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# Synthesis and Structure of a (Diphosphoxane)rhodium(I) Complex. Novel Reaction with CO To Liberate a Phosphinidene Oxide

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*Summary: The synthesis and crystal and molecular structure of* $RhCl[\eta^2\text{-}(Me_2N)_2POP(NMe_2)_2\text{-}P,P'][P(NMe_2)_3]$ *(1) are reported. 1 undergoes a novel reaction with CO in which the diphosphoxane ligand is cleaved, yielding (dimethylamino)phosphinidene oxide and* $Rh[P(NMe_2)_3]_2(CO)Cl$ *(3).*

Recently, we reported that $Rh(PPr^i_3)_2Cl$ catalyzes alkane transfer–dehydrogenation but that the catalytic efficiency is severely limited by ligand decomposition pathways, which appear to involve dehydrogenation of the isopropyl groups.[1] We have also found that $Rh(PMeBu^t_2)_2Cl$ catalyzes alkane transfer–dehydrogenation and that this system too is plagued by ligand decomposition, in this case via P–C bond cleavage.[2] The former, and possibly the latter, decomposition pathways should be disfavored by substitution of the alkyl groups of the phosphine ligands by dialkylamino groups, which may have similar or even more favorable electronic properties; we have begun to investigate the ability of such analogues to catalyze transfer–dehydrogenation.[2] In the course of this work, we inadvertently (and surprisingly) isolated the complex [tetrakis(dimethylamino)diphosphoxane][tris(dimethylamino)phosphine]chlororhodium (1). We report here the crystal and molecular structure of complex 1 and a novel reaction of 1 with CO.

## Experimental Section

**General Procedures.** All manipulations were conducted either under nitrogen atmosphere in a Vacuum Atmospheres Dry-Lab glovebox or by using standard Schlenk techniques. All deuterated solvents were distilled under vacuum from NaK alloy. All other solvents were distilled from dark purple solutions of benzophenone ketyl and stored in the glovebox. Tris(dimethylamino)phosphine (95%) was purchased from Strem Chemicals and used as received. 3,5-Di-*tert*-butyl-1,2-benzoquinone, 3,5-di-*tert*-butylcatechol, and hexamethylphosphoramide were obtained from Aldrich Chemicals and used without further purification.

NMR spectra were recorded on either a Varian XL 200- or 400-MHz spectrometer. IR spectra were obtained on a Mattson Cygnus 100 FTIR spectrometer. GC-MS was performed using a Hewlett-Packard 5890 Series II gas chromatograph/5971 quadrupole mass spectrometer. Elemental analyses were performed by Desert Analytics, and the molecular weight measurement (2) was done using the Signer method.[3]

