***N*-{[4-(Dimethylamino)phenyl]methylene}methanamine *N*-oxide (1a)** was obtained as pale orange solid in 87% yield; R_f (EtOAc/MeOH, 10:1) = 0.25; mp (CH_2Cl_2) 114–116 °C (lit.[18] mp 131.5–134 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ 3.00 (s, 6 H), 3.77 (s, 3 H), 6.66 (d, 2 H, J = 9.0 Hz), 7.17 (s, 1 H), 8.10 (d, 2 H, J = 9.1 Hz).

***N*-{(4-Methoxyphenyl)methylene}methanamine *N*-oxide (1b)** was obtained as pale yellow hydroscopic solid in 80% yield; R_f (EtOAc) = 0.10; mp (CH_2Cl_2) 57–59 °C (lit.[19] mp 69–70 °C); ^1H NMR ($CDCl_3$, 250 MHz) 3.82 (s, 6 H), 6.91 (d, 2 H, J = 9.0 Hz), 7.27 (s, 1 H), 8.19 (d, 2 H, J = 9.0 Hz).

***N*-{(4-Methylphenyl)methylene}methanamine *N*-oxide (1c)** was obtained as pale yellow solid in 87% yield; R_f (EtOAc) = 0.15; mp (CH_2Cl_2) 114–115 °C (lit.[18] mp 116.5–118.5 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ 2.35 (s, 3 H), 3.83 (s, 3 H), 7.20 (d, 2 H, J = 8.1 Hz), 7.30 (s, 1 H), 8.09 (d, 2 H, J = 8.2 Hz).

***N*-(Phenylmethylene)methanamine *N*-oxide (1d)** was obtained as yellow solid in 85% yield; R_f (EtOAc) = 0.14; mp (CH_2Cl_2) 72–75 °C (lit.[20] mp 82.5–83 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ 3.84 (s, 3 H), 7.34–7.39 (m, 4 H), 8.16–8.20 (m, 2 H).

***N*-{(4-Bromophenyl)methylene}methanamine *N*-oxide (1e)** was obtained as white solids: yield 70%; R_f (EtOAc) = 0.10; mp (CH_2Cl_2) 129–130 °C (lit.[20] mp 129.5–130 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ 3.85 (s, 3 H), 7.32 (s, 1 H), 7.52 (d, 2 H, J = 8.7 Hz), 8.08 (d, 2 H, J = 8.7 Hz).

***N*-{(4-Chlorophenyl)methylene}methanamine *N*-oxide (1f)** was obtained as pale yellow solid in 73% yield; R_f (EtOAc) = 0.10; mp (CH_2Cl_2/hexane) 125–127 °C (lit.[20] mp 130–131 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ 3.86 (s, 3 H), 7.37 (d, 2 H, J = 8.8 Hz), 7.34 (s, 1 H), 8.16 (d, 2 H, J = 8.7 Hz).

***N*-{(4-Cyanophenyl)methylene}methanamine *N*-oxide (1g)** was obtained as white solid in 90% yield; R_f (acetone) = 0.58; mp (CH_2Cl_2/hexane) 186–187 °C (lit.[20] mp 187 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ 3.91 (s, 3 H), 7.43 (s, 1 H), 7.67 (d, 2H, J = 8.6 Hz), 8.26 (d, 2 H, J = 8.6 Hz).

***N*-{(4-Nitrophenyl)methylene}methanamine *N*-oxide (1h)** was obtained as white solid in 90% yield; mp (CH_2Cl_2) 207–209 °C (lit.[20] mp 206–207 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ 3.93 (s, 3 H), 7.50 (s, 1 H), 8.24 (d, 2 H, J = 9.0 Hz), 8.36 (d, 2 H, J = 9.1 Hz).

Preparation of *N*-*tert*-Butyl Nitrones. The nitrones were prepared by condensation of the appropriate aldehyde (10 mmol) with *N*-*tert*-butylhydroxylamine[11] (10 mmol) in 40 mL of solvent containing suspended anhydrous $MgSO_4$ (2.0 g) under N_2 according to the procedure of Torssell and Zeuthen.[9] The workup procedure was the same as that of preparation of *N*-methyl nitrone **1**. The yields and reaction conditions are tabulated on Table 2.

