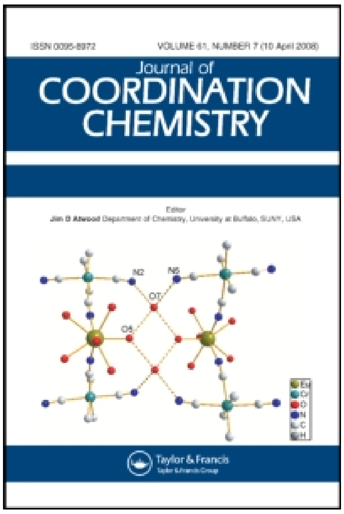

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SYNTHESIS AND CHARACTERIZATION OF THE COORDINATED CHLOROAMIDOPHOSPHINE COMPLEXES $M(CO)_5P(NMe_2)_2$ Cl (M = Cr, W) AND $W(CO)_5P(MeN(CH_2)_2NMe)Cl$, AND THEIR REACTIVITY WITH $AlCl_3$

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SYNTHESIS AND CHARACTERIZATION OF THE COORDINATED CHLOROAMIDOPHOSPHINE COMPLEXES $M(CO)_5P(NMe_2)_2Cl$ (M = Cr, W) AND $W(CO)_5P(MeN(CH_2)_2NMe)Cl$, AND THEIR REACTIVITY WITH $AlCl_3$

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The monosubstituted metal carbonyl complexes $M(CO)_5P(NMe_2)_2Cl$ (M = Cr, W) and $W(CO)_5P(MeN(CH_2)_2NMe)Cl$ have been prepared from the reaction of haloamidophosphine ligands with $M(CO)_5THF$ precursor complexes. The resulting compounds were characterized by infrared and multinuclear NMR (^{31}P, ^{13}C, ^{17}O) spectroscopic methods. Use of ^{13}C NMR spectral data in conjunction with ^{17}O NMR chemical shift values for these compounds gives an indication of σ donor/π acceptor ability relative to other Group VI monosubstituted phosphine complexes. Attempts to form coordinated phosphenium cation complexes from these compounds by chloride abstraction with $AlCl_3$ yielded the unexpected adducts $M(CO)_5L\cdot AlCl_3$.

KEYWORDS: chloroamidophosphine, phosphenium cation, tetrachloroaluminate

INTRODUCTION

Phosphenium cations have been studied extensively as strong π acid ligands when coordinated to Fe(0).[1,2] These ligands offer the unique combination of a lone pair attached to a positively charged phosphorus atom, giving an unprecedented ability to withdraw charge density from transition metal centers. This ability to modify charge on the metal allows for significant alteration of the properties of low-valent transition metal complexes; it would seem natural to extend the coordination chemistry of these interesting ligands to other transition metals. In spite of this, only a few phosphenium cation complexes containing transition metals other than iron have been reported.[3] Of these, there are no reported Group VI complexes in which the phosphenium cation retains its positive charge.

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Precursors for phosphenium cations coordinated to Fe(0) have generally been mixed haloamidophosphine iron carbonyl complexes. The coordinated phosphenium cations are formed by extraction of a halide ion from the phosphine ligand by a suitable Lewis acid:

$$(R_2N)_2P(Cl)Fe(CO)_4 + AlCl_3 \rightarrow [(R_2N)_2PFe(CO)_4]^+ + [AlCl_4]^-$$

In spite of a dearth of such complexes containing metals other than iron, a simple and logical extension for synthesis of analogous complexes using other metal carbonyls appeared reasonable. In this work we report the synthesis and characterization of the precursor complexes $M(CO)_5P(NMe_2)_2Cl$ (M = Cr,W) and $W(CO)_5P(MeN(CH_2)_2NMe)Cl$ and the results of the interaction of these complexes with aluminum chloride.