**$\{Rh[P(NMe_2)_3]_2Cl\}_2$ (2) and $RhCl[\eta^2\text{-}(Me_2N)_2POP(NMe_2)_2\text{-}P,P'][P(NMe_2)_3]$ (1).** Treatment of $[Rh(COE)_2Cl]_2$[4] (COE = cyclooctene; 0.3 g, 0.42 mmol) with 4 equiv (0.31 mL, 1.67 mmol) of $P(NMe_2)_3$ in toluene (10 mL) gave $\{Rh[P(NMe_2)_3]_2Cl\}_2$ (2) in about 80% yield with approximately 12% impurity based on $^1H$ NMR integration. Attempted recrystallization from toluene/pentane at −35 °C gave an orange powder (2) and pale yellow crystals of the impurity. The crystals were isolated, washed with cold pentane, and dried in vacuo. Elemental analysis and $^1H$ and $^{31}P$ NMR spectra are consistent with the single-crystal X-ray diffraction structure, which reveals the complex to be $RhCl[\eta^2\text{-}(Me_2N)_2POP(NMe_2)_2\text{-}P,P'][P(NMe_2)_3]$ (1) (Figure 1). Anal. Calcd for $C_{14}H_{42}ClN_7OP_3Rh$: C, 30.25; H, 7.62; N, 17.64. Found: C, 30.48; H, 7.59; N, 17.64. $^1H$ NMR ($C_6D_6$): $\delta$ 2.60 (d, $J_{P-H}$ = 10.76 Hz, $P^1(NMe_2)_2$), 2.69 (d, $J_{P-H}$ = 9.2 Hz, $P^3(NMe_2)_3$, 2.79 (d, $J_{P-H}$ = 10.76 Hz, $P^2(NMe_2)_2$). $^{31}P$ NMR ($C_6D_6$, $\delta$(85% $H_3PO_4$) = 0): $\delta$ 115.40 (ddd, $P^1$, $J_{Rh-P^1}$ = 230 Hz, $J_{P1-P^2}$ = 117 Hz, $J_{P1-P^3}$ = 39 Hz), $\delta$ 98.79 (ddd, $P^2$, $J_{Rh-P^2}$ = 159 Hz, $J_{P^2-P^3}$ = 582 Hz), 127.02 (ddd, $P^3$, $J_{Rh-P^3}$ = 168 Hz). The orange powder was identified as $\{Rh[P(NMe_2)_3]_2Cl\}_2$ (2). Molecular weight measurement: calculated for $C_{24}H_{72}Cl_2N_{12}P_4Rh_2$, 929.84; found, 902. Anal. Calcd for $C_{24}H_{72}Cl_2N_{12}P_4Rh_2$: C, 30.97; H, 7.74; N, 18.07. Found: C, 31.01; H, 7.75; N, 17.89. $^1H$ NMR ($C_6D_6$): $\delta$ 2.80 (pseudo-t, $J_{P-H}$ = 4 Hz). $^{31}P$ NMR ($C_6D_6$, $\delta$(85% $H_3PO_4$) = 0): $\delta$ 128.5 (d, $J_{Rh-P}$ = 263 Hz).

**Generation of 1 from the Reaction of 2 with $P(NMe_2)_3$ and Water.** A 2.5-$\mu$L (0.014-mmol) portion of $P(NMe_2)_3$ was added to an NMR tube containing 6.5 mg (0.007 mmol) of **2** in 0.5 mL of $C_6D_6$. The solution was shaken, and the $^{31}P$ NMR spectrum was immediately recorded. No formation of 1 was observed. A 0.25-$\mu$L (0.014-mmol) portion of degassed water was added to the NMR tube with shaking, and the formation of 1 was monitored by $^{31}P$ NMR. A second equivalent of water was added after 12 h, and the $^{31}P$ NMR spectrum was observed again. For the control experiment, the same procedure was followed except that no water was added.

**Reaction of 1 with CO.** Under a nitrogen atmosphere, 0.5 mL of a 20 mM solution of 1 in $C_6D_6$ was put in a resealable J. Young NMR tube. The solution was subjected to one cycle of freeze–pump–thaw, 800 Torr of CO was added, and $^1H$ and $^{31}P$ NMR spectra were recorded. All spectroscopic data (NMR, IR) support the formation of the carbonyl complex **3**, which was also independently generated by the reaction of $\{Rh[P(NMe_2)_3]_2Cl\}_2$ (2) with CO. $^1H$ NMR ($C_6D_6$): $\delta$ 2.71 (t, $J_{P-H}$ = 5.13 Hz). $^{31}P$ NMR ($C_6D_6$, $\delta$(85% $H_3PO_4$) = 0): $\delta$ 119.7 (d, $J_{Rh-P}$ = 135.5 Hz). IR ($C_6D_6$): $\nu_{CO}$ = 1958.6 cm$^{-1}$.

**Trapping of "$Me_2NP{=}O$" Formed from the Reaction of 1 with CO.** 3,5-Di-*tert*-butyl-1,2-benzoquinone (4) (1.5 equiv, 3.7 mg) was dissolved in 0.2 mL of toluene-$d_8$, and the solution was syringed into 0.3 mL of a 38 mM solution of 1 at −78 °C in a 5-mL Pyrex reaction vessel sealed with a septum. The mixture was then frozen, the cell was evacuated, and 800 Torr of CO was added. The mixture was allowed to warm slowly to room temperature with shaking. The resulting solution was transferred to an NMR tube, and the $^{31}P$ NMR spectrum was recorded immediately.

