

Reaction of Diazoalkanes with Iron Phosphine Complexes Affords Novel Phosphazine Complexes

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The crystal structures of novel products from the insertion of various diazoalkanes into the iron–phosphorus bond in FeCl_2L_2 (L = phosphine) complexes are presented. Specifically, ethyl diazoacetate and diphenyldiazomethane reacted with $\text{FeCl}_2(\text{PMe}_2\text{Ph})_2$ to afford $\text{FeCl}_2[\text{N}(\text{PMe}_2\text{Ph})\text{NC}(\text{H})\text{CO}_2\text{Et}]_2$ (**1**) and $\text{FeCl}_2[\text{N}(\text{PMe}_2\text{Ph})\text{NCPH}_2]$ (**2**). Interestingly, ethyl diazoacetate inserted into both iron phosphine bonds of $\text{FeCl}_2(\text{d}^i\text{ppe})_2$ to afford the seven-membered metallacycle $\text{FeCl}_2\{\text{N}[\text{NC}(\text{H})\text{CO}_2\text{Et}]\text{P}(\text{Pr})_2\text{CH}_2\text{CH}_2\text{P}(\text{Pr})_2\text{N}[\text{NC}(\text{H})\text{CO}_2\text{Et}]\}_2$ (**3**).

Introduction

Diazoalkanes have proven to be important synthetic reagents in organometallic chemistry.^{1,2} While diazoalkanes are known to coordinate to the metal center in either an η^1 or η^2 fashion,³ in many cases the α -carbon of the diazoalkane undergoes nucleophilic attack by the metal center. Subsequent release of dinitrogen leads to the formation of a transition-metal carbene complex. The metal alkylidene may be generated as a transient intermediate along a reaction pathway or may be formed as a stable and isolable complex.⁴ In our attempts to synthesize an iron analogue to the metathesis catalyst $\text{PCy}_3\text{Cl}_2\text{Ru}=\text{CHPh}$, we examined the reactivity of diazoalkanes with iron chlorides. To our surprise, the diazoalkane inserted into the iron–phosphine bond instead of releasing dinitrogen and forming the expected iron alkylidene. While few examples of diazoalkanes inserting into various metal–ligand systems exist,² only one report involves insertion into a metal–phosphide bond to provide a zirconocene phosphamine complex.⁵ To the best of our knowledge, this is the first example of the formation of a phosphazine complex via insertion of a diazoalkane. In fact, metal phosphazine complexes are rather scarce, although phosphazines have been known for some time.⁶ Herein we report a series of insertion products and their structural characterization.

Results and Discussion

Treatment of $\text{FeCl}_2(\text{PMe}_2\text{Ph})_2$ with 2 equiv of ethyl diazoacetate in benzene afforded $\text{FeCl}_2[\text{N}(\text{PMe}_2\text{Ph})\text{NC}(\text{H})\text{CO}_2\text{Et}]_2$ (**1**) in 82% yield. Addition of only 1 equiv of ethyl diazoacetate to $\text{FeCl}_2(\text{PMe}_2\text{Ph})_2$ still produced