EXPERIMENTAL

General Procedures

All manipulations were performed under an atmosphere of dry nitrogen utilizing standard Schlenk techniques. $Cr(CO)_6$, $W(CO)_6$, PCl_3, and N,N′-dimethylethylenediamine were obtained from Aldrich. Dimethylamine was obtained from Linde. $P(NMe_2)_2Cl$ and $P(MeN(CH_2)_2NMe)Cl$ were prepared according to published methods.[4] Aluminum chloride was purified by sublimation. NMR spectra were recorded as CH_2Cl_2 solutions containing 10% $CDCl_3$ added as a lock and chemical shift reference (with respect to TMS) on a Bruker WM-250 spectrometer. ^{31}P NMR chemical shifts are referenced to external $H_3PO_4(aq)$; ^{13}C NMR chemical shifts are referenced to TMS; ^{17}O NMR chemical shifts are referenced to external H_2O. IR spectra were recorded on a Nicolet MX-1 infrared spectrometer as CH_2Cl_2 solutions. Mass spectra were obtained utilizing electron impact methods on a HP-5859 GC/MS.

Preparation of the $M(CO)_5L$ Derivatives

In a typical reaction, 12 mmol of the metal hexacarbonyl was dissolved in 250 ml of THF and photolyzed under a constant stream of nitrogen in a photochemical reaction vessel (450 W broadband lamp, Hanovia) for eight hours, followed by the addition of 2.00 g of ligand and subsequent stirring for approximately 40 hours. Solvent removal *in vacuo* followed by extraction of the residue with hexane and subsequent evaporation to dryness yields the desired complex. All of these complexes are extremely air and moisture-sensitive and it was not possible to secure satisfactory elemental analyses. However, in each case electron impact mass spectra of these compounds produced a parent ion peak consistent with the $M(CO)_4L$ fragment which was universally the peak of maximum relative abundance. In addition, no impurities were observed in the spectral characterization of the complexes.

$Cr(CO)_5P(NMe_2)_2Cl$: $\delta(^{31}P) = 196.72$ ppm (ref. H_3PO_4); $\delta(^{13}C)$: $(CH_3) = 39.03$ ppm, (CO), *cis* = 213.38 ppm ($^2J_{PC} = 16.36$ Hz), (CO), *trans* = 218.50 ppm; $\nu(CO) = 2055$ (w), 1957 (vs) cm^{-1}.

$W(CO)_5P(NMe_2)_2Cl$: $\delta(^{31}P) = 127.58$ ppm ($^1J_{WP} = 380.0$ Hz); $\delta(^{13}C)$: $(CH_3) =$

38.90 ppm ($^2J_{PC}$ = 5.7 Hz), (CO), *cis* = 194.07 ppm ($^2J_{PC}$ = 5.7 Hz), (CO), *cis* = 194.70 ppm ($^2J_{PC}$ = 8.8 Hz), (CO), *trans* = 197.35 ppm ($^2J_{PC}$ = 49.69 Hz); ν(CO) = 2087 (w), 1962 (vs) cm^{-1}.

$W(CO)_5P(MeN(CH_2)_2NMe)Cl$: $\delta(^{31}P)$ = 141.53 ppm ($^1J_{WP}$ = 366.5 Hz); $\delta(^{13}C)$: (CH_3) = 32.64 ppm ($^2J_{PC}$ = 9.4Hz), (CH_2) = 50.69 ppm ($^2J_{PC}$ = 6.3 Hz), (CO), *cis* = 194.78 ppm ($^2J_{PC}$ = 9.44 Hz), (CO), *trans* = 198.08 ppm ($^2J_{PC}$ = 42.77 Hz); ν(CO) = 2076 (w), 1944 (vs) cm^{-1}.

Reaction of the $M(CO)_5L$ Complexes with $AlCl_3$

0.9 mmol (0.120 g) of freshly sublimed $AlCl_3$ was transferred to a specially modified NMR tube with stopcock/adapter in a Vacuum Atmosphere drybox. This tube was next transferred to a Schlenk/vacuum line, purged with nitrogen, 0.3 ml of CH_2Cl_2 added, and then cooled to −196°C. An equimolar amount of the $M(CO)_5L$ complex dissolved in 2.0 ml of 3:1 $CH_2Cl_2/CDCl_3$ was added with a syringe, and the system subsequently degassed three times. The tube was sealed at a set constriction and allowed to warm very slowly to room temperature. Varying the amount of $AlCl_3$ (in excess), lengthening the reaction time or moderately increasing the temperature had no apparent affect on the course of the reaction. Upon addition of excess $AlCl_3$, a resonance due to $AlCl_3$ is observed in the ^{27}Al NMR spectrum in addition to that of the $M(CO)_5L \cdot AlCl_3$ adduct.

