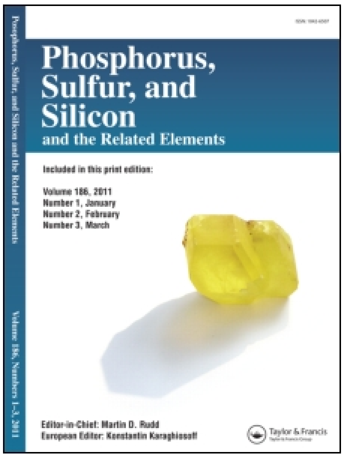

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Sabounchei, Seyyed Javad , Eskandaripour, Farahnaz and Moseybiyan, Parvin(2005) 'A Synthesis and Multinuclear NMR Study of New β -Phosphorus Ylides and Their Palladium (II) Complexes', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 9, 2013 — 2021

To link to this Article: DOI: 10.1080/104265090902778

URL: http://dx.doi.org/10.1080/104265090902778

Phosphorus, Sulfur, and Silicon, 180:2013–2021, 2005
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426509090278

A Synthesis and Multinuclear NMR Study of New β-Phosphorus Ylides and Their Palladium (II) Complexes

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A one-step synthesis of sterically congested phosphorous ylides in moderate-to-good yields by the reaction of CH-acids (Acetylacetone and diethyl malonate), dimethyl acetylenedicarboxylate, and tri-p.tolylphosphine and their palladium (II) complex is reported. The structures of this compound were confirmed by IR and ^1H, ^{31}P, ^{13}C NMR spectroscopy and elemental analysis. The NMR spectra showed that each of these compounds (in $CDCl_3$ as a solvent) contained two rotamers and diastereoisomers with unequal population.

Keywords Acetylacetone; diethyl malonate; palladium; triparatolylphosphine; ylides

INTRODUCTION

Phosphorus ylides are reactive compounds, which take part in many reactions of value in the synthesis of organicproducts.[1–4] Phosphorus ylides are synthetic targets of interest because of their value for a variety of industrial, biological, and chemical synthetic uses.[4–10] Several methods have been developed for the preparation of phosphorus ylides. These ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually obtained from the phosphine and alkyl halid. Phosphonium salts also are prepared by the Michael addition of phosphorus nucleophiles to activated olefins in other ways.[4] The phosphonium salts are most often converted to the ylide by treatment with a strong base, although weaker bases can be used if the salt is acidic enough. We wish to report an efficient synthetic route to phosphorus ylides using triparatolylphosphine,

Received August 10, 2004; in final form September 24, 2004.

We are highly grateful to the University of Bu-Ali-Sina for a grant and Mr. Zebarjadian for recording the NMR spectra.

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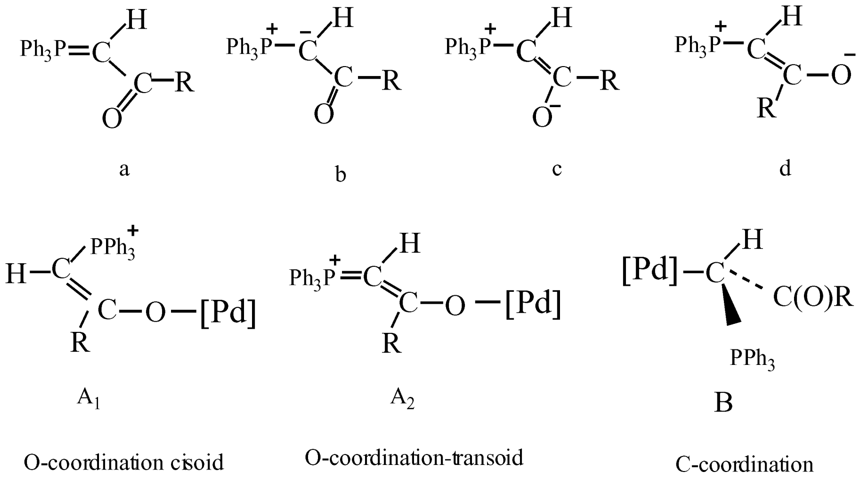
electron-deficient acetylenic esters such as dialkyl acetylenedicarboxylates, and concomitant protonation such as 2,4-pentanedione. Palladium complexes are widely used in catalysis.[11] Examples include the Heck reaction,[12] the Wacker process,[13] and the alkoxy–carbonylation of alkenes.[14] In several of these catalytic processes, palladium-hydrides have been claimed to be involved as key intermediates in the catalytic cycle.[15] The coordination chemistry of the phosphoranes of the type α-keto stabilized ylides $Ph_3P{=}C(H)COR$ have shown useful applications in organometallic chemistry (due to their ambidentate character as ligands) and reactants or valuable key intermediates in metal-mediated organic synthesis. This ambidentate character facilitates the preparation of stable metal complexes in which the ylide could be O-co-ordinated (forms A_1, A_2, Scheme 1) or C-co-ordinated (from B, Scheme 1) with both modes rationalized in terms of the resonance forms a–c together with the isomeric formal. However, while a large number of compounds containing C-coordinated ylides are known, very few examples of O-bonded ones have been reported.[16–19]

