

The Preparation and Properties of Some Mixed Binuclear
Rhodium(II) Acetato- β -diketonato Compounds

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Diamagnetic compounds of formula $[Rh(CH_3COO)(\beta\text{-diketonato})H_2O]_2$ (where $\beta\text{-diketonato}$ is the anion of the enol form of acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone) have been synthesized by reacting $[Rh(CH_3COO)_2H_2O]_2$ with an excess of the $\beta\text{-diketone}$. The compounds exchanged in solution the coordinated water molecules with basic ligands such as pyridine but less easily with other less basic ligands. Some adducts with pyridine and substituted pyridine were isolated in the solid state. Infrared, electronic and n.m.r. spectra are reported and possible structures are proposed.

Introduction

The chemistry of rhodium(II) has not been extensively studied until today because few sure compounds of rhodium(II) were known.

The recent isolation and characterisation¹⁻⁴ of some diamagnetic Rh^{II} carboxylates of formula $[Rh(RCOO)_2L]_2$, where L is a donor ligand, have increased the interest in the chemistry of Rh^{II} derivatives owing to the availability of suitable starting materials.¹

We thought interesting to start from $[Rh(CH_3COO)_2H_2O]_2$ in order to synthesise bis $\beta\text{-diketonatorhodium(II)}$ derivatives and to compare the physical and chemical properties of such compounds with those of related cobalt(II) derivatives which have been extensively studied by Cotton and coworkers.⁵⁻⁷

Unfortunately rhodium(II) carboxylates are very inert to the substitution of carboxylate ligands with other ligands, although they interchange very easily the carboxylate groups.¹⁻³

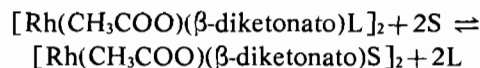
By reacting an aqueous suspension of Rh^{II} acetate with a $\beta\text{-diketone}$, such as acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, only one acetato group was exchanged and brown or green water-insoluble, diamagnetic compounds of formula $[Rh(CH_3COO)(\beta\text{-diketonato})H_2O]_2$ were obtained (Table I).

With other more sterically hindered $\beta\text{-diketones}$ such as benzoylacetone or dibenzoylmethane compounds of a different type, which are still under investigation, were obtained.

Acetylacetone afforded an anhydrous compound and no stable adduct of formula $[Rh(CH_3COO)(C_5H_5O_2)L]_2$, where L is a basic ligand like pyridine, was isolated in the solid state, though it was formed in solution of pyridine (Table IV).

Fluorinated $\beta\text{-diketones}$ gave red adducts, stable in the solid state, by exchange of the water molecule with pyridine or substituted pyridines. These adducts dissociated in benzene solution as shown by the low molecular weights found (Table I).

With other ligands such as N,N-dimethylacetamide and triethylamine the adducts were partially formed in solution as evidenced by the electronic spectra, but they have not been isolated pure in the solid state because the equilibrium



L = basic ligand

S = oxygen donor solvent (H_2O , CH_3OH)

is shifted mainly to the right.

The adducts with water were not enough soluble to be crystallized but the pyridine adducts were easily recrystallised from benzene-pet. ether; the hexafluoroacetylacetone(4) showed the peculiarity of strongly retaining in the lattice molecules of clathrated aliphatic hydrocarbon.

The clathrates lost the hydrocarbon only in vacuo (20 mmHg) at 100°.

This is remarkable since straight chain hydrocarbons are clathrated by urea, while urea is clathrated by acetylacetones.

All the obtained compounds did not react with lithium salts of the halide anions or with other similar anionic ligands. But it was still possible to exchange the residual carboxylato group, for example with the trichloroacetato group.

Experimental Section

The compounds obtained and the relative analytical data are reported in Table I; other properties are given in the same table.

(1) J. H. Chernyaev, E. V. Shenderovskaya, L. A. Nazarova and A. S. Antsyshkina, Abstracts 7th I.C.C.C., Stockholm (1962).

(2) S. A. Johnson, H. R. Hunt and H. M. Neumann, *Inorg. Chem.*, **2**, 960 (1963).

(3) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).

(4) G. Winkhaus and P. Ziegler, *Z. Anorg. Allg. Chem.*, **350**, 51 (1967).