$Cr(CO)_5P(NMe_2)_2Cl \cdot AlCl_3$: $\delta(^{31}P)$ = 195.41 ppm (ref. H_3PO_4) (220K); $\delta(^{13}CO)$: (CO), *cis* = 213.20 ppm, (CO), *trans* = 218.54 ppm (297K); $\delta(^{27}Al)$ = 102.6 ppm (297K), 103.0 ppm (220K).

$W(CO)_5P(NMe_2)_2Cl \cdot AlCl_3$: $\delta(^{31}P)$ = 126.32 ppm ($^1J_{WP}$ = 378.0 Hz) (297K); $\delta(^{13}C)$: (CO), *cis* = 195.0 ppm, (CO), *trans* = 197.7 ppm (297K); $\delta(^{27}Al)$ = 102.9 ppm (297K), 103.0 ppm (220K).

$W(CO)_5P(MeN(CH_2)_2NMe)Cl \cdot AlCl_3$: $\delta(^{31}P)$ = 141.53 ppm ($^1J_{WP}$ = 364.5 Hz) (297K); $\delta(^{13}C)$: (CO), *cis* = 195.0 ppm, (CO), *trans* = 198.5 ppm (297K); $\delta(^{27}Al)$ = 102.5 ppm (297K), 103.0 ppm (220).

RESULTS AND DISCUSSION

Synthesis and Characterization of Haloamidophosphines Coordinated to Chromium(0) and Tungsten(0) Carbonyls

The synthesis of the monosubstituted haloamidophosphine derivatives is readily achieved by photolysis of the parent hexacarbonyl in THF, followed by addition of the appropriate ligand:

$$M(CO)_6 \xrightarrow[h\nu]{THF} \xrightarrow{L} M(CO)_5L,$$

$$L = P((NMe_2)_2Cl \text{ for } M = Cr,W;\ L = P(MeN(CH_2)_2NMe)Cl \text{ for } M = W.$$

Spectroscopic data for these complexes, including ^{13}C and ^{17}O NMR chemical shifts $^1J_{WP}$ and infrared stretching frequencies, are given in Tables 1 and 2. These values are listed along with those of other monosubstituted tungsten/chromium

Table 1 ^{13}CO NMR and IR data of some $M(CO)_5L$ ($M = Cr,W$) complexes, including newly synthesized $M(CO)_5P(NMe_2)_2Cl$ ($M = Cr,W$) and $W(CO)_5P(MeN(CH_2)_2NMe)Cl$.

For M = W, L	δ(CO) *cis*	δ(CO) *trans*	ν(CO)/E mode[b]
PMe_3[a]	197.0	200.0	-
PPh_3[a]	197.2	199.0	1942
$P(OMe)_3$[a]	196.5	199.5	1953
$P(OPh)_3$[a]	194.0	196.5	1959
$P(NMe_2)_2Cl$	194.5	196.9	1962
$P(MeN(CH_2)_2NMe)Cl$	194.8	198.1	1944
For M = Cr, L	**δ(CO) *cis***	**δ(CO) *trans***	**ν(CO)/E mode[b]**
PPh_3[c]	216.5	221.3	-
$P(OPh)_3$[c]	213.8	217.5	-
$P(NMe_2)_2Cl$	213.4	218.5	1957

[a]Ref. 8(a) [b]Ref. 6 [c]Ref. 5

carbonyl complexes containing phosphine ligands possessing varying π-acceptor abilities. The data are presented in this manner in order to ascertain the relative donor/acceptor abilities of these neutral chloroamidophosphines. Previous studies have utilized correlation of $\delta(^{13}CO)$ with $\delta(C^{17}O)$,[5] $^1J_{WP}$ or $^1J_{WC}$ with the corresponding E mode of ν(CO) in the infrared,[6] or $^1J_{WP}$ with the PR_3 substituent electronegativity[7] in order to make these comparisons.