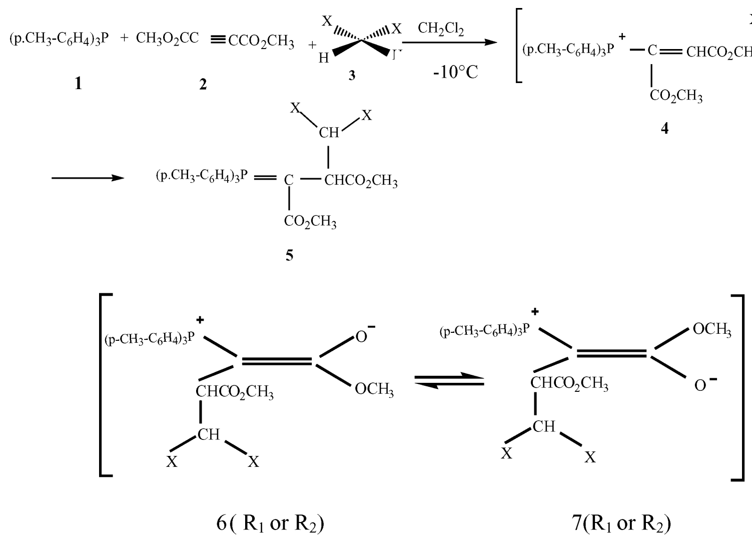


SCHEME 1

The phosphorus ylide complexes have been well investigated. They are versatile ligands for a very small number of catalytic reactions. For example, the hydrogenation of olefins and the cyclotrimerization and polymerization of acetylenes, but the most important application is in the industrially used SHOP[17] process. Data on Pd (II) analogous to Pd(0) complexes studied in the present work can be found in Navarro's and Albanese works.[20] This work reports the complex obtained from the reaction of the β-carbonyl–stabilized ylide with Pd (II).

RESULTS AND DISCUSSION

The ylide may result from the initial addition of tri-p.tolylephosphine **1** to the acetylenedicarboxylate **2** and concomitant protonation of the l:1 adduct, followed by attack of the CH-acid anion on the vinyltri-p.tol phosphonium cation to form the stabilized phosphorane 5a and 5b (5a, X = COMe; 5b, X = CO_2Et, Scheme 2).



SCHEME 2 R_1 = major rotamer and R_2 = minor rotamer.

Spectroscopic techniques such as IR and NMR spectroscopy enable one to distinguish between O(carbonyl) and C-coordination. Coordination of a ylide through carbon causes an increase in ν(CO), while for O-coordination, a lowering of ν(CO) is expected (Table I). The IR spectrum of the complex shows an intense absorption at 1730 cm^{-1} corresponding to the stretching ν(C=O). This absorption has been shifted to slightly higher wave number with respect to the free ylide[16] (ylide, ν(CO) = 1726 cm^{-1}). This suggests that the ylide is coordinated through the carbon atom.