(5) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

(6) F. A. Cotton and R. M. Sodeberg, *Inorg. Chem.*, **3**, 1 (1964).

(7) F. A. Cotton and R. C. Elder, *J. Am. Chem. Soc.*, **86**, 2294 (1964).

Table I.

Compound ^a X	Y	Colour and dec. point (°C)	C ^b	H ^b	N ^b	Rh ^b	Mol. wt. ^b in benzene
(1)	C ₃ H ₇ O ₂	—	dark brown > 250	32.50 32.55	3.86 3.83		
(2)	C ₃ H ₄ F ₃ O ₂	H ₂ O	olive-green > 250	25.20 25.90	2.70 2.90		
(3)	C ₃ HF ₆ O ₂	H ₂ O	green-yellow > 250	21.7 21.2	1.5 1.5	26.4 26.6	
(4)	C ₃ HF ₆ O ₂	C ₅ H ₅ N	brick-red 160	32.27 32.5	2.02 2.2	3.1 2.9	860/896
(5)	C ₃ HF ₆ O ₂	C ₅ H ₄ N-2CH ₃	deep-red c	33.8 34.1	2.4 2.8	3.0 3.1	898/924
(6)	C ₃ HF ₆ O ₂	C ₅ H ₄ N-2Cl	red-brown 210	29.9 30.2	1.6 1.8	2.9 3.0	678/964
(7)	C ₃ H ₄ F ₃ O ₂	C ₅ H ₅ N	brick-red 130	36.6 37.3	3.0 3.2	3.5 3.3	
(8)	C ₃ H ₄ F ₃ O ₂	C ₅ H ₄ N-2CH ₃	red-brown 90-95	38.3 38.6	3.4 3.6	3.4 3.2	

^a All the compounds have the general formula $[Rh(CH_3COO)XY]_2$. ^b Found/calculated. ^c Gradual decomposition up to 150°C.

The compounds were obtained always in nearly quantitative yields.

Infrared spectra (nujol or hexachlorobutadiene mull) were recorded on a Perkin-Elmer 237 grating instrument. ¹H and ¹⁹F n.m.r. spectra were recorded on a Perkin-Elmer R-10 instrument, using tetramethylsilane and CFCl₃ as internal standard, respectively. Melting points were determined on a Leitz Heitztschmikroskop and were not corrected. Molecular weight determinations were carried out with a Mechrolab Osmometer.

All the compounds were found to be diamagnetic in the solid state and in solution.

(1) $[Rh(CH_3COO)(CH_3COCHCOCH_3)]_2$. The sodium salt of acetylacetonate (three times the stoichiometric amount required) was added to the green aqueous solution of $[Rh(CH_3COO)_2(H_2O)]_2$. By refluxing for 12 hr. under nitrogen, a dark brown precipitate was obtained. The colourless solution was filtered and the compound was washed several times with water and then dried in vacuo. The microcrystalline compound is insoluble in the common solvents. It is soluble easily in pyridine and other donor solvents, giving very unstable adducts.

(2) $[Rh(CH_3COO)(CF_3COCHCOCH_3)(H_2O)]_2$. Trifluoroacetylacetonate (6.0 ml), was added to a solution of $[Rh(CH_3COO)_2(H_2O)]_2$ (1.0 g) in water (400 ml). After refluxing under nitrogen for 22 hr. the green precipitate was separated from the colourless solution by filtration. The compound was washed several times with water and then dried under vacuum. The crystalline compound (1.0 g) is practically insoluble in the common organic solvents.

(3) $[Rh(CH_3COO)(CF_3COCHCOCF_3)(H_2O)]_2$. Hexafluoroacetylacetonate (1.65 g) was added to a solution of $[Rh(CH_3COO)_2(H_2O)]_2$ (0.3 g) in water (100 ml.). After refluxing for 20 hr. under nitrogen, a precipitate was filtered. The solution was refluxed for additional 20 hr. with additional hexafluoroacetylacetonate (1.65 g). The now colourless solution was filtered again the combined precipitates were washed several times with water and dried under vacuo.