Comparison of ^{17}O and ^{13}C Chemical Shifts

Based on arguments previously established in terms of the Pople-Santry treatment of the paramagnetic shielding tensor, it is anticipated that the carbonyl carbon *trans* to the substituent ligand L would experience increased π electron density from the metal as they basicity of the ligand increases. This would result in an increased contribution of Q_{MC} in the carbonyl shielding term, and a subsequent downfield shift.[9] Indeed, for the tungsten complexes, the order of observed ^{13}CO chemical shifts follows that expected for the relative sigma donor abilities of the coordinated phosphine ligands:

$$PMe_3 > PPh_3 > P(MeN(CH_2)_2Cl > P(NMe_2)_2Cl > P(OPh)_3$$

Note here that ^{13}CO chemical shifts for the amidochlorophosphines are in the range observed for phosphites coordinated to metal carbonyls. The $\delta(^{17}O)$ of the *trans* CO

Table 2 ^{17}O NMR (ppm) and $^1J_{WP}$ (Hz) data of some $W(CO)_5L$ complexes, including newly synthesized $W(CO)_5P(NMe_2)_2Cl$ and $W(CO)_5P(MeN(CH_2)NMe)Cl$.

For M = W, L	$\delta(^{17}O)$ *cis*	$\delta(^{17}O)$ *trans*	$^1J_{WP}$[b]
PPh_3[a]	353.6	~353.6	280
$P(n\text{-}Bu)_3$[a]	354.1	354.1	200
$P(OMe)_3$[a]	353.7	359.0	398
$P(NMe_2)_2Cl$	353.8	360.4	380
$P(MeN(CH_2)_2NMe)Cl$	350.7	354.0	367

[a]Ref. 12 [b]Ref. 6

of these complexes follow the expected inverse order,[6] again similar to the chemical shift trend exhibited by coordinated phosphite ligand(s):

$$PPh_3 < P(MeN(CH_2)NMe)Cl < P(OMe)_3 \approx P(NMe_2)_2Cl$$

It should be noted that the analogous chromium complexes also parallel the behavior of the tungsten complexes with respect to the $\delta(^{13}CO)$ of the carbonyl *trans* to the phosphine, that is:

$$PPh_3 > P(NMe_2)_2Cl > P(OPh)_3$$

Analysis of the frequencies of the most intense $\nu(CO)$ band for these complexes in the infrared, assumed to be the E mode,[10] is in agreement with this analysis, with the coordinated phosphites and amidochlorophosphines producing the highest energy stretching frequencies:

$$PPh_3 < P(NMe_2)_3 < P(OMe)_3 < P(OPh)_3 \approx P(NMe_2)_2Cl$$

This is expected as the better π-accepting phosphines compete more effectively with CO for charge density from the metal, thus less electron density in available for π donation into the M-CO bond and a correspondingly higher stretching frequency ($\nu(CO)$) is observed.

The one-bond tungsten-phosphorus coupling constants, $^1J_{WP}$, follow the order:

$$PPh_3 < P(NMe_2)_3 < P(MeN(CH_2)_2NMe)Cl < P(NMe_2)_2Cl < P(OMe)_3$$

It is possible to rationalize this trend roughly on the basis of single substituent electronegativities of the atoms bound directly to phosphorus, without invoking π bonding arguments. However, it should be noted that this is the same order observed for the *trans* $\delta(^{13}CO)$ values. Furthermore, substituent electronegativities do not explain the differences between the $P(MeN(CH_2)_2NMe)Cl$ and $P(NMe_2)_2Cl$ complexes. A more reasonable explanation for this observation is that increased donation of π density into the tungsten-phosphorus bond synergistically increases the interactions of spherically symmetric ('s') charge density in the sigma bond, reflected in a larger $^1J_{WP}$ (a function of $\psi_s{}^*\psi_s$).

All of these observations lead to the general conclusion that in these newly synthesized complexes the amidochlorophosphine ligands function as π-acceptors of comparable ability to the phosphites.

