

2,2'-Biphosphinines and 1,4-Diphosphadienes as 8-Electron Donors toward Manganese Carbonyl

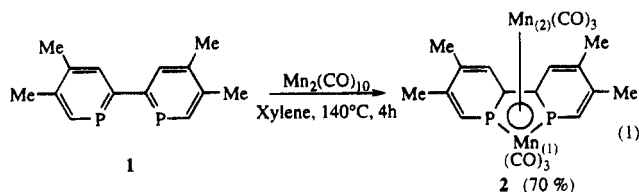
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The reaction of 3,3',4,4'-tetramethyl-2,2'-biphosphinine (tmbp) with $\text{Mn}_2(\text{CO})_{10}$ at 140 °C affords $[\text{Mn}_2(\text{tmbp})(\text{CO})_6]$, a complex where tmbp acts as a 8-electron donor through its central $\text{P}=\text{C}=\text{C}=\text{P}$ 1,4-diphosphadiene unit. An X-ray crystal structure analysis of this complex shows a delocalized 5-membered C_2MnP_2 ring π -complexed to a second $\text{Mn}(\text{CO})_3$ unit, which results in a disruption of the aromaticity of the two phosphinine rings. Similar behavior is observed upon reaction of 1,2-dihydro-1,2-diphosphetes with $\text{Mn}_2(\text{CO})_{10}$. The initial product involves the incorporation of $\text{Mn}(\text{CO})_4$ and $\text{Mn}(\text{CO})_3$ units into the $\text{P}-\text{P}$ bond of the ring and coordination of the $\text{C}=\text{C}$ double bond of the diphosphete to the $\text{Mn}(\text{CO})_3$ unit. Loss of CO occurs upon heating, to yield a 1,4-diphosphadiene- $\text{Mn}_2(\text{CO})_6$ complex whose structure is strictly analogous to the central unit of $[\text{Mn}_2(\text{tmbp})(\text{CO})_6]$.

We have recently developed the chemistry of 2,2'-biphosphinines;¹ these phosphorus analogues of the ubiquitous 2,2'-bipyridines have greater π -backbonding ability than their nitrogen-containing counterparts.² In the course of a systematic investigation of the complexes of 2,2'-biphosphinines with low-valent soft metals, we observed somewhat unusual behavior of these ligands toward manganese carbonyl. The reaction of 4,4',5,5'-tetramethyl-2,2'-biphosphinine **1**³ with $\text{Mn}_2(\text{CO})_{10}$ affords the dinuclear red-orange complex **2** (eq 1), whose structure was established by X-ray analysis (Figure 1).



The tricyclic system is essentially planar and the central $\text{C}_2\text{P}_2\text{-Mn}_{(1)}$ ring is η^5 -bound to the second manganese atom, which lies at 1.8550 (6) Å from the $\text{C}_2\text{P}_2\text{Mn}_{(1)}$ nucleus. At 1.443(3) Å, the $\text{C}_2-\text{C}_2'$ bridging bond is short when compared with either the free cisoid ligand at 1.470(8) Å^{2a} or the $\text{Cr}(\text{CO})_4$ chelate at 1.467(3) Å.¹ Conversely, the internal $\text{P}-\text{C}_2$ bonds are long (1.760(2) Å vs 1.736(4) Å for the free cisoid ligand and 1.737-(2) Å for its $\text{Cr}(\text{CO})_4$ complex respectively). All these data point to a highly delocalized 5-membered central unit, which is consistent with short intracyclic $\text{P}-\text{Mn}_{(1)}$ distances 2.1903-(6) Å by comparison with the $\text{P}-\text{Mn}_{(2)}$ bonds at 2.4062(6) Å. The delocalization apparently takes place at the expense of the