The crystalline compound could be sublimed (260°C/0.1 mm) with considerable decomposition. The com-

pound is slightly soluble in methanol and ethanol and reacts quite fast with NO, (CH₃)₂SO, PPh₃, (C₂H₅)₃N, C₅H₅N and substituted pyridines, always giving red-brown adducts of different stability.

(4) $[Rh(CH_3COO)(CF_3COCHCOCF_3)(C_5H_5N)]_2$. Compound (3) was dissolved in pyridine at room temperature. The dark-red solution was evaporated to dryness and the red oil obtained was dissolved in petroleum ether. On cooling the concentrated solution for many hours to -10°C, a red-violet precipitate in beautiful crystals was obtained. The compound was filtered and dried to constant weight. During this prolonged operation the compound turned brick-red because it released some solvent of crystallisation.

The crystalline compound is very soluble in ether and chlorinated solvents, slightly soluble in alcohol, acetone, benzene and petroleum ether.

(5) $[Rh(CH_3COO)(CF_3COCHCOCF_3)(C_5H_4N-2CH_3)]_2$. Compound (3) slowly dissolves at room temperature in 2-methylpyridine, giving a red-brown solution. Evaporation to dryness under reduced pressure yields a red-brown residue which was then dissolved in petroleum ether. The solution was concentrated and on cooling to -10°C for many hours, deep-red crystals of the analytically pure compound were obtained. The compound has solubilities similar to those of compounds (4).

(6) $[Rh(CH_3COO)(CF_3COCHCOCF_3)(C_5H_4N-2Cl)]_2$. This compound was prepared as the preceding one, obtaining a crystalline red-brown compound with solubilities similar to compounds (4) and (5).

(7) $[Rh(CH_3COO)(CF_3COCHCOCH_3)(C_5H_5N)]_2$. Compound (2) was dissolved in pyridine at room temperature. The cherry-red solution was evaporated to dryness and the residue was dissolved in a mixture of benzene-petroleum ether (1:1). On evaporating and on adding petroleum ether, brick-red crystals of the analytically pure compound were obtained. The compound is generally less soluble than compound (4).

(8) $[Rh(CH_3COO)(CF_3COCHCOCH_3)(C_5H_4N-2CH_3)]_2$. Compound (2) slowly dissolved on heating in C₅H₄N-

2CH₃. By evaporating the resulting red-brown solution, a residue was obtained which was then dissolved in a mixture of benzene-petroleum ether (2:3). On evaporating and on adding petroleum ether, red-brown crystals of the analytically pure compound were obtained. The compound has solubilities similar to compound (7).

Results and Discussion

Infrared spectra. The infrared spectra in the region 1650-1200 cm⁻¹ (Table II) are complex, owing to the overlap of absorption due to the acetato and β-diketonato groups.

The assignments reported in Table II were tentatively made on the basis of the shift to higher frequencies of the bands due to the β-diketonato moiety

atom.⁹ As expected⁸ ν(C≡O) and ν(C≡C) shifted to higher frequencies by substituting methyl with trifluoromethyl groups. However, the assignment of the ν(C≡C) stretchings in the trifluoromethyl derivatives has been made tentatively because of the overlap of this absorption with the asymmetric ν₂(C≡O) stretching of the acetato group (see Table II).

In the compounds with coordinated water two bands were found at 3635-25 cm⁻¹ (sharp) and at nearly 3420 cm⁻¹ (broad); these two bands must be attributed to the coordinated water as they were shifted upon deuteration

to 2800 cm⁻¹ ($-\frac{\nu_H}{\nu_D} = 1.30$) and 2520 cm⁻¹ ($-\frac{\nu_H}{\nu_D} =$

1.36) respectively. Besides, they are absent in the adducts with pyridine.

