% $[Cu(PPh_3)Cl]_4$ (Scheme I). Reflux (ca. 7 h) followed by concentration and chromatography led to the isolation of pyrroline (*S*)-**2** in 66% yield and ≥95% ee. The optical purity of the product and its absolute configuration were determined by ^{1}H NMR chiral solvation studies[9] and chemical correlation.[10] The analogous transformation of *rac*-**3** → *rac*-**4** (59%) established the origin of the C-5 arylmethyl substituent in the pyrroline products, and the isolation of stereochemically homogeneous **6** (42%, $[\alpha]_D$ −96.0° (c = 1.0, ethanol) was indicative of a high level of diastereoselectivity with respect to the alkene component.[12] In each case, the reaction mixture also included a 10–25% yield of the 3-butenyl or 3-pentenyl phenyl ketone corresponding to the starting oxaziridine.

The high level of stereoselectivity obtained in the formation of **2** and **6** was surprising in light of results obtained in other nitrogen radical cyclization reactions.[3a,d,g,o] To gain some insight into the source of stereochemical control, the diastereomeric oxaziridine **1b** was submitted to the same reaction conditions as above (Scheme II). We were astonished to find that aziridine **7** was formed as a single diastereomer in 53% yield, accompanied by only a small amount of the expected **2** in low optical purity.[13,14] The relative configuration of **7** was established by X-ray crystallography. Similar treatment of **1c** also afforded **7** as the major product. This demonstrated that the change in the C-α/C-3 relative stereochemistry (which is the same in **1b** or **1c**) and not the C-α/N-2 relationship (identical in **1a** and **1b**) was responsible for the observed product distributions. Oxaziridines **5b** and **5c** behaved similarly, albeit with lower selectivity.

A mechanistic outline consistent with these results is shown in Scheme III. Single-electron transfer[1,15] (SET) to oxaziridines **1a** or **1b**/**1c** should give rise to radical/alkoxide pairs **9a** or **9b**, respectively (the copper(II) ion generated during the SET step is depicted as the counterion for bookkeeping purposes). The high ee of the final product **2** requires that the cyclization **9a** → **10a** take place with high diastereoselectivity, either in a kinetic or thermodynamic sense. The radical center in **10a** then initiates ipso attack upon the aryl ring followed by 1,4-aryl migration to afford nitrogen-stabilized radical **11**;[16] formal loss of the elements of Cu(I) (available for another catalytic cycle) and acetaldehyde leads to **2**. Radical **9b** should add to the olefin with the same sense of intraannular selectivity to afford **10b**. In this case, however, the transition state required for phenyl transfer is disfavored, possibly due to steric interactions between the α-methyl substituent and the pyrrolidine phenyl substituent. Instead, **10b** undergoes bond reorganization, ultimately resulting in aziridine **7**. The absolute and relative stereochemistries of products **2**, **7**, and **6a** are consistent with the observed face selectivities of the olefin addition reactions.

The two reaction types reported herein constitute new departures in the use of oxaziridines for the stereoselective synthesis of heterocyclic compounds. In addition, these results provide a remarkable demonstration of the effect of stereochemistry on the fate of reactive intermediates.[17]

Acknowledgment. We thank Dr. David Vander Velde for assistance with NMR spectroscopy. We are grateful to the National Institutes of Health for the financial support of this work (GM 39402). J.A. acknowledges an Eli Lilly Granteeship (1989–1991).

Supplementary Material Available: Details of the synthesis and structure elucidations of oxaziridines **1a–c** and X-ray crystallographic data for the LAH reduction product of compounds **6**[12] and **7** (33 pages). Ordering information is given on any current masthead page.

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(9) Pirkle, W. H.; Rinaldi, P. L. *J. Org. Chem.* **1978**, *43*, 4475.