***N*-{[4-(Dimethylamino)phenyl]methylene}-2-methyl-2-propanamine *N*-oxide (2a)** was obtained as yellow solid in 47% yield; R_f (EtOAc) = 0.45; mp (CH_2Cl_2) 134–136 °C; IR (KBr) 1104, 1126, 1188, 1357, 1520, 1602 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.56 (s, 9 H), 2.98 (s, 6 H), 6.66 (d, 2 H, J = 9.0 Hz), 7.35 (s, 1 H), 8.18 (d, 2 H, J = 9.0 Hz); mass spectrum m/z (rel intensity) 220 (M^+, 79), 204 (32), 189 (71), 164 (100), 148 (25). Anal. Calcd for $C_{13}H_{20}N_2O$: C, 70.87; H, 9.15; N, 12.72. Found: C, 70.91; H, 9.27; N, 12.73.

***N*-{(4-Methoxyphenyl)methylene}-2-methyl-2-propanamine *N*-oxide (2b)** was obtained as yellow solid in 63% yield; R_f (EtOAc) = 0.46; mp (CH_2Cl_2) 94–96 °C (lit.[21] mp 94–96 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.54 (s, 9 H), 3.77 (s, 3 H), 6.86 (d, 2 H, J = 9.0 Hz), 7.41 (s, 1 H), 8.23 (d, 2 H, J = 8.9 Hz).

(17) Tsuji, J.; Takahashi, M.; Takahashi, T. *Tetrahedron. Lett.* **1980**, *21*, 849.

(18) Castro, C.; Dixon, M.; Erden, I.; Ergonenc, P.; Keeffe, J. R.; Sukhovitsky, A. *J. Org. Chem.* **1989**, *54*, 3732.

(19) Tsuge, O.; Sone, K.; Urano, S.; Matsuda, K. *J. Org. Chem.* **1982**, *47*, 5171.

(20) Yijima, C.; Tsujimoto, T.; Suoa, K.; Yamauchi, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2165.

***N*-{(4-Methylphenyl)methylene}-2-methyl-2-propanamine *N*-oxide (2c)** was obtained as yellow-brown solid in 90% yield; R_f (hexane/EtOAc, 5:1) = 0.18; mp (CH_2Cl_2) 70–73 °C (lit.[21] mp 70–73 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.57 (s, 9 H), 2.34 (s, 3 H), 7.19 (d, 2 H, J = 8.0 Hz), 7.43 (s, 1 H), 8.15 (d, 2 H, J = 8.2 Hz).

***N*-{(4-Methylphenyl)methylene}-2-methyl-2-propanamine *N*-oxide (2d)** can be purchased from Aldrich or prepared in excellent yield from oxidation of *N*-benzyl-*tert*-butylamine by hydrogen peroxide in the presence of sodium tungstate catalyst.[10]

***N*-{(4-Bromophenyl)methylene}-2-methyl-2-propanamine *N*-oxide (2e)** was obtained as pale-yellow solid in 61% yield; R_f (CH_2Cl_2) = 0.17; mp (CH_2Cl_2) 60–62 °C (lit.[22] mp 61–62 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.58 (s, 9 H), 7.49–7.53 (m, 3 H), 8.16 (d, 2 H, J = 9.1 Hz).

***N*-{(4-Chlorophenyl)methylene}-2-methyl-2-propanamine *N*-oxide (2f)** was obtained as white solid in 75% yield; R_f (hexane/EtOAc, 4:1) = 0.24; mp (CH_2Cl_2) 72–73 °C (lit.[23] mp 112–115 °C); IR (KBr) 891, 1197, 1249, 1362, 1388, 1398, 1410, 1483, 1548 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.49 (s, 9 H), 7.26 (d, 2 H, J = 8.6 Hz), 7.43 (s, 1 H), 8.15 (d, 2 H, J = 8.6 Hz); mass spectrum m/z (rel intensity) 211 (M^+, 5), 155 (5), 57 (100). Anal. Calcd for $C_{11}H_{14}ClNO$: C, 62.41; H, 6.67; N, 6.62. Found: C, 62.20; H, 6.62; N, 6.49.