complex **1**, although in reduced yield. A characteristic absorption at 1560 cm^{-1} , indicative of a $\nu(\text{C}=\text{N})$ stretch, was observed in the infrared spectrum (KBr pellet) of **1**. Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a saturated solution of **1** in benzene at room temperature (Figure 1; crystallographic data and selected bond distances and angles are given in Tables 1 and 2, respectively). The crystal structure unambiguously indicated that the ethyl diazoacetate inserted into both iron–phosphine bonds. Analysis of the structure revealed two geometries for **1**; each structure differed only by a slight rotation of the ethyl group. Complex **1** adopted a distorted-tetrahedral geometry with angles ranging from $100.32(10)$ to $120.63(5)^\circ$. Notably, the $\text{Cl1}-\text{Fe}-\text{Cl2}$ angle in **1** ($120.63(5)^\circ$) is substantially larger than it is in $\text{FeCl}_2(\text{P}^i\text{Bu}_2\text{Me})_2$ ($110.97(3)^\circ$),⁷ which may be due to the increased steric bulk of the $\text{P}^i\text{Bu}_2\text{Me}$ ligands relative to the phosphazine ligands. The $\text{Cl1}-\text{Fe}-\text{Cl2}$ angle resembles the $\text{Br}-\text{Fe}-\text{Br}$ angle in $\text{FeBr}_2(\text{PETe}_3)_2$ ($121.9(1)^\circ$).⁸ $\text{Fe}-\text{N}$ bond lengths ($2.088(4)\text{ \AA}$) are as expected for a single bond, indicating that a dative bond formed between the N1 and the metal center. As expected, the $\text{N1}-\text{N2}-\text{C1}$ linkage adopted a geometry similar to a free phosphazine rather than a free diazoacetate. First, the $\text{N}-\text{N}$ bond ($1.391(5)\text{ \AA}$) resembles the $\text{N}-\text{N}$ bond in benzophenone triphenylphosphazine (1.390 \AA)⁹ and is considerably longer than the $\text{N}-\text{N}$ bond in a free diazo compound (1.12 \AA).¹ Second, the $\text{N}-\text{N}-\text{C}$ angle is bent ($116.0(3)^\circ$) rather than linear, as it is in free diazo compounds. In classical η^1 -bound diazo complexes, the $\text{M}-\text{N}-\text{N}$ angle deviates only marginally from linearity ($153-177^\circ$).¹ In complex **1**, however, this angle is much smaller ($127.6(3)^\circ$), suggesting the hybridization of N1 changed from sp to sp^2 .

In analogy to the formation of complex **1**, reaction of $\text{FeCl}_2(\text{PMe}_2\text{Ph})_2$ with 1 equiv of diphenyldiazomethane

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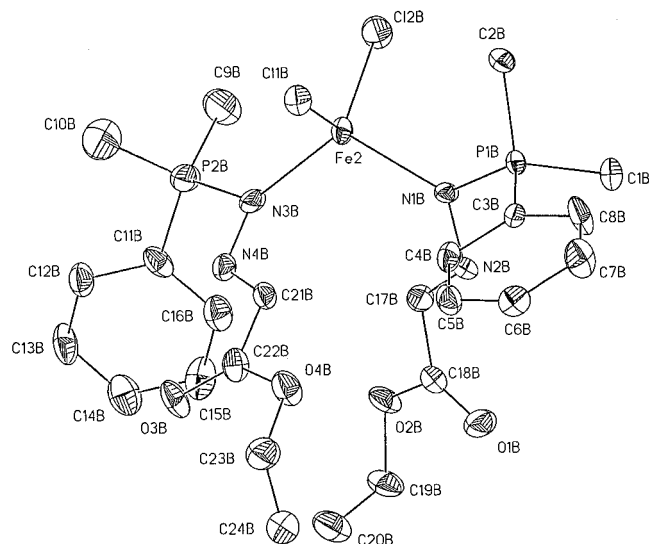


Figure 1. ORTEP view of complex **1**. Ellipsoids are drawn at 50% probability.

Table 1. Crystallographic Data for Complexes 1–3

	1	2	3
formula	C ₂₄ H ₃₄ Cl ₂ Fe-N ₄ O ₄ P ₂	C ₂₁ H ₂₁ Cl ₂ Fe-N ₂ P	C ₂₂ H ₄₄ Cl ₂ Fe-N ₄ O ₄ P ₂
fw	631.26	459.14	617.32
space group	P1	P2 ₁ /c	P1
a (Å)	10.7582(14)	9.2172(5)	9.9648(7)
b (Å)	15.807(2)	9.3944(5)	10.0839(7)
c (Å)	18.193(2)	24.7708(1)	17.7501(1)
β (deg)	99.717(2)	98.8290(1)	95.5510(1)
V (Å ³)	3011.6(7)	2119.5(2)	1603.57(2)
Z	4	4	2
radiation (Kα, Å)	0.710 73	0.710 73	0.710 73
T (K)	98(2)	98(2)	98
D _{calcd} (Mg m ⁻³)	1.392	1.439	1.353
μ _{calcd} (mm ⁻¹)	0.820	1.047	0.772
F ₀₀₀	1312	944	688
R1	0.1056	0.0344	0.1354
wR2	0.1375	0.0669	0.1398
GOF	1.878	1.993	2.310