(10) An authentic sample of (*R*)-**2** was prepared from *N*-Boc-phenylalaninal[11] ((1) KO-*t*-Bu, $(EtO)_2P(O)CH_2C(O)Ph$, THF; (2) H_2, Pd/C, acetone; (3) trifluoroacetic acid) and shown to have $[\alpha]_D$ + 83.8° (c = 1.0, ethanol) (cf. $[\alpha]_D$ −82.8° (c = 1.0, ethanol) for (*S*)-**2** as prepared according to Scheme I).

(11) Fehrentz, J.-A.; Castro, B. *Synthesis* **1983**, 676–678.

(12) Pyrroline **6** was reduced with LAH to afford its *cis*-pyrrolidine derivative, the structure of which was elucidated by X-ray crystallography (supplementary material). The ee was ascertained by chiral solvation studies and the absolute configuration assigned in analogy to **2**.

(13) For a single example of a related reaction, see: Schmitz, E.; Janisch, K. *Chem. Heterocycl. Compds.* (*Engl. Transl.*) **1976**, *12*, 1432–1439; *Khim. Geterosikl. Soedin.* **1974**, *12*, 1629–1638.

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(15) A variety of intermediates related to those suggested in Scheme III can also be envisioned, such as copper-associated radicals or copper-containing metallocycles; future work will attempt to differentiate between these various possibilities.

(16) For some examples of the addition of radicals to arenes and radical-mediated ipso substitution, see: (a) Surzur, J.-M.; Stella, L. *Tetrahedron Lett.* **1974**, 2191–2194. (b) Ishibashi, H.; Nakamura, N.; Ito, K.; Kitayama, S.; Ikeda, M. *Heterocycles* **1990**, *31*, 1781–1784. (c) Ishibashi, H.; So, T. S.; Okochi, K.; Sato, T.; Nakamura, N.; Nakatani, H.; Ikeda, M. *J. Org. Chem.* **1991**, *56*, 95–102. (d) Lauk, U.; Dürst, D.; Fischer, W. *Tetrahedron Lett.* **1991**, *32*, 65–68. (e) Curran, D. P.; Liu, H. *J. Am. Chem. Soc.* **1991**, *113*, 2127–2132. (f) Bertrand, M. P.; Surzur, J.-M.; Oumar-Mahamat, H.; Moustrou, C. *J. Org. Chem.* **1991**, *56*, 3089–3097. (g) Curran, D. P.; Abraham, A. C.; Liu, H. *J. Org. Chem.* **1991**, *56*, 4335–4337. (h) Curran, D. P.; Morgan, T. M.; Schwartz, C. E.; Snider, B. B.; Dombroski, M. A. *J. Am. Chem. Soc.* **1991**, *113*, 6607–6617. (i) Motherwell, W. B.; Pennell, A. M. K. *J. Chem. Soc., Chem. Commun.* **1991**, 877–879. (j) Bowman, W. R.; Heaney, H.; Jordan, B. M. *Tetrahedron* **1991**, *47*, 10119–10128.

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Formation of Cyclic Acetylene Complexes from the Reactions between Cycloalkeno-1,2,3-selenadiazoles and $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$[1]

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Whereas cycloalkynes containing five, six, and seven carbon atoms are kinetically unstable compounds only observed as transient species, they may be stabilized by complexation to metal atoms. In 1964 Wilkinson et al. observed the $Co_2(CO)_8$-mediated transformation of octafluorocyclohexa-1,3-diene to (hexafluorohex-1-yn-3-ene)$Co_2(CO)_6$,[2] and more general methodologies for stabilizing cycloalkynes have been established by the Bennett (eq 1),[3] Buchwald (eq 2),[4] and Chisholm groups (eq 3).[5] A ring closure route involving precoordinated triple bonds has been reported by Schreiber et al.[6]

Attractive precursors for the thermal generation of such cycloalkynes, and cycloalkenynes, are 4,5-cycloalkeno-1,2,3-selenadiazoles, I.[7] We, and others, have studied the reactions of selenadiazoles with transition metal complexes and shown that they are able to form a series of compounds dependent upon the nature of the 4,5-substituents and the transition metal complex.[8]