Reaction of Alkynyl Carbene Complex with Nitrone. General Procedure. A solution of the chromium complex **4a** (54 mg, 161 μmol) and the nitrone, H-PBN **2d** (29 mg, 164 μmol) in THF (2 mL) was stirred at rt under nitrogen. The reaction was closely monitored by TLC. The red solution changed to orange after 3 h. The solvent was then evaporated, and the residue was flashed chromatographed on silica gel with CH_2Cl_2/hexane (1:1) to give the red viscous oil **5d** (79 mg, 95%): R_f (hexane/CH_2Cl_2, 1:1) = 0.77; IR (KBr) 1935, 1959, 1996, 2061 cm^{-1}; ^{1}H NMR (acetone-d_6, 250 MHz) δ 1.27 (s, 9 H), 4.34 (s, 3 H), 6.08 (s, 1 H) and 7.26–7.70 (m, 10 H); ^{13}C NMR (acetone-d_6, 62.9 MHz) δ 25.24, 40.51, 61.25, 65.43, 71.59, 112.69, 127.68, 128.08, 128.58, 129.96, 130.92, 147.36, 150.26, 216.60, 223.23, 339.01; mass spectrum m/z (rel intensity) 429 ([M – 3CO]$^+$, 1), 373 (2), 279 (18), 261 (21), 204 (64), 146 (54), 105 (100). Anal. Calcd for $C_{26}H_{23}CrNO_7$: C, 60.82; H, 4.52; N, 2.73. Found: C, 60.40; H, 4.17; N, 2.90.

Reaction of Complex 4a with NMe_2-PBN 2a. The reaction mixture was stirred for 15 min. The red viscous oil **5a** was collected in 94% yield: R_f (hexane/CH_2Cl_2, 2:1) = 0.42; IR (neat) 1933, 2059 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.27 (br s, 9 H), 2.91 (br s, 3 H), 3.97 (br s, 1 H), 6.11 (br s, 1 H), 6.68–7.40 (br m, 9 H); ^{13}C NMR (acetone-d_6, 50 MHz) δ 26.57, 63.20, 66.04, 73.91, 129.52, 129.80, 130.32, 130.64, 130.92, 132.89, 218.53, 215.43, 339.28; mass spectrum m/z (rel intensity) 500 ([M – 2CO]$^+$, 1), 472 (4), 444 (1), 416 (5), 380 (9).

Reaction of Complex 4a with MeO-PBN 2b. The reaction mixture was stirred for 30 min. The red viscous oil **5b** was collected in 90% yield: R_f (hexane/CH_2Cl_2, 1:1) = 0.44; IR (neat) 1936, 2059 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.27 (s, 9 H), 3.78 (s, 3 H), 4.02 (s, 1 H), 6.12 (s, 1 H), 6.81–7.41 (m, 9 H); mass spectrum m/z (rel intensity) 543 ([M$^+$, 0.7), 515 ([M – CO]$^+$, 2), 459 ([M – 3CO]$^+$, 26), 431 (2), 403 (12). Anal. Calcd for $C_{27}H_{25}CrNO_8$: C, 59.67; H, 4.64; N, 2.58. Found: C, 59.36; H, 4.73; N, 2.58.

Reaction of Complex 4a with Me-PBN 2c. The reaction mixture was stirred for 40 min. The red viscous oil **5c** was collected in 98% yield: R_f (hexane/CH_2Cl_2, 1:1) = 0.53; IR (neat) 1939, 1984, 2059 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.26 (s, 9 H), 2.30 (s, 3 H), 3.97 (s, 3 H), 6.12 (s, 1 H), 7.14–7.40 (m, 9 H); mass spectrum m/z (rel intensity) 471 ([M – 2CO]$^+$, 0.3), 443 (4), 415 (1), 387 (10) 372 (13). Anal. Calcd for $C_{27}H_{25}CrNO_7$: C, 61.48; H, 4.78; N, 2.66. Found: C, 61.32; H, 4.92; N, 2.59.