Reaction of Coordinated Haloamidophosphines with Aluminum Chloride

Formation of Lewis acid-base adducts with the nitrogen and/or phosphorus lone pairs was anticipated upon addition of aluminum chloride to methylene chloride solutions of haloamidophosphines. The acid-base reaction which dominates, however is between Cl^- and $AlCl_3$, resulting in the formation of $[(R_2N)_2P]^+ [AlCl_4]^-$.[11] This is unexpected on the basis of a simple donor/acceptor model, and must depend thermodynamically on the formation of the stable solvated $[AlCl_4]^-$ anion, and the ability of the N-P-N π system to delocalize the positive charge which would otherwise reside on the phosphorus atom. Coordination to a metal center would serve to enhance the stability of the cation by further neutralizing positive charge through metal dπ – ligand dπ back donation. Despite this, to date, there have been no reports of a cationic phosphenium complex involving a Group VI transition metal, although the corresponding iron derivatives are well known,[1,2] and a nickel carbonyl derivative was recently reported[3]. Somewhat surprisingly, the reaction of $M(CO)_5P(NMe_2)_2Cl$ (M = Cr,W) or $W(CO)_5P(MeN(CH)_2)_2NMe)Cl$ with either a stoichiometric or excess amount of $AlCl_3$ in CH_2Cl_2 did *not* produce the anticipated phosphenium cation complex!

Haloamidophosphines experience tremendous downfield ^{31}P chemical shifts upon abstraction of the halide ion, usually on the order of 100 ppm downfield from H_3PO_4.[11] ^{13}CO resonances also shift upfield as a consequence of the loss of π electron density,[12] which is polarized toward the phosphenium cation. In contrast, addition of $AlCl_3$ to CH_2Cl_2 solutions of the haloamidophosphine carbonyl complexes of chromium and tungsten yielded virtually no shift in the observed ^{13}CO resonances and only a 1 ppm shift for the ^{31}P signal, thus ruling out the possibility that a coordinated amidophosphenium cation is formed with any of the neutral complexes.

While only small changes are observed for NMR active nuclei in the $M(CO)_5P(NR_2)_2Cl$ complexes, ^{27}Al NMR spectra of the mixtures indicates that aluminum chloride undergoes a significant modification. $AlCl_3$ in methylene chloride exhibits a ^{27}Al resonance at 93 ppm with an extremely large linewidth of 1489 Hz at 220 K. This is due in large part to relaxation broadening resulting from the interaction of the ^{27}Al quadrupole with an asymmetric electric field gradient about the aluminum. If the field gradient becomes symmetric, the resonance sharpens as this interaction decreases. In $[AlCl_4]^-$, where the charge density about the nucleus is tetrahedral, the ^{27} Al resonance shifts approximately 10 ppm from the $AlCl_3$ resonance and sharpens to an 8.0 Hz linewidth.

The ^{27}Al NMR spectrum of the $Cr(CO)_5P(NMe_2)_2Cl/AlCl_3$ mixture is shown in Figure 1. The resonance has shifted to within 1 ppm of $[AlCl_4]^-$, and has narrowed to 354 Hz at 220 K. This behavior is observed for all of the haloamidophosphines in this study. Very minor perturbations can result in significant line broadening, and it is clear that the ^{27}Al nucleus is in an environment closer to that of tetrachloroaluminate than aluminum chloride. On the other hand, the modest shift in the ^{31}P resonance of the haloamidophosphine complexes indicates that the chloride ion has not been extracted from the phosphine ligand. It appears that a pseudo-symmetric four-coordinate aluminium species forms, probably in the form of a $M(CO)_5$ $P(NR_2)_2Cl{:}AlCl_3$ adduct. A proposed structure is shown in Figure 2.

As the temperature is raised to ambient conditions, the linewidths decrease for the $M(CO)_5P(NR_2)_2Cl{:}AlCl_3$ adducts and for free aluminum chloride. As illustrated in Table 3, the resonances sharpen by a factor of four for the adduct and $AlCl_3$ alike. In the case of aluminum chloride, this is probably due to shorter correlation times, and decreased *external* perturbations to the electric field gradient about the ^{27}Al nucleus. The sharpening of the adduct resonance is probably due to a similar effect,

Table 3 Temperature effects on the ^{27}Al NMR chemical shift* (ppm) and corresponding linewidth (Hz) of several aluminum-containing compounds

Complex	220K δ(ppm)/$\Delta\nu$	240K δ(ppm)/$\Delta\nu$	270K δ(ppm)/$\Delta\nu$	297K δ(ppm)/$\Delta\nu$
$W(CO)_5P(NMe)_2)_2Cl\cdot AlCl_3$	103.0/354	103.0/244	102.9/171	102.9/73
$AlCl_3$	93.4/1489	93.3/1001	93.0/879	92.7/397
$[Et_4N]$ $[AlCl_4]$	102.4/8.0	102.4/8.0	102.4/10	102.4/10

*All chemical shifts are referenced with respect to $AlCl_4^-$ and normalized to $Al(H_2O)_6^+$.