Table 2. Selected Bond Lengths (Å) and Angles (deg) for FeCl₂[N(PMe₂Ph)NC(H)CO₂Et]₂ (1)

Bond Distances			
Fe–N1	2.088(4)	Fe–N3	2.090(4)
Fe–Cl2	2.2775(1)	Fe–Cl1	2.2920(1)
N1–N2	1.391(5)	N3–N4	1.402(5)
P1–N1	1.661(4)	P2–N3	1.656(4)
N2–C17	1.292(5)	N4–C21	1.281(5)
Bond Angles			
N1–Fe–N3	114.23(1)	N3–N4–C21	118.5(4)
N1–Fe–Cl2	100.32(1)	N2–N1–P1	106.8(3)
N3–Fe–Cl2	114.03(1)	N4–N3–P2	103.1(3)
N1–Fe–Cl1	107.60(1)	N2–N1–Fe	127.6(3)
N3–Fe–Cl1	100.52(1)	N4–N3–Fe	127.2(3)
Cl2–Fe–Cl1	120.63(5)	P1–N1–Fe	125.28(2)
N1–N2–C17	116.0(3)	P2–N3–Fe	128.45(2)

in benzene afforded FeCl₂[N(PMe₂Ph)NCPPh₂] (**2**) in 65% yield. A characteristic absorption at 1552 cm⁻¹, indicative of a ν(C=N) stretch, was observed in the infrared spectrum (KBr pellet) of **2**. X-ray analysis (Figure 2; crystallographic data and selected bond distances and angles are given in Tables 1 and 3, respectively) revealed that the steric bulk of the diphenyl unit and ligand lability prevented more than one phosphazine unit from binding to the metal. Interaction between

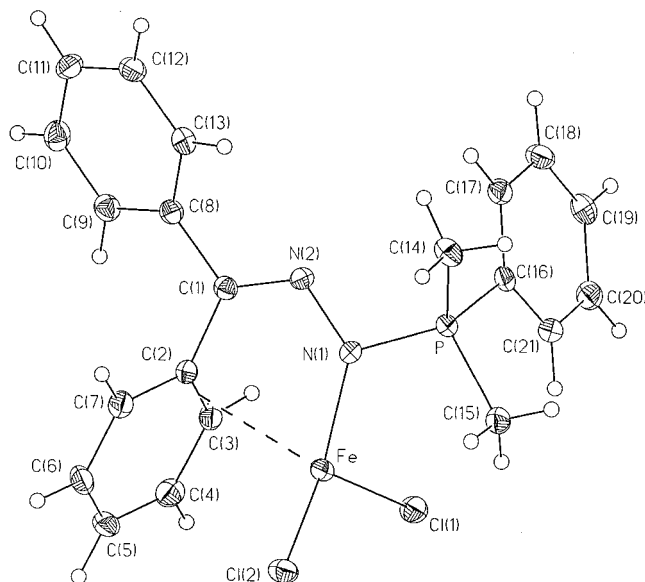


Figure 2. ORTEP view of complex **2**. Ellipsoids are drawn at 50% probability.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for FeCl₂[N(PMe₂Ph)NCPPh₂] (2)

Bond Distances			
Fe–N1	2.0104(1)	P–N1	1.6439(1)
Fe–Cl2	2.2355(4)	Fe–Cl1	2.2621(4)
Fe–C2	2.4394(2)	N1–N2	1.4045(2)
Fe–C3	2.6544(2)	N2–C1	1.288(2)
Fe–C4	3.0314(2)		
Bond Angles			
N1–Fe–Cl2	121.36(4)	Cl2–Fe–C2	105.45(4)
N1–Fe–Cl1	109.55(4)	Cl1–Fe–C2	126.02(3)
Cl2–Fe–Cl1	116.341(2)	N1–N2–C1	117.14(1)
N1–Fe–C3	92.04(5)	N2–N1–P	109.09(9)
Cl2–Fe–C3	115.38(4)	N2–N1–Fe	126.87(1)
Cl1–Fe–C3	97.08(4)	P–N1–Fe	122.06(7)
N1–Fe–C2	71.53(5)		