(21) Cherry, W. R.; Huie, R. *J. Org. Chem.* **1985**, *50*, 1532.
(22) Boyd, D. R.; Campbell, R. M.; Coulter, P. B.; Grimshaw, J.; Neill, D. C. *J. Chem. Soc. Perkin Trans 1* **1985**, 849.
(23) Toda, F.; Tanaka, K. *Chem Lett.* **1987**, 2283.

Reaction of Complex 4a with Br-PBN 2e. The reaction mixture was stirred for 5 h. The red viscous oil **5e** was collected in 94% yield: R_f (hexane/CH_2Cl_2, 2:1) = 0.85; IR (neat) 1937, 2066 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.24 (s, 9 H), 4.07 (s, 3 H), 6.07 (s, 1 H), 7.29–7.48 (m, 9 H); mass spectrum m/z (rel intensity) 509 ([M – 3CO]$^+$, 2), 507 (2), 451 (3), 417 (6), 415 (6). Anal. Calcd for $C_{26}H_{22}BrCrNO_7$: C, 52.72; H, 3.74; N, 2.36. Found: C, 52.72; H, 3.93; N, 2.12.

Reaction of Complex 4a with Cl-PBN 2f. The reaction mixture was stirred for 5 h. The red viscous oil **5f** was collected in 99% yield: R_f (hexane/CH_2Cl_2, 4:1) = 0.33; IR (neat) 1940, 2059 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.24 (br s, 9 H), 4.07 (br s, 3 H), 6.08 (br s, 1 H), 7.34–7.41 (br m, 9 H); mass spectrum m/z (rel intensity) 407 ([M – 5CO]$^+$, 0.2), 371 (2), 207 (12), 204 (11), 182 (23), 180 (68). Anal. Calcd for $C_{26}H_{22}ClCrNO_7$: C, 57.00; H, 4.05; N, 2.57. Found: C, 57.30; H, 4.22; N, 2.49.

Reaction of Complex 4b with NMe_2-PBN 2a. The reaction mixture was stirred for 5 min. The red viscous oil **6a** was collected in 99% yield: R_f (hexane/CH_2Cl_2, 1:1) = 0.25; IR (neat) 1925, 1977, 2063 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.25 (s, 9 H), 2.91 (s, 6 H), 4.15 (s, 3 H), 5.92 (s, 1 H), 6.69–6.72 (m, 2 H), 7.22–7.25 (m, 2 H), 7.43–7.55 (m, 5 H); mass spectrum m/z (rel intensity) 662 ([M – CO]$^+$, 0.3), 602 (2), 322 (2). Anal. Calcd for $C_{28}H_{28}N_2O_7W$: C, 48.85; H, 4.10; N, 4.07. Found: C, 48.55; H, 4.10; N, 3.99.

Reaction of Complex 4b with MeO-PBN 2b. The reaction mixture was stirred for 15 min. The red viscous oil **6b** was collected in 95% yield: R_f (hexane/CH_2Cl_2, 1:1) = 0.46; IR (neat) 1920, 1977, 2063 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.22 (s, 9 H), 3.76 (s, 3 H), 4.16 (s, 3 H), 5.91 (s, 1 H), 6.85–6.89 (d, 2 H), 7.41–7.54 (m, 5 H), 7.26–7.31 (d, 2 H); mass spectrum m/z (rel intensity) 590 ([M – 3CO]$^+$, 9), 535 (4), 477 (9), 464 (8) 434 (7). Anal. Calcd for $C_{27}H_{25}NO_8W$: C, 48.02; H, 3.73; N, 2.07. Found: C, 48.42; H, 3.82; N, 2.05.

Reaction of Complex 4b with Me-PBN 2c. The reaction mixture was stirred for 40 min. The red viscous oil **6c** was collected in 95% yield: R_f (hexane/EtOAc, 10:1) = 0.43; IR (neat) 1916, 2063 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.25 (s, 9 H), 2.32 (s, 3 H), 4.18 (s, 3 H), 5.94 (s, 1 H), 7.41–7.54 (m, 5 H), 7.26–7.31 (d, 2 H); mass spectrum m/z (rel intensity) 631 ([M – CO]$^+$, 15), 603 (2), 575 (66), 547 (3), 519 (39). Anal. Calcd for $C_{27}H_{25}NO_7W$: C, 49.18; H, 3.82; N, 2.12. Found: C, 48.83; H, 3.88; N, 2.12.