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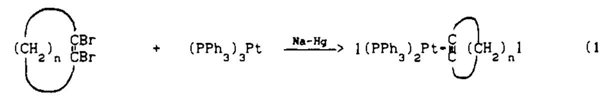
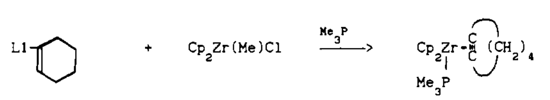


(1)



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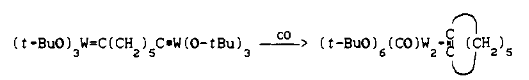


(3)

Intact selena(thia)diazole complexes of Cr, Mo, and W pentacarbonyls and cyclopentadienyldicarbonylmanganese have been isolated and characterized.[8a-c] Reactions of the diazoles with iron carbonyls led to a series of α-selena(thia) keto carbene,[8d-f] ketene,[8f] imine,[8g] and hydrazonato complexes,[8ℓ] presumably formed via ring opening of the selena(thia)diazoles to form transient α-diazoselena(thia) ketones. An example of this latter type of previously unknown organic fragment, stabilized by transition metal complexation, was recently reported.[8h] Despite this attention, no evidence has been obtained for the production of acetylenic complexes.

We now report that 4,5-R_2-1,2,3-selenadiazoles readily react with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$ in diglyme to form a series of complexes culminating in the formation of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2(RC_2R)$, V.[9] When R = Ph, H, the reactions are fast and the yields of the final acetylenic complex good. When $R_2 = (CH_2)_n$, n = 4–6, the reactions leading to Va (n = 4), Vb (n = 5), and Vc (n = 6) are slower, and intermediate complexes II–IV may be isolated, Scheme I, for n = 4.[10]

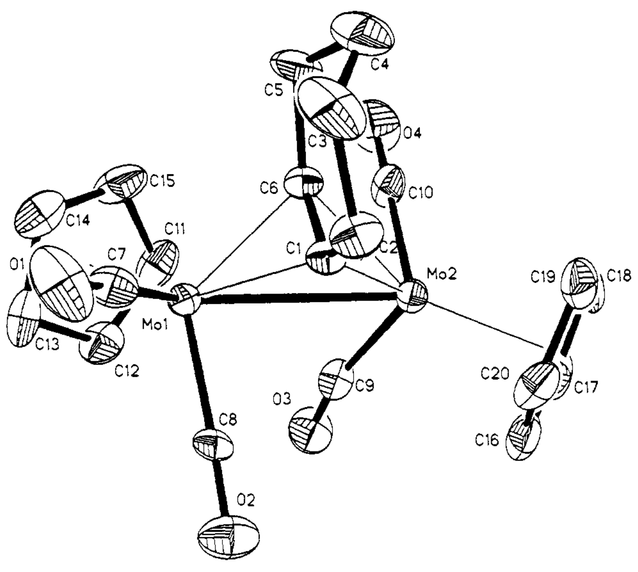
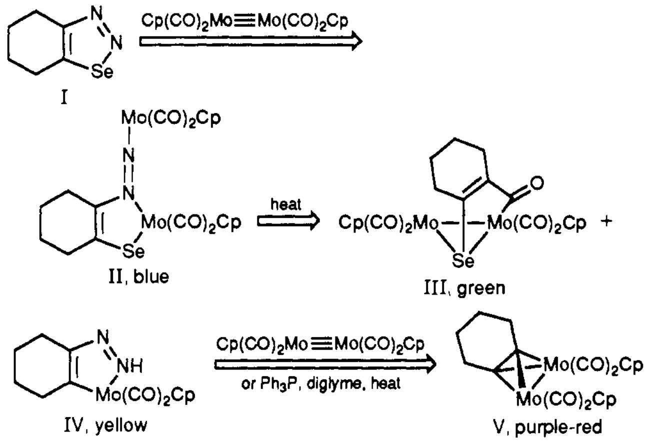