The ^{31}P NMR spectrum of complex 5c exhibited two singlets at $\delta_1 = 26.05$ ppm and $\delta_2 = 26.67$ ppm (Figure 1(a)), and complex 5d exhibited two singlets at $\delta_1 = 29.64$ ppm and $\delta_2 = 27.76$ ppm which were related to major and minor rotamers, and shifted downfield relative to the free ylide $\delta_P = 20.0$ ppm (Figure 1(b)) and are in agreement with C-coordinations (Table II). The ^1H NMR spectrum of 5c shows 2 broad singlet resonances attributed to the methane proton $CH(COCH_3)_2$ at

TABLE I ν**(CO) of Selected Phosphoranes and Their Metal Complexes**

Compound	ν (CO) cm^{-1}	Ref.
$Ph_3CHCOPh$(BPPY)	1525	19
Free ylide (5a)	1726	This article
Free ylide (5b)	1732	This article
C-coordination		
BPPY.$HgCl_2$	1635	14
BPPY.$HgBr_2$	1630	14
Complex [($C_{32}H_{35}O_6P$)$PdCl_2$]	1730	This article
Complex [($C_{34}H_{39}O_8P$)$PdCl_2$]	1736	This article
O-coordination		
[(Sn(CH_3·BPPY]Cl	1480	20
[(Sn(Ph_3·BPPY]Cl	1470	20

5.4 ppm and 5.81 ppm (product major and minor) and a multiplet signal at 3.45 ppm to the $CHCO_2CH_3$. This broad resonance probably arises from very close chemical shifts of the methinic proton of the two diastereoisomers (Figure 2).

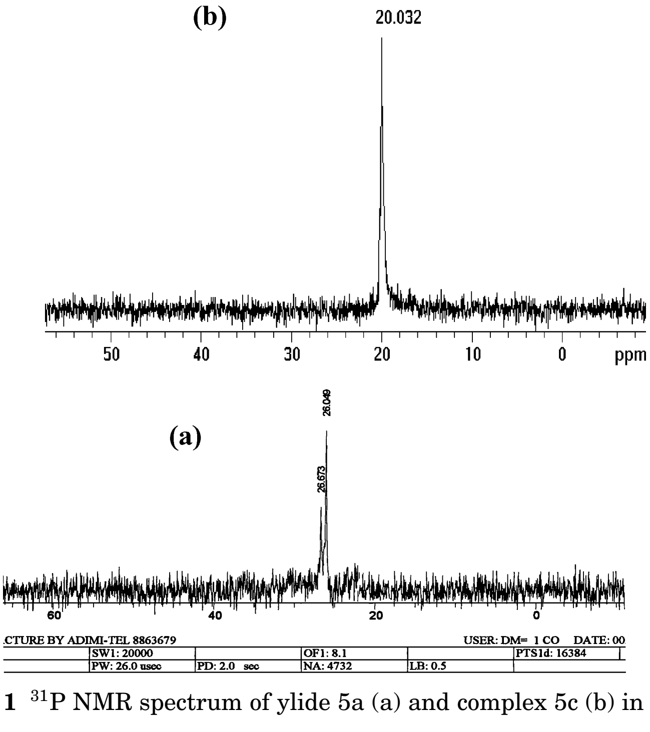
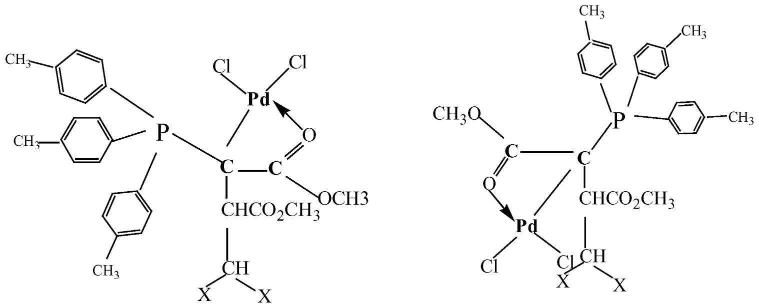


FIGURE 1 ^{31}P NMR spectrum of ylide 5a (a) and complex 5c (b) in $CDCl_3$ at 25°C.



5c **5d**

FIGURE 2 The suggested structures (diastereoisomers) for 5c and 5d.