**Synthesis of 2-(Dimethylamino)-4,6-bis(1,1-dimethylethyl)-1,3,2-benzodioxaphosphole 2-Oxide (5) from 3,5-Di-*tert*-butylcatechol and $O{=}P(NMe_2)_3$.** A 2.0-g (9.0-mmol) sample of 3,5-di-*tert*-butylcatechol was mixed with 1.56 mL (8.97 mmol) of $O{=}P(NMe_2)_3$ in 5 mL of toluene, and the mixture was refluxed under argon for 24 h. The $^{31}P$ NMR of the resulting solution was

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[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1994.

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**Table 1. Crystal Data and Collection Parameters for RhCl[$\eta^2$-$(Me_2N)_2POP(NMe_2)_2$-$P,P'$][$P(NMe_2)_3$]**

| | |
|---|---|
| formula | $C_{14}H_{42}N_7OP_3RhCl$ |
| mol wt | 555.82 |
| space group | $P2_1/c$ |
| temp (°C) | −100(5) |
| $a$ (Å) | 8.521(2) |
| $b$ (Å) | 16.031(2) |
| $\beta$ (deg) | 102.51(2) |
| $c$ (Å) | 18.994(3) |
| $V$ (Å$^3$) | 2533.0(8) |
| $Z$ | 4 |
| $\mu$ (cm$^{-1}$) | 9.9 |
| cryst dimens (mm) | 0.35 × 0.17 × 0.23 |
| reflcns measd | $\pm h,+k,+l$ |
| scan rate (deg min$^{-1}$) | 2.4–5.5 |
| 2$\theta$ range (deg) | 4–52 |
| scan type | $\omega$ |
| no. of reflcns measd | 4573 |
| no. of unique reflcns | 4436 |
| no. of reflcns used | 3747 ($I > 2\sigma(I)$ |
| no. pf params | 258 |
| $R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$ (%) | 3.3 |
| $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$ (%) | 7.2 |
| GOF = $[\sum w(F_o^2 - F_c^2)^2/(NO - NP)]^{1/2}$ | 1.016 |

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for RhCl[$\eta^2$-$(Me_2N)_2POP(NMe_2)_2$-$P,P'$][$P(NMe_2)_3$]**

| | | | |
|---|---|---|---|
| Rh–P(1) | 2.170(1) | Rh–Cl | 2.400(1) |
| Rh–P(2) | 2.235(1) | P(1)–P(2) | 2.508(1) |
| Rh–P(3) | 2.335(1) | | |
| P(1)–O | 1.679(2) | P(2)–O | 1.662(2) |
| P(1)–Rh–P(2) | 69.40(3) | P(1)–Rh–Cl | 164.74(4) |
| P(1)–Rh–P(3) | 104.31(4) | P(2)–Rh–Cl | 95.83(3) |
| P(2)–Rh–P(3) | 166.42(3) | P(3)–Rh–Cl | 90.93(3) |
| O–P(1)–Rh | 97.58 (8) | P(1)–O–P(2) | 97.32(12) |
| O–P(2)–Rh | 95.64(9) | | |