Table II. Infrared spectra ^a

Compound	C≡O acetato		C≡O β-diketonato ^b		C≡C diketonato ^b	
	ν ₂ asym.	ν ₁ sym.	ν _{symm.}	ν _{asymm.}	ν _{C≡C}	ν _(C≡C+C-R)
(1)	1560-1570 (doublet)	1440	1540	1420 (broad)	1510	1250
(2)	1560 ^c	1425	1610	1485	1540 ^c	1310
(3)	1560 ^c	1420	1620-1600 (doublet)	1480	1550 ^c	1350 (doublet)
(4)	1560 ^c	1450-1420	1610	1490	1550 ^c	1345
(5)	1565 ^c	1450	1610	1485	1550 ^c	1350
(6)	1570 ^c	1440	1612	1490	1560 ^c	1345
(7)	1570	1440	1605	1485	1530	1310
(8)	1570	1430	1607	1480	1530	1310

^a Nujol mull. ^b See ref. (9). ^c The absorptions could be interchanged.

when a methyl group was substituted by a trifluoromethyl group and by comparison of the spectrum of [Rh(CH₃COO)(C₅H₇O₂)₂] with that of [Rh(CH₃COO)₂]₂.

The asymmetric ν₂(C≡O) stretching of the acetato group is at lower frequency than that found for [Rh(CH₃COO)₂]₂ (e.g. 1560-1570 cm⁻¹ against 1588-1580 cm⁻¹)^{1,2,3,4} and the difference Δ(ν₂ - ν₁) has lower values than that found in [Rh(CH₃COO)₂]₂ (e.g. 130-145 cm⁻¹ against 162-150 cm⁻¹)^{1,3,4}. These data confirm that the acetato group is still symmetrically bound as a bidentate ligand, although it is not possible³ to deduce surely from the infrared spectra if it is a bridging or a chelated group.

The low values found here for ν₂ and Δ(ν₂ - ν₁) seem to support the view that less electronic charge is on the C≡O groups, possibly because the β-diketonato ligand is more able to accept the negative charge than acetato group. However, no appreciable variations of ν₂ and Δ(ν₂ - ν₁) have been detected by change of the methyl groups on the β-diketonato ligand with the trifluoromethyl groups or by change of the neutral ligand bound to the rhodium atom.

The absorptions due to the β-diketonato ligands are not very different from those reported for other chelated β-diketonato compounds.⁸ Our assignments are based on those of recent papers.⁹

The β-diketonato ligands appear, in our compounds, to be bound to the metal through the oxygen atoms of the carbonyl groups and not through the γ carbon

In [Rh(CH₃COO)₂H₂O]₂ only a broad absorption at nearly 3400 cm⁻¹ due to the coordinated water was observed.

The sharp band at nearly 3600 cm⁻¹ is rather unusual although a similar sharp band was observed in some nickel(II) derivatives with EDTA having a coordinated water molecule.¹⁰ Further, an absorption at 3610 cm⁻¹ was recently found¹¹ on the dimeric rhodium(III) acetylacetonate of formula [Rh₂(C₅H₇O₂)₄Cl₂ · 3H₂O].

Electronic spectra. The electronic spectra (Table III) generally show three bands in the visible region.

Table III. Electronic Spectra

Compound	Solvent	λ _{max}	ε
(1)	CH ₃ OH	688	52
(1)	C ₅ H ₅ N	535	526
		400 (sh)	2650
(2)	CH ₃ OH	682	130
		420 (sh)	2250
		360	4100
(7)	»	560	137
		420 (sh)	2380
		353	3590
(3)	»	600-610 (sh)	210
		450	2950
		390	2580
(4) ^a	»	445	2970
		440	3890

^a The absorption band at nearly 600 mμ is completely covered by the strong absorption at 445 mμ.

(8) K. Nakamoto, «Infrared Spectra of Inorganic and Coordination Compounds», J. Wiley and Sons., N.Y., p. 216 (1963).

(9) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 6, 433 and 440 (1967).

(10) F. P. Dwyer and D. P. Mellor, «Chelating Agents and Metal Chelates», Academic Press, p. 320 (1964).

(11) S. C. Chatteray and R. E. Sievers, *Inorg. Chem.*, 6, 408 (1967).

The band at nearly 600-550 $m\mu$ is at higher value than the related band in the homologous bisacetato compounds.¹ This absorption shifts to lower wavelength by substituting the oxygen donor atom of the monodentate ligand (H_2O or CH_3OH) with nitrogen donor atom (pyridine). A similar behaviour was shown¹ by the adducts of the bisacetato compound.