TABLE II ^{1}H NMR and ^{31}P NMR Data of Ylides and Their Complexes With Palladium

Compound	δ (CH)	$^2J_{PH}$	$^3J_{PH}$	δ (^{31}P)	Reference
$Ph_3PCHCOPh$(BPPY)	4.44(d)	24.5	—	15.59	20
$HgCl_2$.BPPY	5.24(d)	10.4	—	23.41	20
Free β-ylide (5a)	5.01	—	11.74	20.01	This article
	5.44	—	10.93		
	3.02	—	m		
Free β-ylide (5b)	4.33	—	15.2	22.23, 28.65	This article
	4.80	—	16.12		
	3.30	—	m		
Complex (5c)	5.40	—	br	26.05, 26.67	This article
	5.81	—	br		
	3.45	—	m		
Complex (5d)	5.66	—	br	27.76, 29.64	This article
	5.88	—	br		
	3.8	—	m		

In $CDCl_3$, 90 MHz values (ppm) are relative to internal TMS and are relative to external 85% phosphoric acid. d, doublet; m, multiplet; br, broad.

TABLE III ^{13}C NMR Data of Ylide and Their Complexes

Compound	P-^{13}C	Ph	C=O	Reference
BPPY	50.21(d)	126.18–132.66	184.37	20
BPPY.$HgCl_2$	46.98(d)	127.70–133.12	189.69	20
Ylied 5a	39.82(R_1)	126.5–134.9	170,174(R_1)	This article
	40.41(R_2)		171,174.(R_2)	
Complex 5c	33.27(R_1)	115–146(R_1,R_2)	191.52,166.8(R_1)	This article
	31.70(R_2)		191.52,171.2(R_2)	

In $CDCl_3$; values (ppm); d, doublet.

Finally, the ^{13}C NMR data of the complex and the title ylide are listed in Table III along with possible assignments. The most interesting aspect of the ^{13}C NMR of the complex is the upfield shift of the CH's signals due to ylidic carbon, while the adjacent carbonyl carbon (175 ppm in ylide) is shifted down field (191 ppm in complex), indicating much lower shielding of carbon of the CO group in the complex, as expected for C-coordination. Attempts to get good ^{13}C NMR spectra for 5b and 5d were unsuccesfull because of low solubility.

EXPERIMENTAL

Melting points were measured with a SMPI apparatus. Solid-state FT-IR spectra in the region of 400–4000 cm^{-1} using KBr pellets were obtained on a (Shimadzu-435) spectrophotometer. ^{1}H and ^{31}P spectra were obtained using a 90 MHz instrument with a regional sophisticated instrumentation at Bu-Ali Sina University, and ^{13}C NMR spectra were measured with a BRUKER DRX–500 spectrometer of Sharip University in Tehran. Elemental analyses were carried out at the Research Institute of Petroleum Industry.

SYNTHESIS

Dimethyl 2-(1-Acetyl-2-oxopropyl)-3-(tri-p.tolylphosphineanylidene) Succinate 5a

To a magnetically stirred solution of tri-p-tolyl phosphine (0.304 gr, 1 mmol) and 2,4-pentanedione (0.1 ml, 1 mmol) in CH_2Cl_2 (5 mL) was added drop wise to a mixture of dimethyl acetylenedicarboxylate (0.12 ml, 1 mmol) in CH_2Cl_2 (3 mL) at −10°C over 15 min. The mixture was allowed to warm up to room temperature. The solvent was removed under reduced pressure and the residue was crystallized from ethylacetate-light petroleum ether (1:3). Crystals were collected by filtration. White crystals (0.345 g), m.p. 152–154°C yield 69%. IR (KBr)(υ_{max}.cm^{-1}): 1726 (CO ester): 1625 (CO keton); 1430 (P—C = arom). ^{31}P NMR ($CDCl_3$) δ_P: 20.01. ^{1}H NMR ($CDCl_3$, major rotamer (R_1) 53.5% and minor rotamer (R_2) 46.5%: δ_H: 2.10, 2.20 (6H, 2s, 2CH_3); 3.02 (1H, m, $CHCO_2Me$); 3.54 (R_1) and 3.02 (R_2)(6H, 2s, 2OCH_3); 5.4 (R_1, d, br, $^{3}J_{HH}$ = 10.93 Hz) and 5.01 (R_2, d, br, $^{3}J_{HH}$ = 11.74 Hz) (1H, 2br, 2$CH(COCH_3)_2$); 2.329 (H, 1s, 3CH_3); 7.2–7.5 (12H, m, arom).^{13}C NMR ($CDCl_3$)δ_C: 21.20 (3CH_3), 30.61 (R_1) and 30.36 (R_2) (4CH_3); 39.82 (R_1, d, $^{1}J_{PC}$ = 124.4 Hz) and (R_2, d, $^{1}J_{PC}$ = 132.5 Hz)(P = C); 44.73(R_1, d, $^{2}J_{PC}$ = 13.3 Hz) and 43.63 (R_2, d, $^{2}J_{PC}$ = 13.2 Hz) (P = C-^{13}C); 48.76(R_1), 51.78 (R_2)(4OCH_3); 67.16 (R_1) and 68.56 (R_2) ($^{13}CH(COCH_3)_2$);