iron and the two carbons (C2 and C3) of the diphenyldiazomethane phenyl ring appears to stabilize the compound, preventing it from forming a highly unstable 12-electron species. The Cl–Fe–Cl angle (116.341(2)°) is shortened relative to complex **1** (120.63(5)°) and may be due to an increase in steric bulk of the phosphazine unit. However, **2** still adopted a distorted-tetrahedral geometry.

The insertion of diazo compounds into iron–phosphine bonds was not limited to monodentate phosphines. A soluble iron(II) chloride possessing a bidentate phosphine ligand, FeCl₂(d'ppe)₂,¹⁰ was treated with 2 equiv of ethyl diazoacetate in benzene to afford complex **3** in 93% yield. A characteristic absorption at 1563 cm⁻¹, indicative of a ν(C=N) stretch, was observed in the infrared spectrum (KBr pellet) of **3**. Single-crystal X-ray diffraction analysis revealed the diazoacetates inserted into both iron–phosphine bonds to produce an unusual seven-membered metallacycle (Figure 3; crystallographic data and selected bond distances and angles are given in Tables 1 and 4, respectively). A striking feature is that the Cl–Fe–Cl angle is 109.21(5)°, remarkably smaller and closer to an expected tetrahedral angle than observed in complexes **1** and **2**. The increased ring size

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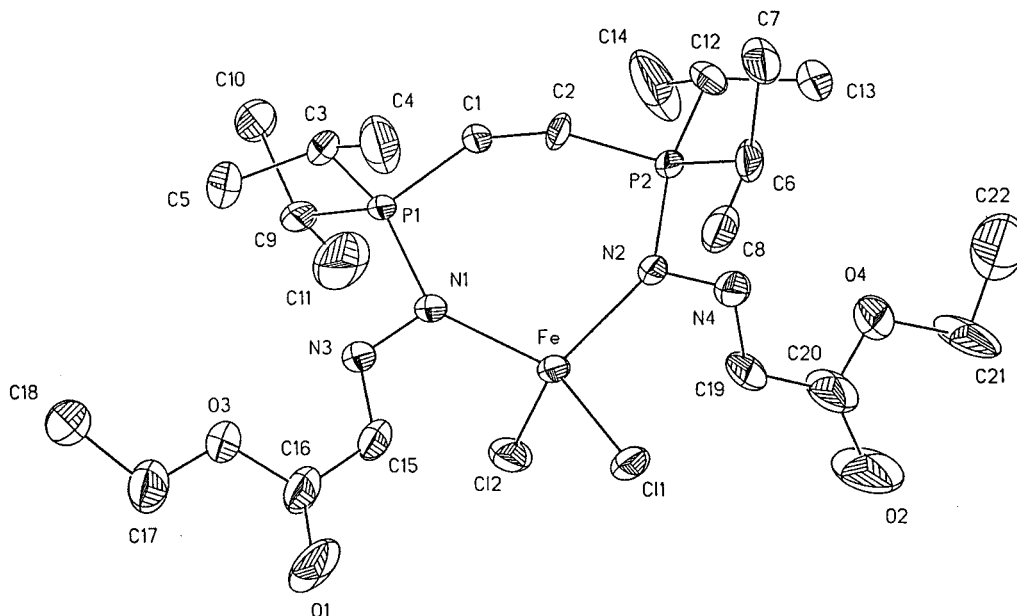


Figure 3. ORTEP view of complex **3**. Ellipsoids are drawn at 50% probability.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 3