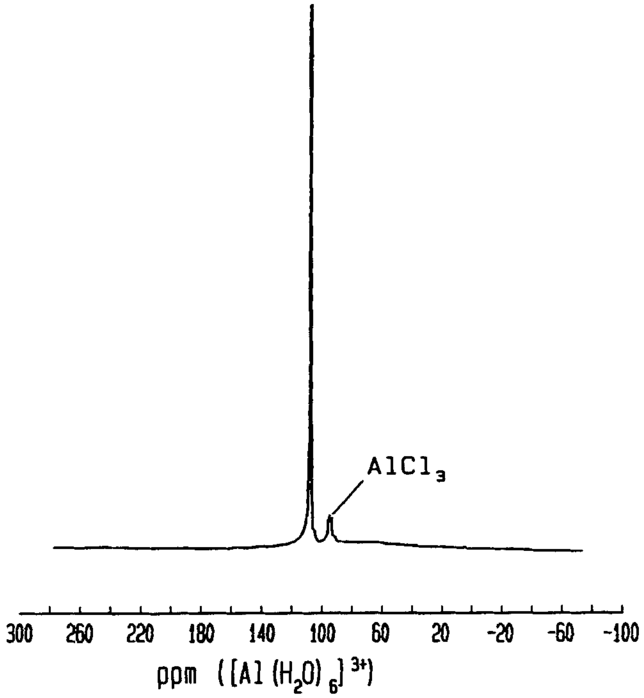

Figure 1 ^{27}Al NMR spectrum of $Cr(CO)_5P(NMe_2)_2Cl\cdot AlCl_3$ at 220 K

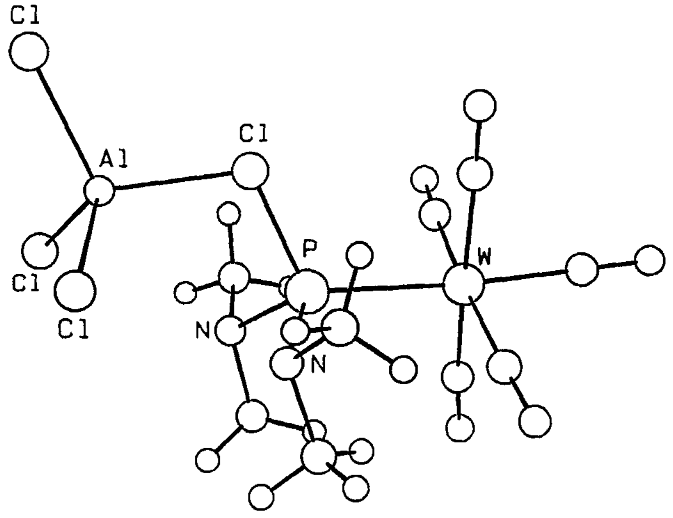

Figure 2 Proposed structure for $M(CO)_5P(NR_2)_2Cl$:$AlCl_3$ adduct

since no chemical shift change is observed. If the complex was undergoing a dynamic exchange process with $AlCl_3$, a change in the chemical shift toward free aluminum chloride would be expected, and this is *not* observed.

CONCLUDING REMARKS

In contrast to the haloamidophosphine complexes of iron, it appears that under the conditions of this study, similar complexes of chromium and tungsten form Lewis acid-base adducts rather than phosphenium cations. Even so, the apparent coordination of $AlCl_3$ to the halogen on the ligand rather than an amido nitrogen is surprising. On the other hand, this is perfectly consistent with the formation of phosphenium ions in the case of free haloamidophosphine ligands and their iron carbonyl complexes. While these observations suggest a possible explanation for the paucity of phosphenium ion complexes in the literature, other routes, such as the utilization of the fluoroamidophosphine derivatives and halide abstraction by suitable Lewis acids such as PF_5 might yield greater success.

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