125.97-133.62 (fairly complex, aromatic); 170.09 (R_1, d, $^2J_{PC} = 13.8$ Hz), 174.40 (R_1, d,$^3J_{PC} = 3.9$ Hz), 171.16 (R_2, d, $^2J_{PC} = 18.6$ Hz) and 174.5 (R_2, d, $^3J_{PC} = 5.9$ Hz) (4CO of esters), 202.45, 204.20 (R_1) and 204.37 (R_2) (4CO of ketones). Analysis: Calc. for $C_{32}H_{35}O_6P$ (546): C, 70.33%; H, 6.41%. Found: C, 70.74%; H, 6.82%.

1,1-Diethyl 2,3-Dimethyl-3-(tri-p.tolylphosphineanylidene)-1,1,2,3-propanetetracarboxylate 5b

White crystals (0.21 g), m.p 181.3–182.4°C. yield 37%. IR (KBr) (υ_{max}, cm^{-1}): 1732 (CO ester); 1602(CO keton); 1436(P—C=C arom). ^{31}P NMR ($CDCl_3$)δ_P: 28.65 (R_1) and 22.23 (R_2). ^{1}H NMR ($CDCl_3$, major rotamer (R_1) 77.1% and minor rotamer (R_2) 22.9%) δ_H: 1.24 (R_1) and 0.83 (R_2) (6H, m, $4CH_3$); 2.28 (9H, s, $3CH_3$); 3.31–3.36 (R_1) and 3.23–3.29 (R_2) (1H, m, $CHCO_2CH_3$); 3.53 (R_1), 3.69 (R_1) and 3.46 (R_2) 3.78 (R_2)(6H,m ,$4OCH_3$); 4.14(R_1) and 3.96 (R_2) (4H, m, $4OCH_2$); 4.33 (R_1, d, ^{3} $J_{HH} = 15.2$ Hz) 4.80 (R_2, d, $^3J_{HH} = 16.12$ Hz) (1H, $CH(CO_2Et)_2$); 7.17–7.56(12H, m, arom). ^{13}CNMR($CDCl_3$)δ_C; 13.98(R_1), 10.91(R_2)($4CH_3$); 21.53 (R_1) and 21.46 (R_2) ($3CH_3$); 25.92 (R_1, d, $^1J_{PC} = 134.7$ Hz); 27.0 (R_2, d, $^1J_{PC} = 149.31$ Hz) (P=C); 38.76 (R_1, d, $^2J_{PC} = 13.7$) and 34.92 (R_2, d, $^2J_{PC} = 13.8$)(P = C-^{13}C); 51.12–53.24 (R_1, R_2, m) ($4OCH_3$); 60.84 (R_1, d, $^3J_{PC} = 5.2$ Hz) and 60.29 (R_1, d, $^3J_{PC} = 4.4$ Hz) ($^{13}CH(CO_2Et)_2$); 68.12 (R_1) and 67.99 (R_2)($4OCH_2$); 128.85–142.10 (fairly complex, arom); 167.83 (R_1, br) and 167.06 (R_2, br) ($4^{13}CO_2Me$); 190.37 (R_1), 190.46 (R_1) and 191.20 (R_2), 191.47 (R_2) (4 $^{13}CO_2Et$). Analysis: Calc. for $C_{34}H_{39}O_8P$ (606): C, 67.30%; H, 6.44%. Found: C, 67.71%; H, 6.58%.