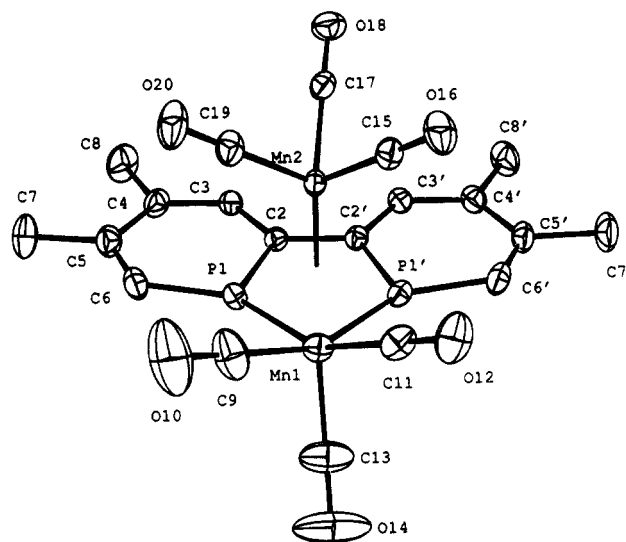


Figure 1. ORTEP drawing of one molecule of **2**. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) are as follows: $\text{Mn}(1)-\text{Mn}(2) = 2.8128(5)$, $\text{Mn}(1)-\text{P}(1) = 2.1903(6)$, $\text{Mn}(1)-\text{P}(1') = 2.2038(7)$, $\text{P}(1)-\text{C}(2) = 1.760(2)$, $\text{C}(2)-\text{C}(2') = 1.443(3)$, $\text{P}(1')-\text{C}(2') = 1.762-(2)$, $\text{P}(1)-\text{C}(6) = 1.747(2)$, $\text{P}(1')-\text{C}(6') = 1.749(2)$, $\text{Mn}(2)-\text{P}(1) = 2.4062(6)$, $\text{Mn}(2)-\text{C}(2) = 2.219(2)$. Bond angles (deg): $\text{P}(1)-\text{Mn}(1)-\text{P}(1') = 79.75(2)$, $\text{Mn}(1)-\text{P}(1)-\text{C}(2) = 117.13(7)$, $\text{Mn}(1)-\text{P}(1')-\text{C}(2') = 116.29(7)$, $\text{P}(1)-\text{C}(2)-\text{C}(2') = 112.6(1)$, $\text{C}(2)-\text{C}(2')-\text{P}(1') = 113.3(1)$, $\text{Mn}(2)-\text{Mn}(1)-\text{P}(1) = 55.84(2)$, $\text{Mn}(2)-\text{P}(1)-\text{C}(2) = 62.11(7)$, $\text{Mn}(2)-\text{C}(2)-\text{C}(2') = 71.2(1)$, $\text{Mn}(2)-\text{C}(2')-\text{P}(1') = 73.74-(7)$, $\text{Mn}(2)-\text{Mn}(1)-\text{P}(1') = 56.10(2)$.

aromaticity of the phosphinine rings. Indeed, C_3-C_4 and C_5-C_6 become localized double bonds at 1.372(3) and 1.360(3) Å respectively and the C_4-C_5 bond is long at 1.447(3) Å. It must be recalled that the $\text{C}-\text{C}$ bonds of the free cisoid ligand all fall within the range 1.388–1.396 Å. This electronic relocation within the phosphinine rings is rather unexpected because, according to recent *ab initio* calculations, the aromaticity of phosphinine is *ca.* 90% of that of benzene or pyridine.⁴

From a ligating standpoint, the 2,2'-biphosphinine acts as a 1,4-diphosphadiene 8-electron donor in complex **2**. We thus

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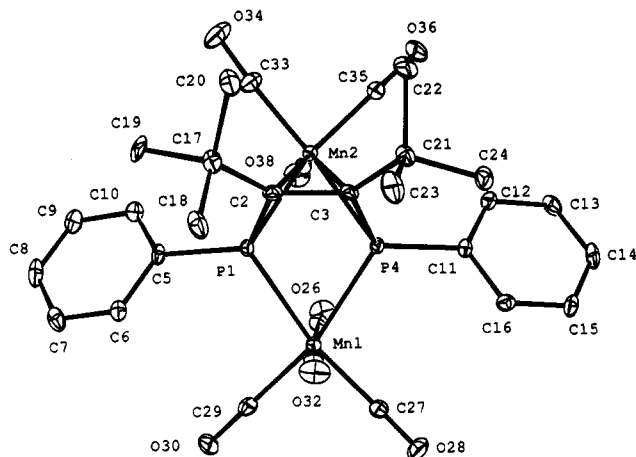
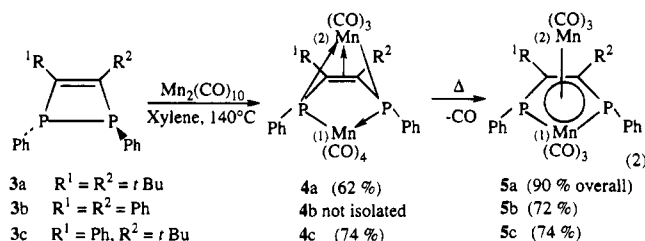