Figure 1. Structure of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2C_6H_8$. Crystal deep violet plate, space group $Pna2_1$, a = 15.699 (2) Å, b = 9.014 (1) Å, c = 26.681 (3) Å, Z = 8, R_0 = 0.035. Selected bond lengths (Å) and angles (deg): Mo(1)–Mo(2) = 2.975 (1); Mo(2)–C(1) = 2.149 (9); Mo(2)–C(6) = 2.213 (9); C(2)–C(6) = 1.35 (1); C(1)–C(2) = 1.51 (1); C(5)–C(6)–C(1) = 125; C(2)–C(1)–C(6) = 124; C(1)–C(2)–C(3) = 109.

Scheme I



A single-crystal structure of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2(C_6H_8)$, Va, is presented in Figure 1. The structure is similar to those reported for noncyclic acetylenic Mo_2 complexes for the non-acetylenic portion of the molecule.[11] Thus, it contains a single Mo–Mo bond, 2.975 (1) Å, cf. 2.984 (1) Å for $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2(C_2H_2)$,[11] and two semibridging CO groups that may also be noted from the infrared spectrum of the complex, ν(CO) 1777 cm^{-1}. The cyclohexyne portion of the molecule possesses a structure identical to that of an uncomplexed cyclohexene C=C bond of 1.35 (1) Å, with a similar conformation as determined by simple MMX calculations which are very accurate for such simple organic molecules. The overall bond lengths and angles of this portion of the molecule are somewhat different from those reported for the Pt and Zr complexes noted above. For example, the "acetylenic" C–C bond lengths for the Pt and Zr complexes are reported as 1.295 (25) Å (Zr) and 1.297 (8) Å (Pt).[3a,4c] Using such values, the authors suggested that a metallocyclopropene type of structure best represented the bonding pattern. In the present case the binding of two metal atoms to the acetylenic group further reduces the C–C bond order, but only to that expected for free cyclohexene. A similar observation was noted by Chisholm from the structure of the (μ-cycloheptyne)ditungsten complex, eq 3.[5] It would seem that coordination of the acetylenic π system to a single transition metal center results in a greater C–C bond order than implied by a cyclopropene arrangement.

Since transient colors are observed for the reactions of all the selenadiazoles with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$, we presume that they all proceed via the same type of intermediates illustrated in Scheme I for the cycloalkeno-substituted compounds. It seems that the greater stability of the linear acetylenes renders the decomposition of the corresponding intermediates II and III more kinetically favorable relative to the cycloalkyne complexes. In the sequence leading to the formation of the cycloalkyne complexes it is re-

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(9) In a typical reaction, 2.0 g of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (4.08 mmol) was dissolved in 50 mL of diglyme and heated to reflux for 3 h to convert the starting material to $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$. The progress of this reaction was monitored by infrared spectroscopy, the appearance of CO stretching frequencies at 1889 and 1854 cm^{-1} being noted. After cooling to room temperature, 0.38 g of cyclohexeno-1,2,3-selenadiazole (2 mmol) was added to the solution of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$ and the mixture was stirred for 4 h, after which time a dark blue color was observed. This solution was heated to 100 °C for 2.5 h. The solvent was removed in vacuum, and the dark residue was dissolved in a minimum of CH_2Cl_2/hexane, 1:9, placed upon a silica gel column, 2 × 15 cm, and eluted with the same solvent mixture at –20 °C. The eluate was further purified by recrystallization from the same solvent mixture to yield Va, 0.24 g (19%), mp 183–4 °C dec. Anal. Found (calcd): C, 47.02 (46.71); H, 3.72 (3.53). NMR (C_6D_6): ^1H, 5.24 (s, C_5H_5, 10 H), 2.88 (m, 4 H), 1.47 (m, 4 H); ^{13}C, 231.5 (CO), 91.99 (C_5H_5), 83.50 (C≡C), 36.45 (CH_2), 24.76 (CH_2). IR (hexane): ν(CO) 1987, 1919, 1911, 1847; FD-MS m/e (^{92}Mo), 506. Analysis by Galbraith Laboratories, Knoxville, TN.