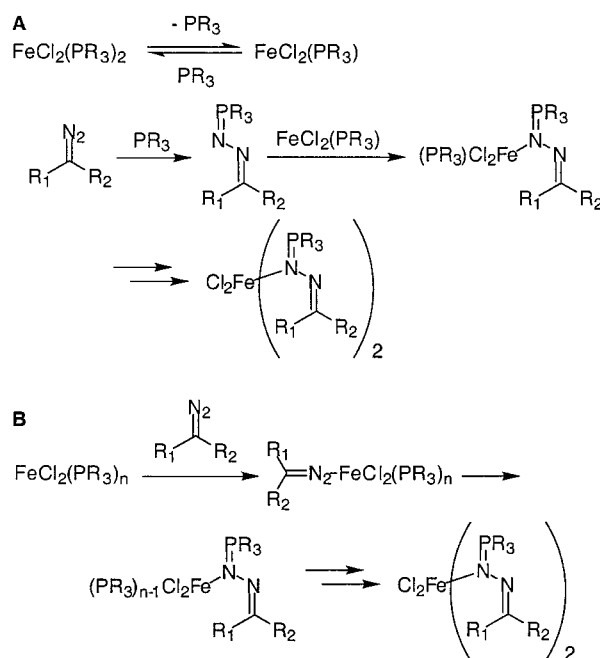
Bond Distances			
Fe–N1	2.088(4)	Fe–N2	2.080(3)
Fe–Cl1	2.2970(1)	Fe–Cl2	2.2895(1)
N1–N3	1.392(5)	N2–N4	1.389(5)
P1–N1	1.657(4)	P2–N2	1.646(3)
N3–C15	1.263(5)	N4–C19	1.281(5)
Bond Angles			
N2–Fe–N1	112.02(1)	N2–N4–C19	119.5(4)
N2–Fe–Cl2	111.49(1)	N3–N1–P1	103.3(3)
N1–Fe–Cl2	106.08(1)	N4–N2–P2	104.5(3)
N2–Fe–Cl1	103.47(1)	N3–N1–Fe	124.6(2)
N1–Fe–Cl1	114.67(1)	N4–N2–Fe	124.0(3)
Cl2–Fe–Cl1	109.21(5)	P1–N1–Fe	129.7(2)
N1–N3–C15	117.7(4)	P2–N2–Fe	130.5(2)

of the phosphazine ligand in complex **3** may force the chlorine atoms closer together. All other angles and bond lengths are similar to those of complexes **1** and **2**.

While complexes **1–3** display similar structural characteristics, it is clear that the sterics of the phosphazine unit affect the Cl–Fe–Cl bite angle as seen in the trend $120.63(5)^\circ > 116.341(2)^\circ > 109.21(5)^\circ$ for **1–3**, respectively. A notable structural feature is the shortened C–N bond length (~ 1.28 Å) as compared to free phosphazine (1.314 Å). Although complexes **1–3** are paramagnetic, which precluded the use of NMR spectroscopy, the infrared spectrum displayed diagnostic bands ($1552\text{--}1563\text{ cm}^{-1}$) of the C=N stretch that are similar to those of η^1 -bound diazoalkane complexes ($\sim 1570\text{ cm}^{-1}$). While crystals suitable for X-ray analysis were not obtained, the reaction of $\text{FeCl}_2(\text{dppe})$ (dppe = diphenylphosphinoethane) with diphenyldiazomethane and ethyl diazoacetate afforded two powders with stretching frequencies of 1554 and 1560 cm^{-1} , respectively, in their IR spectra. These results suggest that insertion of diazo compounds into iron–phosphine bonds may be a general reaction.

Possible pathways for the formation of phosphazine complexes are shown in Scheme 1. Phosphines are labile ligands that rapidly dissociate and are in equilibrium with a low-valent iron center. Phosphines also react

Scheme 1. Possible Pathways for Product Formation



with diazoalkanes to form phosphazines.¹¹ Thus, phosphine dissociation and reaction with diazoalkane would produce free phosphazine. Binding of this free phosphazine to a low-valent iron would afford a phosphazine complex (pathway A). Alternatively, diazoalkane could initially bind to the iron dichloride in an η^1 fashion. Subsequent phosphine migration from the iron center to the nitrogen atom would afford a phosphazine complex (pathway B). Although we cannot rule out either mechanism, we feel product formation follows pathway B for two reasons: (1) iron compounds have a high affinity for nitrogen and (2) bidentate phosphines, which are less labile and less likely to dissociate than monodentate phosphines, also yield phosphazine complexes.