**Table 3. Positional Parameters for RhCl[$\eta^2$-$(Me_2N)_2POP(NMe_2)_2$-$P,P'$][$P(NMe_2)_3$]**

| | $x$ | $y$ | $z$ | $B_{eq}{}^a$ (Å$^2$) |
|---|---|---|---|---|
| Rh | 0.21675(3) | 0.69267(2) | 0.40164(1) | 1.285(6) |
| Cl | 0.31908(12) | 0.65378(6) | 0.52504(5) | 2.35(2) |
| P(1) | 0.11165(10) | 0.69257(5) | 0.28688(4) | 1.33(2) |
| P(2) | 0.20651(10) | 0.56307(5) | 0.35746(4) | 1.38(2) |
| P(3) | 0.26936(10) | 0.83314(5) | 0.42972(5) | 1.44(2) |
| O | 0.1180(3) | 0.5892(1) | 0.2736(1) | 1.54(4) |
| N(1) | −0.0775(3) | 0.7216(2) | 0.2562(2) | 1.61(5) |
| N(2) | 0.1925(3) | 0.7230(2) | 0.2180(2) | 1.67(5) |
| N(3) | 0.0844(3) | 0.4840(2) | 0.3700(2) | 1.67(5) |
| N(4) | 0.3729(3) | 0.5132(2) | 0.3553(2) | 1.84(5) |
| N(5) | 0.2156(3) | 0.8673(2) | 0.5042(2) | 1.78(5) |
| N(6) | 0.4715(3) | 0.8527(2) | 0.4505(2) | 1.78(5) |
| N(7) | 0.2165(4) | 0.9059(2) | 0.3639(2) | 1.97(6) |
| C(1) | 0.1831(5A) | 0.8117(2) | 0.1982(2) | 2.32(6) |
| C(2) | 0.3524(4) | 0.6889(3) | 0.2166(2) | 2.44(6) |
| C(3) | −0.1853(4) | 0.7284(2) | 0.3057(2) | 1.98(6) |
| C(4) | −0.1623(4) | 0.7113(2) | 0.1811(2) | 2.19(6) |
| C(5) | −0.0839(4) | 0.5108(2) | 0.3639(2) | 2.13(6) |
| C(6) | 0.1440(5) | 0.4374(2) | 0.4373(2) | 2.61(7) |
| C(7) | 0.5290(4) | 0.5500(2) | 0.3859(2) | 2.52(7) |
| C(8) | 0.3799(5) | 0.4387(2) | 0.3124(2) | 2.80(7) |
| C(9) | 0.2546(5) | 0.9501(2) | 0.5333(2) | 2.54(7) |
| C(10) | 0.0784(4) | 0.8297(2) | 0.5258(2) | 2.29(6) |
| C(11) | 0.5550(5) | 0.8337(3) | 0.3931(2) | 2.78(8) |
| C(12) | 0.5633(4) | 0.8219(2) | 0.5198(2) | 2.35(6) |
| C(13) | 0.0432(4) | 0.9136(2) | 0.3364(2) | 2.36(6) |
| C(14) | 0.2954(5) | 0.9862(3) | 0.3641(2) | 3.25(9) |

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$.

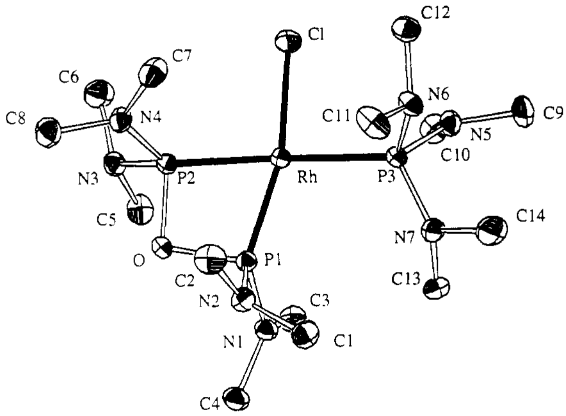

**Figure 1.** ORTEP diagram of RhCl[$(Me_2N)_2POP(NMe_2)_2$]P$(NMe_2)_3$, excluding H atoms.

run with external $C_6D_6$ sealed in a capillary tube. GC-MS was also recorded for the resulting solution.

**X-ray Crystallography.** A crystal of 1 was sealed in a capillary in a glovebox and then placed in the low-temperature nitrogen stream on a CAD4 diffractometer (graphite-monochromatized Mo K$\alpha$ radiation, $\lambda$ = 0.710 73 Å). Three intensity standard reflections were checked every hour and showed approximately 3% decay. The 4573 measured reflections were corrected for Lorentz effects, polarization, decay, and adsorption, the last employing the numerical method found in SHELX76. The structure was solved by direct methods (SHELXS86) and refined by least-squares and Fourier techniques based upon $F^2$ (SHELXL93). All non-H atoms were refined with anisotropic displacement parameters. The H atoms were fixed to their calculated positions with isotropic displacement parameters equal to 1.2 times the isotropic equivalent displacement parameters of the C atoms to which they were bound. The largest peak on the final difference Fourier map had an electron density of 0.59 e/Å$^3$ (near the Cl atom), and the lowest excursion was −0.39 e/Å$^3$. There were no significant indications of extinction. The ORTEP diagram in Figure 1 was drawn with ellipsoids at the 50% probability level. Crystal packing in 1 is characterized by channels of methyl–methyl interactions.