Reaction of Complex 4b with H-PBN 2d. The reaction mixture was stirred for 3 h. The red viscous oil **6d** was collected in 92% yield: R_f (hexane/CH_2Cl_2, 4:1) = 0.18; IR (neat) 1919, 2063 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.20 (s, 9 H), 4.13 (s, 3 H), 5.91 (s, 1 H), 7.21–7.53 (m, 10 H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 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 Hz), 202.12, 303.04; mass spectrum m/z (rel intensity) 645 (M^+, 0.5), 617 (5), 563 (15), 561 (18), 505 (15); HRMS calcd for $C_{26}H_{23}NO_7W$ m/z 645.0978, measd m/z 645.0931.

Reaction of Complex 4b with Br-PBN 2e. The reaction mixture was stirred for 5 h. The red viscous oil **6e** was collected in 99% yield: R_f (hexane/CH_2Cl_2, 1:1) = 0.56; IR (neat) 1918, 2064 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.20 (s, 9 H), 4.20 (s, 3 H), 5.88 (s, 1 H), 7.26–7.55 (m, 9 H); mass spectrum m/z (rel intensity) 637 ([M – 2CO]$^+$, 3), 585 (2), 224 (17), 184 (8). Anal. Calcd for $C_{26}H_{22}BrNO_7W$: C, 43.12; H, 3.06; N, 1.93. Found: C, 43.11; H, 3.19; N, 1.91.

Reaction of Complex 4b with Cl-PBN 2f. The reaction mixture was stirred for 5 h. The red viscous oil **6f** was collected in 96% yield: R_f (hexane/CH_2Cl_2, 1:1) = 0.63; IR (neat) 1924, 1978, 2064 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.20 (s, 9 H), 4.19 (s, 3 H), 5.89 (s, 1 H), 7.24–7.54 (m, 9 H); mass spectrum m/z (rel intensity) 623 ([M – CO]$^+$, 0.3), 595 (4), 594 (12), 539 (7), 483 (14). Anal. Calcd for $C_{26}H_{22}ClNO_7W$: C, 45.94; H, 3.26; N, 2.06. Found: C, 46.23; H, 3.35; N, 2.03.

Reaction of Complex 4a with PBnN 3. The reaction was stirred for 10 min. The product was very unstable when the solvent was removed at rt. The hexane/EtOAc eluate was removed over vacuum at 0 °C. The red liquid **8** was collected in 73% yield: ^{1}H NMR (acetone-d_6, 250 MHz) δ 4.34 (s, 3 H),

4.50 (d, 1 H, J = 13 Hz), 4.64 (d, 1 H, J = 13 Hz), 6.08 (s, 1 H), 7.28–7.52 (m, 15 H). Satisfactory elemental analysis could not be obtained for repeated analysis.

Reaction of Complex 4b with PBnN 3. The reaction was stirred for 10 min and red viscous oil **9** was obtained in 92% yield: R_f (hexane/CH_2Cl_2, 2:1) = 0.45; IR (neat) 1939, 2064 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 4.24 (s, 3 H), 4.35 (d, 1 H, J = 13.1 Hz), 4.56 (d, 1 H, J = 13.1 Hz),5.84 (s, 1 H), 7.20–7.53 (m, 15 H).

Reaction of Complex 4b with NMe_2-PMN 1a. The reaction mixture was stirred for 5 min for the titled reaction and other PMNs unless otherwise noted. The red viscous oil **7a** was collected in 50% yield: R_f (hexane/EtOAc, 5:2) = 0.33; IR (neat) 1908, 2067 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 2.92 (s, 6 H), 3.00 (s, 3 H), 4.18 (s, 3 H), 5.53 (s, 1 H), 6.73–7.43 (m, 9 H).