[($C_{32}H_{35}O_6P$)$PdCl_2$] (5c)

To a solution of $K_2[PdCl_4]$ (0.163 g, 0.5 mmol) in $CHCl_3$ (5 mL) a solution of ylide (0.273 g, 0.5 mmol) in $CHCl_3$ (5 mL) was added and the pale red solution was stirred for 72 h under a N_2 atmosphere at room temperature. The final reaction mixture was filtered off; the residue was washed several times with diethylether and dried under a vaccum to give a yellow-brown precipitate (0.21 g, 54% yield). IR(KBr)(ν_{max}.cm^{-1}): 1730(CO ester); 1625(CO keton); 1433(P—C=C arom). ^{31}P NMR ($CDCl_3$)δ_P: 26.05 (R_1) and 26.67 (R_2). ^{1}H NMR ($CDCl_3$, major complex (R_1) 59.09 and minor complex (R_2) 40.91): δ_H: 2.18 (R_1), 2.20 (R_1) and 2.10(R_2), 2.20 (R_2) (6H, 3s, $2CH_3$); 2.40 (9H, s, 3p-CH_3); 3.45–3.50 (1H, m, $CHCO_2CH_3$); 3.59 (R_1) and 3.08 (R_2)(6H, 2s, $4OCH_3$); 5.81 (R_1) and 5.40 (R_2) (1H, 2br, $CH(COCH_3)_2$); 7.27–7.51(12H, m, arom). ^{13}C NMR ($CDCl_3$)δ_C: 21.87 (R_1) and 22.29 (R_2) (2s, 3p-CH_3);

31.73 (R_1), 30.96 (R_1) and 30.10 (R_2), 29.76 (R_2) (4s, 2CH_3); 33.27(R_1, d, $^1J_{PC} = 84.5$ Hz) and 31.70 (R_2, d, $^1J_{PC} = 89.4$ Hz); 46.45(R_1), 53.09 (R_1) and 42.40 (R_2), 49.20 (R_2) (2OCH_3); 52.40 (R_1) and 53.99 (R_2) (P—C); 66.5 (R_1) and 66.4 (R_2) (P—C-^{13}C); 191.52 (R_1), 166.79 (R_1) and 191.52 (R_2), 171.20 (R_2) (2CO ester); 202 (R_1) and 204 (R_2) (2CO keton); 115–146 (fairly complex, arom). Analysis Calc. for [($C_{32}H_{35}O_6P$)$PdCl_2$] (723.4): C, 53.08%; H, 4.83%. Found: C, 53.1%; H, 5.32%.

[($C_{34}H_{39}O_8P$)$PdCl_2$] (5d)

The red-brown precipitate (0.19 g, 48.47% yield). IR(KBr)(ν_{max}.cm^{-1}): 1736 (CO ester); 1600 (CO keton); 1437 (P—C=C arom). ^{31}P NMR ($CDCl_3$)δ_P: 29.64 (R_1) and 27.76 (R_2). ^{1}H NMR ($CDCl_3$, major complex (R_1) 83.87% and minor complex (R_2) 16.13%): δ_H; 1.18 (R_1) and 0.81(R_2) (6H, m, 4CH_3); 2.32 (R_1) and 2.44 (R_2) (9H, 2s, 3 p-CH_3); 3.81–3.86 (1H, m, $CHCO_2CH_3$); 3.70(R_1) and 3.99 (R_2) (6H, m, 4OCH_3); 4.08 (R_1), and 4.17 (R_2) (4H, m, 4OCH_2); 5.66 (R_1) and 5.88 (R_2) (1H, 2br, $CH(CO_2Et)_2$); 7.17–7.56 (12H, m, arom). Analysis Calc. for [($C_{34}H_{39}O_8P$)$PdCl_2$] (783.4): C, 52.085%; H, 4.98%. Found: C, 52.60%; H, 5.48%.

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