## Results and Discussion

RhCl[$\eta^2$-$(Me_2N)_2POP(NMe_2)_2$-$P,P'$][$P(NMe_2)_3$](1) is apparently formed from the reaction of $[Rh(COE)_2Cl]_2$ with $P(NMe_2)_3$ containing $(Me_2N)_2POP(NMe_2)_2$ impurity, a hydrolysis product present in the commercially obtained $P(NMe_2)_3$ (as indicated by GC-MS). Additionally, some 1 may have formed via a hydrolysis pathway involving residual water in the dried solvent, as indicated by the following experiment. One equivalent each of $P(NMe_2)_3$ and water (per rhodium) were added to a $C_6D_6$ solution of 2 in an NMR tube. $^{31}P$ NMR spectroscopy revealed the formation of complex 1 (30% yield based on 2 after ca. 10 min; 73% after 12 h). After 12 h, a second equivalent of $H_2O$ was added, and 2 was no longer observable; 1 was the exclusive product. Complex 1 was quite stable to excess water, with no further changes in the $^{31}P$ NMR spectrum after 2 days. In a control experiment with no water added, 11% yield of 1 was observed 36 h after mixing.

The coordination sphere of 1 (see Figure 1) may be considered as a severely distorted square-planar arrangement with a dihedral angle of 13° between the Rh–P(1)–P(2) and Rh–P(3)–Cl planes. The oxygen atom is almost in the P(1)–Rh–P(2) plane, and the Rh atom is 0.1 Å out of the P(1)–P(2)–P(3)–Cl plane. The Rh–Cl and Rh–P bond lengths are as expected and similar to those in, e.g., $RhCl(PPh_3)_3$.[5] The structural feature of greatest interest is the four-membered Rh–P–O–P ring. Because of the very narrow bite angle of the chelating ligand, the P(1)–Rh–P(2) angle is only 69.40(3)°; the P(1)–O–P(2) angle is

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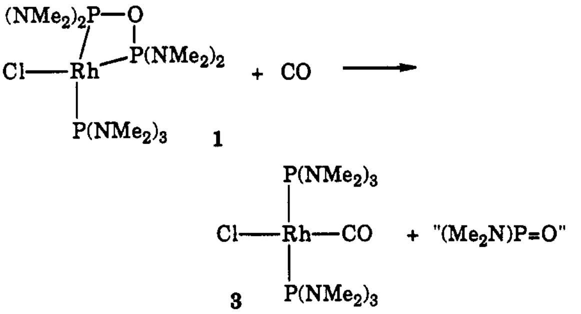
97.32(12)°. The crystal structure of the most closely related complex previously reported, $RhCl(Ph_2POPPh_2)PPh_3$, is strikingly similar.[6] For that complex the P(1)–Rh–P(2) and P(1)–O–P(2) angles are 68.4(2) and 95.4(5)°, respectively.

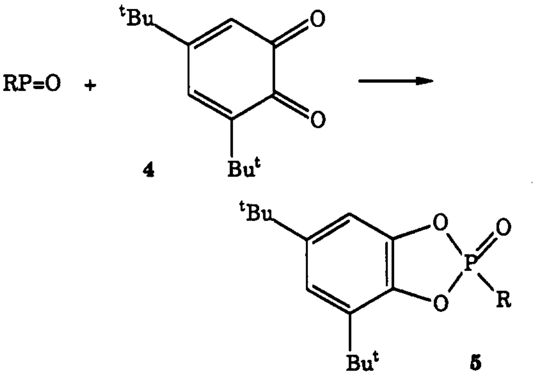
Complex 1 undergoes a remarkable reaction with carbon monoxide. For example, 800 Torr of CO was added to a resealable NMR tube containing a 20 mM solution of 1 in $C_6D_6$. Both $^1H$ and $^{31}P$ NMR revealed that a clean reaction occurred; bis[tris(dimethylamino)phosphine]carbonylchlororhodium (3) formed within 10 min. The stoichiometry of the reaction requires that complex 1 must lose a "$(Me_2N)P{=}O$" unit ((dimethylamino)phosphinidene oxide).