Reaction of Complex 4b with MeO-PMN 1b. The red viscous oil **7b** was collected in 65% yield: R_f (hexane/EtOAc, 10:1) = 0.10; IR (neat) 1920, 1977, 2063 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.03 (s, 3 H), 3.78 (s, 3 H), 4.22 (s, 3 H), 5.58 (s, 1 H), 6.82–7.48 (m, 9 H).

Reaction of Complex 4b with Me-PMN 1c. The red viscous oil **7c** was collected in 85% yield: R_f (hexane/CH_2Cl_2, 3:1) = 0.25; IR (neat) 1921, 1978, 2064 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 2.31 (s, 3 H), 3.03 (s, 3 H), 4.20 (s, 3 H), 5.57 (s, 1 H), 7.13–7.51 (m, 9 H).

Reaction of Complex 4b with H-PMN 1d. The red viscous oil **7d** was collected in 86% yield: R_f (hexane/EtOAc, 10:1) = 0.21; mp (ethanol) 94.5 °C; IR (neat) 1919, 2065 cm^{-1}; ^1H NMR (benzene-d_6, 250 MHz) δ 2.71 (s, 3 H), 3.64 (s, 3 H), 5.49 (s, 1 H), 7.00–7.41 (m, 10 H). Anal. Calcd for $C_{23}H_{17}NO_7W$: C, 45.80; H, 2.84; N, 2.32. Found: C, 45.62; H, 2.84; N, 2.27.

Reaction of Complex 4b with Br-PMN 1e. The red viscous oil **7e** was collected in 97% yield: R_f (hexane/CH_2Cl_2, 2:1) = 0.44; IR (neat) 1925, 2064 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 2.98 (s, 3 H), 4.17 (s, 3 H), 5.48 (s, 1 H), 7.15–7.44 (m, 9 H).

Reaction of Complex 4b with Cl-PMN 1f. The red viscous oil **7f** was collected in 75% yield: R_f (hexane/EtOAc, 10:1) = 0.40; IR (neat) 1922, 2064 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.05 (s, 3 H), 4.24 (s, 3 H), 5.57 (s, 1 H), 7.21–7.52 (m, 9 H). Anal. Calcd for $C_{23}H_{16}ClNO_7W$: C, 43.32; H, 2.53; N, 2.20. Found: C, 43.60; H, 2.76; N, 2.10.

Reaction of Complex 4b with CN-PMN 1g. The reaction mixture was stirred for 1 h. The red viscous oil **7g** was collected in 91% yield: R_f (hexane/EtOAc, 10:1) = 0.12; IR (neat) 1940, 1980, 2075 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.98 (s, 3 H), 4.17 (s, 3 H), 5.50 (s, 1 H), 7.18–7.45 (m, 9 H). Anal. Calcd for $C_{24}H_{16}N_2O_7W$: C, 45.88; H, 2.57; N, 4.46. Found: C, 45.46; H, 2.57; N, 4.37.

Reaction of Complex 4b with NO_2-PMN 1h. A volume of 15 mL solvent was used instead of 2 mL as **1f** was less soluble in THF and the reaction mixture was stirred for 5 h. The red viscous oil **7h** was collected in 90% yield: R_f (hexane/EtOAc, 10:1) = 0.29; IR (neat) 1921, 2065 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.08 (s, 3 H), 4.26 (s, 3 H), 5.65 (s, 1 H), 7.41–7.56 (m, 2 H), 8.20–8.23 (m, 7 H). Anal. Calcd for $C_{23}H_{16}N_2O_9W$: C, 42.59; H, 2.47; N, 4.32. Found: C, 42.69; H, 2.64; N, 4.40.

Reaction of Complex 4c with H-PBN 2d. The reaction mixture was stirred for 3.5 h. The red viscous oil **10** was collected in 88% yield: R_f (hexane) = 0.15; IR (neat) 1939, 1984, 2059 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.27 (s, 9 H), 2.38 (s, 3 H), 3.97 (s, 3 H), 6.13 (s, 1 H), 7.20–7.43 (m, 9 H); mass spectrum (70 eV) m/z (rel intensity) 443 ([M – 3CO]$^+$, 2), 387 (2), 351 (9), 274 (27), 218 (100). Anal. Calcd for $C_{27}H_{25}CrNO_7$: C, 61.48; H, 4.78; N, 2.66. Found: C, 61.76; H, 4.90; N, 2.61.