(10) If the reaction above is worked up at the stage of the blue solution obtained at room temperature, complex IIa is obtained, 55% yield, mp >200 °C dec. Anal. Found (calcd): C, 38.29 (38.67); H, 2.96 (2.92); N, 4.36 (4.51). Full details of the spectroscopic, analytical, and structural data for complexes II, III, and IV will be the subject of a full paper dealing with the mechanism of the overall reaction.

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markable that the initial complexes formed, IIa–c, do not contain a Mo–Mo bond. This type of complex, in which Se is replaced by O, has previously been observed from the reactions of α-diazo ketones with $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$,[12] thereby illustrating the similarity of complexing behavior of the ring-closed selenadiazoles and ring-opened α-diazo ketones. The second complex formed in the sequence, IIIa–c, represents a transition metal complexed α-seleno keto ketene, similar to those isolated from the reactions of 1,2,3-selenadiazoles with iron carbonyls. The hydrazonato complex IV is a dead end in the transformation since it decomposes without formation of isolable products.

Overall we have been able to secure a new route to the formation of metal-stabilized alkynes and, more interesting, ring-strained cycloalkynes which act as bridging ligands as opposed to the "normal" terminal examples. The detailed mechanism of the process and the chemistry of the complexed cycloakynes are currently under investigation.

Acknowledgment. This research has been supported by the Robert A. Welch Foundation, Houston, TX.

Supplementary Material Available: Crystallographic experimental data, tables of crystal data, data collection, least-squares parameters, atomic coordinates, complete bond lengths and bond angles, and anisotropic thermal parameters (10 pages); listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Bromine Perbromate: Synthesis and Bromine K-Edge EXAFS Studies

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Although first reported in the 1930s,[2] bromine oxides remain the least well characterized series of main-group oxides, reflecting both their thermal instability and intractability. We recently reported[3] a detailed spectroscopic study of brown dibromine monoxide, Br_2O, which demonstrated that both the solid and vapor consist of C_{2v} molecules. Bromine K-edge EXAFS (extended X-ray absorption fine structure) data was refined to give d(Br–O) = 1.85 Å and d(Br···Br) = 3.07 Å, and hence by triangulation a Br–O–Br angle at 112°. Here we report preliminary spectroscopic and EXAFS data on solid bromine dioxide.

Schwarz and Schmeisser obtained yellow BrO_2 by passing a mixture of bromine and oxygen through a discharge tube cooled in liquid air,[4] and Schmeisser and Joerger[5] subsequently prepared what appeared to be the same compound by ozonization of bromine in Freon-11 at low temperature. The material usually given the name "bromine dioxide" is stable at low temperatures, but decomposes above ca. −50 °C to Br_2O and O_2. It is EPR silent, and since the BrO_2 monomer is an odd electron molecule, it has been assumed to be the dimeric species $O_2Br{-}BrO_2$. A preliminary Raman study[6] supported this formulation.