(1)

Phosphinidene oxides are not isolable as monomers but some well-defined oligomers have been isolated; of these, the closest analog to "$Me_2NP{=}O$" is "$Pr^i_2NP{=}O$", isolated as a trimer.[7] In our case, however, a complex mixture of products appeared to form in reaction 1. The $^1H$ NMR spectrum revealed several broad signals overlapping with the triplet of methyl protons of 3, and the $^{31}P$ NMR spectrum contained some poorly resolved signals at $\delta$ 123, 128–129, and 159, as well as the doublet of 3 ($\delta$ 119.7).

Quast and Heuschmann have reported that "$Bu^tP{=}O$" can be trapped quantitatively in benzene-$d_6$ using 3,5-di-*tert*-butyl-1,2-benzoquinone (eq 2; R = $Bu^t$).[8] When 1 is reacted with CO in the presence of 4, $Me_2NP{=}O$ is trapped analogously (eq 2; R = $NMe_2$). Preliminary results revealed that 4 reacts rapidly with 1 at room temperature, giving an unidentified product (singlet at $\delta$ −23.7 in the $^{31}P$ NMR spectrum). (The carbonyl complex 3, however, does not react with 4 at ambient temperature.) The trapping experiment was therefore carried out at low temperature. A 1.5-equiv quantity of 4 was mixed with 1 in toluene-$d_8$ at −78 °C under 800 Torr of CO. The mixture was allowed to warm slowly to room temperature with shaking. The $^{31}P$ NMR spectrum revealed the complete disappearance of 1 and the formation of 3 (ca. 55% yield based on integration of all peaks) along with a singlet at $\delta$ 12.7 with an integrated area equal to 50% of that of the doublet attributable to 3 ($\delta$ 119.7), as well as some uncharacterized, probably rhodium-containing, species. The only species detected by GC-MS analysis showed a parent peak with $m/e$ = 311 (the major peak was $m/e$ = 296, attributable to loss of $CH_3$), presumably the trapped product 5. 5 was independently synthesized by refluxing 3,5-di-*tert*-butylcatechol and $O{=}P(NMe_2)_3$ in toluene for 24 h with a conversion of 40%; its GC-MS and NMR spectroscopic properties were identical to those of the product of the reaction of CO, 1, and 4. The ratios of 5 to unreacted $O{=}P(NMe_2)_3$ obtained by GC-MS and by $^{31}P$ NMR were in good agreement (GC-MS 0.68, $^{31}P$ NMR 0.64), further supporting the assignment of the $^{31}P$ NMR signal at $\delta$ 12.7 to the species with parent peak $m/e$ = 311 observed by GC-MS.



(2)

A plausible mechanism for the formation of 3 from the reaction of 1 with CO (eq 1) may be suggested. CO readily displaces phosphines from complexes of the form $RhL_3Cl$.[9] Displacement of one of the chelating phosphorus groups from 1, as opposed to the monodentate $P(NMe_2)_3$ ligand, would be favored by strain in the RhPOP ring (the P(1)–Rh–P(2) and P(1)–O–P(2) angles are 69.40(3) and 97.32(12)°, respectively) and by the strong driving force for the trans-phosphine configuration in complexes of the type $RhL_2(CO)Cl$.[9] The dangling $P(NMe_2)_2$ moiety which would result may then attack (at P) the coordinated $P(NMe_2)_2$ group; such behavior would be consistent with the known nucleophilic character of the nitrogen-based lone pairs of aminophosphines[10] and the electrophilic character of the phosphorus atom[10] (which is probably greatly enhanced by coordination).

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**Supplementary Material Available:** Tables of intramolecular distances and angles, torsion angles, least-squares planes, anisotropic displacement parameters, and H atom parameters (7 pages). Ordering information is given on any current masthead page.

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