Reaction of Complex 4d with H-PBN 2d. The reaction mixture was stirred for 1 h. The red viscous oil **11** was collected in 98% yield: R_f (hexane/CH_2Cl_2, 4:1) = 0.2; IR (neat) 1910, 1950, 2075 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.25 (s, 9 H), 2.43 (s, 3 H), 4.27 (s, 3 H), 5.91 (s, 1 H), 7.51–7.63 (m, 9 H); mass spectrum m/z (rel intensity) 659 (M$^+$, 20), 631 ([M – CO]$^+$, 47), 575 ([M – 3CO]$^+$, 100), 519 ([M – 5CO]$^+$, 55). Anal. Calcd for $C_{27}H_{25}NO_7W$: C, 49.18; H, 3.82; N, 2.12. Found: C, 49.33; H, 3.83; N, 2.07.

Demetalation of Cycloadduct 5d. The procedure was same as below but with reaction time of 1 d. The colorless solid **13** was collected in 96% yield: R_f (hexane/EtOAc, 8:1) = 0.5; mp 67.5–69.5 °C; ^1H NMR ($CDCl_3$, 60 MHz) δ 1.23 (s, 9 H), 3.53 (s, 3 H), 5.50 (s, 1 H), 7.36–8.20 (m, 10 H).

Demetalation of Cycloadduct 6d. Complex **6d** (50 mg, 0.08 mmol) was stirred in DMSO (0.5 mL, 7.05 mmol) at rt for 2 d. The crude product mixture was subjected to silica gel chromatograph using hexane/EtOAc (5:1) as eluent to yield colorless solid **13** in 59% yield: R_f (hexane/EtOAc, 8:1) = 0.5; mp 67.5–69.5 °C; ^1H NMR ($CDCl_3$, 60 MHz) δ 1.23 (s, 9 H), 3.53 (s, 3 H), 5.50 (s, 1 H), 7.36–8.20 (m, 10 H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 25.75, 51.54, 62.19, 69.46, 105.18, 128.05, 128.22, 128.61, 129.05, 130.26, 131.63, 144.45, 163.49, 164.72; IR (neat) 2975, 1696, 1638, 1493, 1366, 1357, 1240, 1075 cm^{-1}; mass spectrum (70 eV) m/z (rel intensity) 337 (M$^+$, 4), 281 (18), 260 (17), 204 (67), 105 (100), 77 (72), 57 (41); HRMS calcd for $C_{21}H_{23}NO_3$ m/z 337.1688, measd m/z 337.1698.

Reaction of Methyl 2-Phenylethynecarboxylate (12) with H-PBN 2d. The organic ester (100 mg, 0.63 mmol) and nitrone (122.7 mg, 0.69 mmol) were dissolved in THF (3.0 mL). The solution was stirred for 75 d. After removal of solvent, the crude product was chromatographed on silica gel using hexane/EtOAc (10:1) as eluent. The colourless solid **13** (67.2 mg, 0.2 mmol) was collected in 32% yield accoomplished with starting material **12** recovered (5 mg).

Reaction of Complex 14 with H-PMN 1d. A solution of complex **14** (71 mg, 152 μmol) and the nitrone, H-PMN **1d** (24 mg, 160 μmol), in THF (2 mL) was stirred at room temperature under nitrogen. The brown solution changed to yellow after 1 h. The solvent was then evaporated and the residue was flashed chromatographed on silica gel with hexane/CH_2Cl_2, (4:1) to give the pale yellow liquid **15** (21 mg, 22%): R_f (hexane/CH_2Cl_2, 4:1) = 0.4; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.79 (s, 3 H), 6.42 (d, 1 H), 7.33–7.52 (m, 5 H, J = 16.1 Hz), 7.68 (d, 1 H, J = 16.0 Hz).

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