It can be explained by assuming that this absorption comes from a $d-d$ transition, which is supported also by the low values of the extinction coefficient. In this case, the spectrochemical properties of oxygen or nitrogen donor atoms predict an increase of the d orbital splitting in the order $O < N$.

One of the other two bands (at nearly 360 $m\mu$) must be assigned to some charge-transfer transition between the metal and the β -diketonato ligand; the other one (at nearly 420 $m\mu$) can be compared with the related band present in the adducts of $[Rh(CH_3COO)_2]_2$.¹

The very high extinction coefficients found for this latter absorption in the β -diketonato compounds must be attributed to the overlap with the strong absorption at nearly 360 $m\mu$.

Table IV. 1H n.m.r. spectra^a (τ values)

Compound	γ H	CH_3 on the pyridine ring	acetato CH_3	β -diketonato CH_3
(4)	4.20	—	7.88	—
(5)	4.24	7.2	7.87	—
(6)	4.13	—	7.85	—
(7)	4.62	—	7.89-7.92-7.97	8.14-8.16
(8)	4.58	7.18	7.86-7.87-7.90	8.08-8.10

^a TMS as internal standard; $CDCl_3$ solutions. ^b All the compounds gave absorptions due to the pyridine ring protons in the expected region (1-3 τ).

Table V. ^{19}F n.m.r. spectra

Compound	Solvent	δ (p.p.m.) ^a
(2)	CH_3OH	7.28 - 7.35
(3)	CH_3OH	7.48
(4)	$CHCl_3$	7.60
(5)	$CHCl_3$	7.57
(6)	$CHCl_3$	7.52
(7)	$CHCl_3$	7.40 - 7.46 (ratio 1.3 - 1.4)
(8)	$CHCl_3$	7.35 - 7.41 (ratio 1.1 - 1.0)

^a $CFCl_3$ as internal standard.

N.m.r. spectra. The 1H (Table IV) and ^{19}F (Table V) n.m.r. spectra of compounds (4), (5), (6) agreed very well with a completely symmetrical structure also in the case of substituted pyridine ligands. This can be explained by a rotation or better a fast dissociation of these ligands as evidenced also by molecular weight measurements.

From the n.m.r. spectra it is confirmed that the β -diketonato ligand is bound to the metal through the oxygen atoms of the carbonyl groups and not through the γ carbon atom. In fact no Rh-H coupling was detected.

Compound (7) showed a more complex spectrum (Figure 1) which can be explained only by the presence of a mixture of two isomeric compounds:

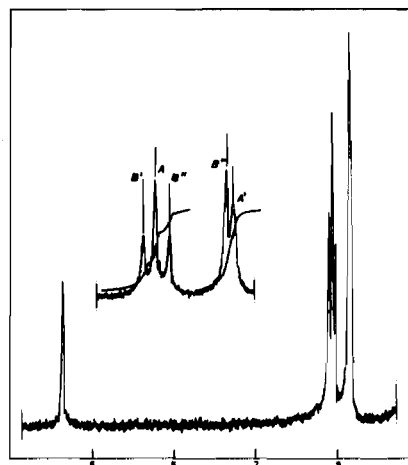


Figure 1. 1H n.m.r. spectrum of the mixture of reaction of formula $[Rh(CH_3COO)(C_5H_4F_3O_2)(C_5H_5N)]_2$.

Indeed only one signal due to the γ proton of the β -diketonato ligand, was detected, but (Figure 1) three methyl signals of acetato (peaks B', B'', A) and two signals of methyl of β -diketonato group (peaks B''', A') were detected.

Peaks B' and B'' were of equal area and their total area corresponded to the area of peak B''', similarly peak A corresponded to peak A'. The ^{19}F spectrum (Table V) showed two trifluoromethyl groups with a ratio 1.4-1.3 which corresponds to the area ratio of peaks B''' and A'.

Similar spectra, but less resolved, were found for compound (8).

These spectra can be explained by assuming that one isomer has two non-equivalent acetato groups (peaks B' and B'') and two equivalent β -diketonato groups (peak B'''), while the other isomer has both kinds of groups completely equivalent (peaks A and A').