Figure 2. ORTEP drawing of one molecule of **4a**. Selected bond lengths (Å) are as follows: Mn(1)–P(1) = 2.325(2), Mn(1)–P(4) = 2.326(2), Mn(2)–P(1) = 2.297(2), Mn(2)–P(4) = 2.295(2), Mn(2)–C(2) = 2.185(7), Mn(2)–C(3) = 2.208(7), P(1)–C(2) = 1.828(7), C(2)–C(3) = 1.438(9), C(3)–P(4) = 1.830(7). Bond angles (deg): P(1)–Mn(1)–P(4) = 66.73(7), Mn(1)–P(1)–C(2) = 111.4(2), P(1)–C(2)–C(3) = 108.1(5), C(2)–C(3)–P(4) = 107.5(4), Mn(1)–P(4)–C(3) = 111.1(2), Mn(1)–P(1)–Mn(2) = 109.92(8), Mn(1)–P(4)–Mn(2) = 109.97(8), Mn(2)–P(1)–C(2) = 62.7(2), Mn(2)–C(2)–C(3) = 71.8(4), Mn(2)–C(3)–P(4) = 68.5(2).

decided to check whether genuine 1,4-diphosphadienes would react similarly with $\text{Mn}_2(\text{CO})_{10}$. Both theoretical calculations⁵ and experiments on their P-coordination compounds⁶ indicate that 1,2-dihydro-1,2-diphosphetes serve as synthetic equivalents of 1,4-diphosphadienes through an easy electrocyclic ring opening. We thus investigated the reaction of a series of 1,2-dihydro-1,2-diphosphetes **3a–c** with $\text{Mn}_2(\text{CO})_{10}$ (eq 2).



The reaction proceeds in two steps. Initially, complexes **4a–c** are formed through the formal insertion of two manganese units into the P–P bond of the diphosphete ring. In each case, the ligand acts as a (3 + 3)-electron donor via its two phosphorus atoms (the two Mn being in the oxidation state +1) and as a 2-electron donor via its C=C double bond. The ring electron density is fully localized, as shown by an X-ray crystal structure analysis of **4a** (Figure 2): internal P–C bonds, 1.828(7) and 1.830(7) Å; internal Mn(1)–P bonds, 2.325(2) and 2.326(2) Å; internal C=C bond, 1.438(9) Å (this elongation reflects the η^2 -complexation by Mn₂). There is no bond between the two manganese atoms, Mn(1)–Mn(2) 3.784 Å, as confirmed by the ³¹P chemical shifts to high fields of H₃PO₄.⁷

Heating of complexes **4** results in the loss of one CO ligand; this gives a new series of complexes **5**, whose downfield-shifted ³¹P resonances fall in the same range as complex **2**: $\delta(^{31}\text{P})$ (**2**), +146.9 (CH₂Cl₂); $\delta(^{31}\text{P})$ (**5a**), +167.4 (CDCl₃); $\delta(^{31}\text{P})$ (**5b**), +148.5 (CD₂Cl₂); $\delta(^{31}\text{P})$ (**5c**), +171.4 and +140.7, ²J(P–P) = 41 Hz (CDCl₃). The X-ray crystal structure analysis of **5c**