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Experimental Section

All operations were performed under an inert atmosphere in a nitrogen-filled drybox or by using standard Schlenk techniques. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Solvents were dried over aluminum columns.¹² Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Samples for elemental analysis were submitted to Midwest Microlab, Inc. $\text{FeCl}_2(\text{d}^i\text{ppe})$ was prepared according to the literature procedure.¹⁰

$\text{C}_{24}\text{H}_{34}\text{Cl}_2\text{FeN}_4\text{O}_4\text{P}_2$ (1). Ethyl diazoacetate (100 μL , 0.78 mmol) was added to a solution of $\text{FeCl}_2(\text{PMe}_2\text{Ph})_2$ (150 mg, 0.37 mmol) in benzene (10 mL) via syringe. The pale green reaction turned orange immediately. The reaction mixture was stirred at room temperature for 1 h and layered with pentane. The pentane was allowed to slowly diffuse into the solution at room temperature to afford yellow crystals of **1** in 82% yield after filtration. IR (KBr): 2990 (m), 2916 (m), 1721 (s), 1560 (s), 1438 (m), 1371 (w), 1344 (w), 1295 (m), 1203 (s), 1120 (m), 1043 (s), 996 (s), 956 (s), 936 (s), 877 (w), 747 (m), 690 (m), 536 (m), 482 (w) cm^{-1} . Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{Cl}_2\text{FeN}_4\text{O}_4\text{P}_2$: C, 45.67; H, 5.43; N, 8.88. Found: C, 45.80; H, 5.37; N, 8.74.

$\text{C}_{21}\text{H}_{21}\text{Cl}_2\text{FeN}_2\text{P}$ (2). Diphenyldiazomethane (78 mg, 0.40 mmol) and $\text{FeCl}_2(\text{PMe}_2\text{Ph})_2$ (135 mg, 0.33 mmol) were reacted in a procedure analogous to that given for **1** to afford yellow crystals of **2** in 65% yield. IR (KBr): 3041 (w), 2978 (m), 2912 (m), 1581 (w), 1552 (w), 1493 (m), 1436 (s), 1389 (w), 1322 (w),

1308 (m), 1166 (m), 1120 (s), 1018 (s), 935 (s), 887 (s), 773 (s), 744 (s), 686 (s), 637 (m), 535 (w), 487 (s), 455 (m) cm^{-1} . Anal. Calcd for $\text{C}_{21}\text{H}_{21}\text{Cl}_2\text{FeN}_2\text{P}$: C, 54.94; H, 4.61; N, 6.10. Found: C, 54.74; H, 4.71; N, 5.47.

$\text{FeCl}_2\{\text{N}[\text{NC}(\text{H})\text{CO}_2\text{Et}]\text{P}(\text{Pr})_2\text{CH}_2\text{CH}_2\text{P}(\text{Pr})_2\text{N}[\text{NC}(\text{H})\text{CO}_2\text{Et}]\}_2$ (3). Ethyl diazoacetate (36 mg, 0.32 mmol) and $\text{FeCl}_2(\text{d}^i\text{ppe})$ (60 mg, 0.15 mmol) were reacted in a procedure analogous to that given for **1** to afford yellow crystals of **3** in 93% yield. IR (KBr): 2979 (m), 2937 (w), 2884 (w), 1702 (s), 1563 (s), 1466 (m), 1394 (w), 1371 (w), 1329 (w), 1280 (vs), 1198 (m), 1045 (vs), 934 (s), 885 (m), 859 (w), 771 (m), 708 (w), 678 (w), 625 (w), 568 (w), 542 (w), 499 (w) cm^{-1} . Anal. Calcd for $\text{C}_{22}\text{H}_{44}\text{Cl}_2\text{FeN}_4\text{O}_4\text{P}_2$: C, 42.81; H, 7.18; N, 9.08. Found: C, 42.93; H, 6.99; N, 9.22.

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Supporting Information Available: Experimental details for the X-ray structure determination, tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, and anisotropic displacement parameters, and figures giving additional views for compounds **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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