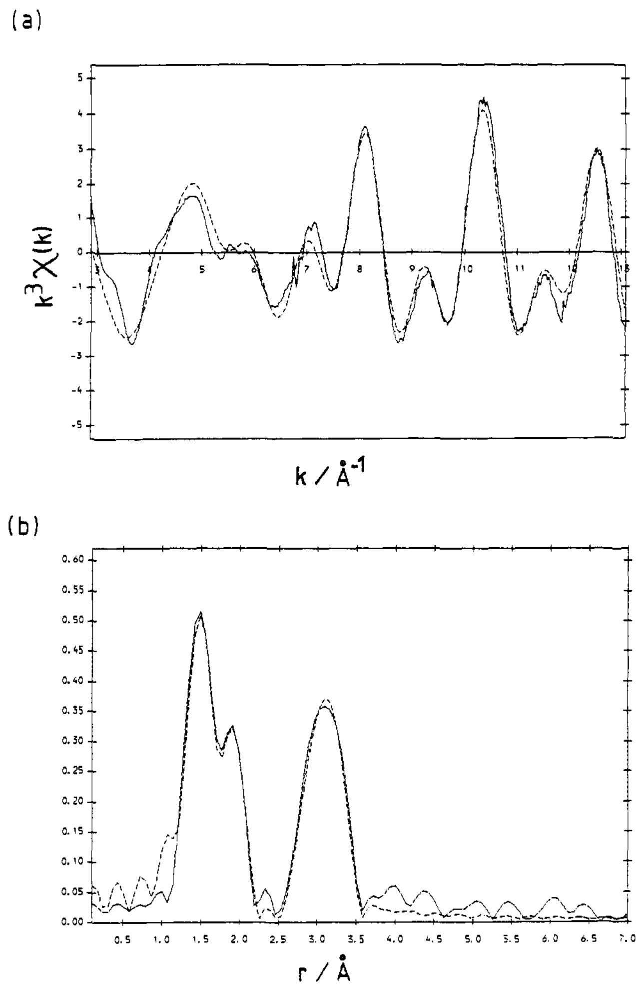

Figure 1. Background-subtracted k^3-weighted EXAFS data (a) and corresponding Fourier transform (b) obtained from an unsmoothed X-ray absorption spectrum of $BrOBrO_3$. Solid line, experiment; broken line, theory.

Our "bromine dioxide" was made by the discharge route, as described previously,[3,7] and its composition was confirmed by measuring the ratio Br_2:O_2 formed upon complete decomposition. The yellow solid is violently hydrolyzed by 2 mol dm^{-3} aqueous NaOH. Immediate examination of the solution thus produced using a combination of ^{81}Br and ^{17}O NMR spectroscopy[8] identified Br^-, BrO^-, some BrO_3^-, and most surprisingly, BrO_4^-. After 2 days, only Br^- and BrO_3^- remain, as reported previously.[9,10] The presence of BrO_4^- was confirmed by a Raman spectrum obtained from the freshly hydrolyzed solution. Perbromate, BrO_4^-, has never been observed as a product of the disproportionation of lower oxidation states of bromine, and its presence among the hydrolysis

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[1] (a) University of Southampton. (b) University of Strathclyde. (c) University of Manchester.

[2] For a review of the older literature, see: Schmeisser, M.; Brandle, K. *Adv. Inorg. Chem. Radiochem.* **1963**, *5*, 41–89.

[3] Levason, W.; Ogden, J. S.; Spicer, M. D.; Young, N. A. *J. Am. Chem. Soc.* **1990**, *112*, 1019–1022.

[4] Schwarz, R.; Schmeisser, M. *Ber.* **1937**, *70*, 1163–1166.

[5] Schmeisser, M.; Joerger, K. *Angew. Chem.* **1959**, *71*, 523–524.

[6] Pascal, J.-L.; Potier, J. *J. Chem. Soc., Chem. Commun.* **1973**, 446–447.

[7] A 1:3 Br_2/O_2 mixture at ca. 1 mm of pressure was subjected to high-voltage discharge (1600 V, 30 mA), and the product condensed at low temperature. For Raman studies a glass cell fitted with an optically flat outer window and a central glass cold-finger cooled to −126 °C (methylcyclohexane slush) was used since liquid nitrogen cooling also condenses excess ozone, which is unpredictably explosive. Cautious warming in high vacuum removed any co-condensed bromine.

[8] Levason, W.; Ogden, J. S.; Spicer, M. D.; Young, N. A. *J. Chem. Soc., Dalton Trans.* **1990**, 349–353.

[9] Independent experiments demonstrated that in basic solution BrO^- and BrO_4^- slowly react to form BrO_3^-.

[10] Schwarz, R.; Weile, H. *J. Prakt. Chem.* **1939**, *152*, 157–176.

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