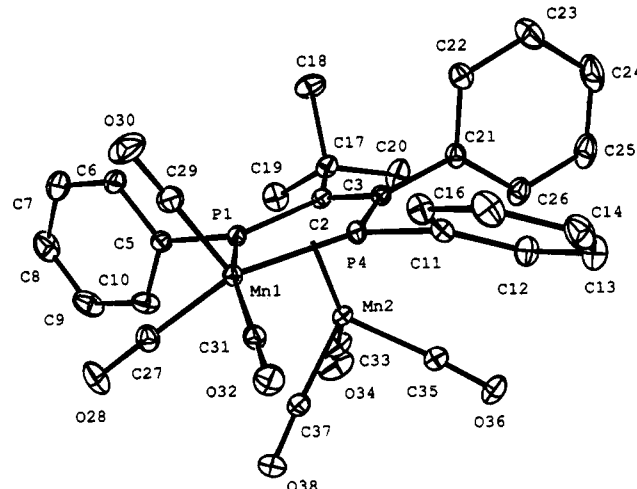


Figure 3. ORTEP drawing of one molecule of **5c**. Selected bond lengths (Å) are as follows: Mn(1)–Mn(2) = 2.8761(3), Mn(1)–P(1) = 2.1931(4), Mn(1)–P(4) = 2.1755(4), P(1)–C(2) = 1.793(1), C(2)–C(3) = 1.424(2), C(3)–P(4) = 1.782(1), Mn(2)–P(1) = 2.3523(4), Mn(2)–C(2) = 2.250(1), Mn(2)–C(3) = 2.233(1), Mn(2)–P(4) = 2.3630(4). Bond angles (deg): P(1)–Mn(1)–P(4) = 79.53(1), Mn(1)–P(1)–C(2) = 118.36(5), Mn(1)–P(4)–C(3) = 117.02(5), Mn(1)–P(1)–Mn(2) = 78.42(1), Mn(1)–P(4)–Mn(2) = 78.53(1), P(1)–C(2)–C(3) = 110.3(1), C(2)–C(3)–P(4) = 114.8(1), Mn(2)–Mn(1)–P(1) = 53.25(1), Mn(2)–Mn(1)–P(4) = 53.63(1), Mn(2)–P(1)–C(2) = 64.10(4), Mn(2)–C(2)–C(3) = 70.83(8), Mn(2)–C(3)–P(4) = 71.09(5).

(Figure 3) shows a close relationship between the geometries of **5c** and **2**: for **2**, Mn–Mn 2.8128(5) Å; Mn(1)–P 2.1903(6), 2.2038(7) Å; P–C 1.760, 1.762(2) Å; C–C (bridge) 1.443(3) Å; for **5c**, Mn–Mn 2.8761(3) Å; Mn(1)–P 2.1755–2.1931(4) Å; P–C 1.782–1.793(1) Å; C–C 1.424(2) Å. The C₂P₂Mn(1) ring of **5c** and the external P–Ph bonds lie in a plane. Cyclic delocalization is shown by the shortening of the Mn(1)–P and P–C bonds when passing from **4a** to **5c**.

To summarize briefly: we describe a novel 8-electron coordination mode for both 2,2'-biphosphinines and 1,4-diphosphadienes. Until now 2,2'-biphosphinines were only known to act as (2 + 2)-electron chelating ligands through their phosphorus atoms^{1,2,8} and, additionally, this unexpected 8e bonding mode has no parallel in the coordination chemistry of 2,2'-bipyridines to the best of our knowledge.⁹ Furthermore, only complexes involving the phosphorus lone pairs were known for 1,4-diphosphadienes or their ring-closed 1,2-dihydro-1,2-diphosphete isomers,¹⁰ although an 8-electron coordination mode has been described for 1,4-diazadienes.¹¹

Experimental Section

All the reactions were performed under argon; the solvents were purified, dried and degassed by standard techniques. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker AC 200 SY spectrometer

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Table 1. Reaction Conditions for the Preparation of Compounds **4** and **5**

	compound 3		compound 4		compound 5	
	R ¹	R ²	<i>t</i> (h)	<i>T</i> (°C)	<i>t</i> (h)	<i>T</i> (°C)
a	<i>t</i> -Bu	<i>t</i> -Bu	3	130	20	140
b	Ph	Ph			3	130
c	Ph	<i>t</i> -Bu	16	130	4	140

operating at 200.13, 50.32, and 81.01 MHz, respectively. All chemical shifts are reported in ppm downfield from internal TMS (¹H and ¹³C) and external 85% H₃PO₄ (³¹P). Mass spectra and elemental analyses were performed by the "Service d'analyse du CNRS".