Conclusion

The molecular weights, the diamagnetism and the electronic spectra of the compounds here reported confirm that the basic structure of $[Rh(CH_3COO)_2L]_2$ with a strong metal-metal bond and two monodentate ligands L is still present. On the other hand, infrared and n.m.r. spectra show that in the compounds which have a β -diketonato ligand with a two-fold axis, there is always a high molecular symmetry. Indeed only one type of acetato and β -diketonato group is detected.

If only non-bonding interactions of the ligands are considered, structures (c), (d) and (f) should be more stable than structures (a), (b) and (e) (Figure 2).

Indeed with a probable Rh-Rh distance¹² of 2.4-2.6 Å the non-bonding repulsion of the π system of the chelated rings should be very strong, if no distortion is present. However a staggered configuration of the chelated rings by a rotation of 90° around the

(12) M. A. Porai-Koshits and A. S. Antsyshkina, *Dokl. Akad. Nauk. SSSR*, 146, 1102 (1962); L. M. Dikarjeva, Abstracts 7th Int. Congress and Symposium on Crystal Growth, Moscow (1966).

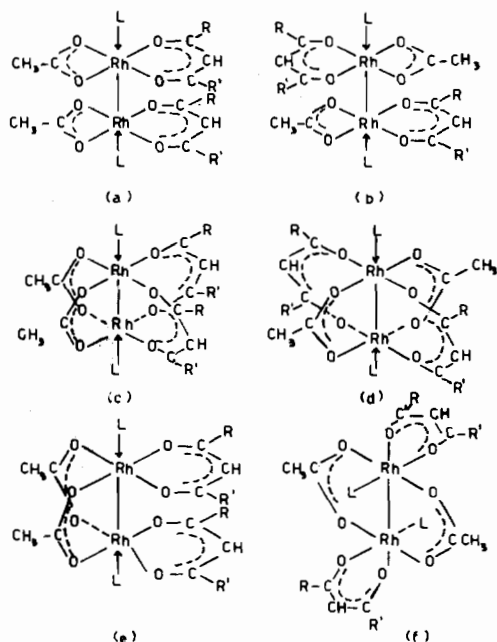


Figure 2. Possible structures.

L-Rh-Rh-L axis) should decrease the non-bonding repulsions of structures (a) and (b).

On the other hand structures (a) and (b) are not very probable because they need a complete rearrangement of the «cage» structure¹ of $[\text{Rh}(\text{CH}_3\text{COO})_2\text{H}_2\text{O}]_2$.

Also structure (c) and (d) are not very probable because with a metal-metal bond of 2.5-2.6 Å the bridging β -diketonato group would be very distorted, since its bite is 2.8-2.9 Å. Besides, only one compound with a β -diketonato group bridging in such a way was briefly reported¹³ in the literature.

(13) J. P. Fackler, *Progress in Inorganic Chemistry*, Ed. F. A. Cotton, vol. 7, 371 (1966).

If the n.m.r. spectra are considered the *trans*-isomer must be in a conformation such to have only one type of acetato and β -diketonato signals, while the *cis* isomer must have two different methyl signals corresponding to the acetato groups, but only one methyl or trifluoromethyl signal corresponding to the β -diketonato groups.

Structure (f) must then be ruled out for the following reasons: the *trans* isomer has a center of symmetry, to which corresponds a n.m.r. spectrum with only one type of acetato and β -diketonato groups, but the *cis* isomer has a symmetry plane perpendicular to the plane in which the acetato groups lie. This situation corresponds to an n.m.r. spectrum with only one signal for the methyls of the acetato groups and two signals for the methyls of the β -diketonato groups (the same number of signals for the trifluoromethyls).

Also structures (c) and (d) and the eclipsed structure (a) and (b) must be definitively ruled out because both *cis* and *trans* isomers have a similar n.m.r. spectrum with one signal for the acetato groups and one signal for the β -diketonato groups.

Besides the staggered structure derived from (a) or (b) has, whatever is the orientation of the ligands, equivalent methyl groups from the acetato ligands.

Only structure (e), even if distorted as to remove the non bonding repulsion of the two chelated rings (which should form a dihedral angle) agrees very well with the n.m.r. spectra found.

It is possible that this structure corresponds to the real structure in solution of these rhodium(II) acetato β -diketonato compounds. In the solid state the compounds are probably polymeric, when anhydrous.

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