[Mn₂(tmbp)(CO)₆] **2**. Biphosphinine **1** (0.6 g, 2.44 mmol) and Mn₂(CO)₁₀ (0.95 g, 2.44 mmol) were heated in 20 mL of xylene at 140 °C for 4 h. During this period, an orange powder precipitated. After cooling to 25 °C, 60 mL of xylene were added and the resulting orange solution was heated at 140 °C for 10 min and then slowly cooled to room temperature (15 h). Complex **2** (0.88 g 70%) was recovered as red orange crystals after filtration, mp 100 °C. Anal. Calcd for C₂₀H₁₆O₆P₂Mn₂: C, 45.83; H, 3.08. Found: C, 45.74; H, 2.99. ¹H NMR (C₆D₆O): 2.47 (s, 6H, CH₃), 2.52 (s, 6H, CH₃), 8.00 (AA'XX', ΣJ_{HP} = 34.7 Hz, H_{6,6'}), 8.67 (AA'XX', ΣJ_{HP} = 13.10 Hz, H_{3,3'}). ³¹P NMR (CH₂Cl₂): 146.93. IR (CH₂Cl₂): ν(CO) 2023 (s), 1985 (vs), 1948 (vs) cm⁻¹.

General Procedure for Compounds 4 and 5. In a Schlenk tube, 3 mmol of 1,2-dihydro-1,2-diphosphete (**3a–c**)¹² and 3 mmol of Mn₂(CO)₁₀ in 25 mL of xylene were stirred and heated following the conditions presented in Table 1. After evaporation the residue was chromatographed through silica gel (250 g, 60 mesh) with hexane/toluene (80:20).

4a was recovered as a yellow solid in 62% yield, mp 206 °C. Anal. Calcd for C₂₉H₂₈O₇P₂Mn₂: C, 52.73; H, 4.24; P, 9.39. Found: C, 52.88; H, 4.34; P, 9.36. ¹H NMR (CDCl₃): 1.41 (s, 18H, CH₃), 7.2–7.8 (m, 10H, C₆H₅). ¹³C NMR (CDCl₃): 37.07 (s, CH₃), 39.92 (|¹J_{CP} + ³J_{CP}| = 9.8 Hz, CMe₃), 104.99 (b, :C), 221 (b, CO). ³¹P NMR (CDCl₃): -31 (b). Mass spectrum 70 eV, *m/z* (relative intensity): 660 (M, 2.5), 632 (M - CO, 4), 576 (M - 3CO, 100). IR (hexane): ν(CO) 2065 (s), 1995 (s), 1980 (s), 1965 (s), 1935 (s) and 1920 (s) cm⁻¹.

4c was recovered as a yellow solid in 74% yield. ¹H NMR (CDCl₃): 1.01 (s, 9H, CH₃), 6.9–8.0 (m, 15H, C₆H₅). ¹³C NMR (CDCl₃): 33.04 (s, CH₃), 39.68 (d, ²J_{CP} = 6 Hz, CMe₃), 101.50 (|¹J_{CP} + ²J_{CP}| = 68.3 Hz, :C-*t*Bu), 111.27 (|¹J_{CP} + ²J_{CP}| = 29.2 Hz, :C-Ph), 126–135 (m, C₆H₅), 212 (b, CO), 224 (b, CO). ³¹P NMR (CDCl₃): -32.46 and -37.06 (b, P₁ and P₂).

5a was recovered as a red-orange solid in 90% yield, mp 214 °C. Anal. Calcd for C₂₈H₂₈O₆P₂Mn₂: C, 53.16; H, 4.43; P, 9.81. Found: C, 52.74; H, 4.61; P, 9.36. ¹H NMR (CDCl₃): 1.49 (s, 18H, CH₃), 7.3–8 (m, 10H, C₆H₅). ¹³C NMR (CDCl₃): 37.92 (s, CH₃), 41.56 (|²J_{CP} + ³J_{CP}| = 13.4 Hz, CMe₃), 118.38 (|¹J_{CP} + ²J_{CP}| = 7.4 Hz, :C), 221.7 (b, CO), 222.7 (b, CO). ³¹P NMR (CDCl₃): 167.4. Mass spectra 70 eV, *m/z* (relative intensity): 632 (M, 11), 576 (M-2CO, 19), 548 (M-3CO, 41). IR (hexane) ν(CO) 2020 (s), 1987 (vs), 1960 (vs), 1940 (s), 1925 (vs).

Table 2. X-ray Crystal Data^a

	2	4a	5c
formula	C ₂₀ H ₁₆ Mn ₂ O ₆ P ₂	C ₂₉ H ₂₈ Mn ₂ O ₇ P ₂	C ₃₀ H ₂₄ Mn ₂ O ₆ P ₂
space group	P2 ₁ /n	P4/n	P1
<i>a</i> (Å)	12.098(1)	25.303(2)	8.985(1)
<i>b</i> (Å)	11.122(1)		10.844(1)
<i>c</i> (Å)	16.302(2)	9.582(1)	16.169(2)
α (deg)			105.43(1)
β (deg)	102.97(1)		97.43(1)
γ (deg)			103.50(1)
<i>V</i> (Å ³)	2137.62(71)	6135.31(1.61)	1445.5(7)
<i>Z</i>	4	8	2
<i>D</i> _{calc} (g/cm ³)	1.629	1.430	1.499
μ (cm ⁻¹)	13.2	9.3	9.9
<i>F</i> ₀₀₀	1056	2704	664
max 2θ (deg)	60.0	54.0	60.0
no. of reflns measd	6795	7491	8921
no. of reflns included	4553	3380	6870
no. of reflns params refined	335	361	361
<i>R</i>	0.031	0.050	0.026
<i>R</i> _w	0.041	0.083	0.043
GOF	1.08	1.59	1.14
instrument instability factor, <i>p</i>	0.05	0.08	0.06

^a The unweighted agreement factor $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. The weighted agreement factor $R_w = [\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2}$, where $w = 4F^2/\sigma^2(F^2)$.

5b was recovered as an orange solid in 72% yield, mp 98–100 °C. ¹H NMR (CD₂Cl₂): 6.9–7.7 (m, C₆H₅); ¹³C NMR (CD₂Cl₂): 112.53 (|¹J_{CP} + ²J_{CP}| = 35.6 Hz, :C), 128.5–136 (m, C₆H₅), 222.87 (b, CO); ³¹P NMR (CD₂Cl₂): 148.5.

5c was recovered as an orange solid in 74% yield. ¹H NMR (CDCl₃): 0.98 (s, 9H, CH₃), 6.9–7.7 (m, 15H, C₆H₅). ¹³C NMR (CDCl₃): 34.87 (s, CH₃), 41.28 (d, ²J_{CP} = 9 Hz, CMe₃), 107.24 (|¹J_{CP} + ²J_{CP}| = 40.7 Hz, :C-*t*Bu), 122.95 (|¹J_{CP} + ²J_{CP}| = 41.3 Hz, :C-Ph), 128–135.7 (m, C₆H₅), 222.34 (b, 3CO), 222.99 (s, 3CO). ³¹P NMR (CDCl₃): 140.72 and 171.41 (²J_{PP} = 41 Hz).

X-ray Structure Determinations. All data were collected at -150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator. The crystal structures were solved and refined using the Enraf-Nonius MOLEN package. Lorenz and polarization corrections were applied in all cases and direct methods yielded a solution for most atoms. For compound **2**, the hydrogen atoms positional parameters were refined. For compounds **4a** and **5c**, the hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement. All other atoms were assigned anisotropic temperature factors and refined using reflections having $F_o^2 > 3.0\sigma(F_o^2)$. Relevant crystallographic data are included in Table 2.

Supporting Information Available: X-ray structure determination for **2**, **4a**, and **5c**, including tables of crystal data, positional parameters, bond distances and angles for all non-hydrogen atoms, and β_{ij} values (15 pages). Ordering information is given on any current masthead page.

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