

[CONTRIBUTION FROM THE UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, B. C., AND THE MELLON INSTITUTE, PITTSBURGH 13, PENNSYLVANIA]

Phosphorus- and Arsenic-Bridged Complexes of Metal Carbonyls. IV.¹ Reactions of Tetrakis(trifluoromethyl)diarsine with Some Metal Carbonyl Compounds

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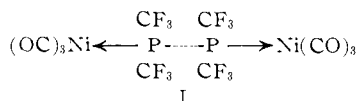
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$\text{As}_2(\text{CF}_3)_4$ reacts with $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2]_2$ to give the mononuclear complexes $[\text{C}_5\text{H}_5\text{M}\{\text{As}(\text{CF}_3)_2\}(\text{CO})_n]$ ($\text{M} = \text{Fe}$, $n = 2$; $\text{M} = \text{Mo}$, $n = 3$) which dimerize on irradiation with ultraviolet light to form $[\text{C}_5\text{H}_5\text{M}\{\text{As}(\text{CF}_3)_2\}(\text{CO})_{n-1}]_2$. $\text{Mn}_2(\text{CO})_{10}$ and $[\text{Fe}(\text{CO})_2(\text{NO})_2]$ react with $\text{As}_2(\text{CF}_3)_4$ to give $[\text{Mn}\{\text{As}(\text{CF}_3)_2\}(\text{CO})_4]_2$ and $[\text{Fe}\{\text{As}(\text{CF}_3)_2\}(\text{NO})_2]_2$, respectively. The reactions of $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ with $\text{As}_2(\text{CF}_3)_4$ have also been investigated. The infrared and nuclear magnetic resonance spectra of the compounds are discussed.

In the previous papers of this series, the reactions of tetrasubstituted-diphosphine and -diarsine ligands with metal carbonyls and cyclopentadienyl metal carbonyls have been investigated. Many novel, usually binuclear, complexes were obtained from these reactions and it was shown that the two metal atoms are linked by phosphorus or arsenic bridges.¹ There were some indications that electronegative substituents on the ligand atom tend to facilitate P-P or As-As bond cleavage.³ It is also possible that such substituents might sufficiently decrease the donor power of the ligand atom so as to inhibit bridge formation. In order to study these effects, we have carried out reactions of tetrakis(trifluoromethyl)diarsine, $\text{As}_2(\text{CF}_3)_4$, with a selected group of metal carbonyl compounds.

In general, trifluoromethyl-substituted arsines are very poor donor ligands and thus usually do not form adducts with mercuric chloride.⁴ The donor properties of $\text{As}_2(\text{CF}_3)_4$ have not been investigated in detail, although it does not form an adduct with methyl iodide at 75° and is not expected to differ greatly in this respect from other arsines of this type. This behavior is usually attributed to the high electronegativity of the trifluoromethyl group which decreases the availability of the lone pair of electrons for donation.⁶ However, if the current view that π -bonding makes a significant contribution to the bonding between transition metals and suitable π -acceptor ligands is valid, then the trifluoromethyl arsines, like PF_3 ,⁷ should behave as reasonably good ligands toward, for example, metal carbonyl compounds.

Some indication of the interesting potential of trifluoromethyl-substituted phosphines and arsines as ligands come from the work of Burg and Mahler.⁸ They investigated the reactions of nickel carbonyl with $\text{P}(\text{CF}_3)_3$, $\text{P}_2(\text{CF}_3)_4$, and $(\text{PCF}_3)_4$ and obtained a series of stable complexes. Of particular interest is the reaction of $\text{Ni}(\text{CO})_4$ with $\text{P}_2(\text{CF}_3)_4$ to give a complex (of proposed structure I) which is red-black in color, a very unusual color for a zerovalent nickel complex. More recently, the reactions of $(\text{CF}_3)_2\text{PI}$ with iron and



manganese carbonyls were found to give stable binuclear complexes, probably containing bridging phosphorus.⁹

Experimental

Microanalyses¹⁰ and molecular weight measurements were by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and Dr. A. Bernhardt, Max-Planck Institut für Kohlenforschung, Mülheim, Germany. Melting points were determined in sealed capillaries under nitrogen and are uncorrected.

Infrared spectra were measured on a Beckman IR-9 spectrophotometer. ¹⁹F nuclear magnetic resonance spectra were measured at 56.4 Mc./sec. on a Varian Associates V-4311 instrument using CCl_3F as both solvent and standard. The chemical shifts were expressed on the ϕ scale,¹¹ although no extrapolation to infinite dilution was carried out. The ¹H n.m.r. spectra were measured on a Varian Associates A-60 spectrometer using CCl_3F as solvent and tetramethylsilane as an internal reference.

All operations, except the handling of the solid complexes, were carried out in a nitrogen atmosphere. Merck acid-washed alumina was used for chromatographic purifications. The irradiations were carried out in a Vycor reaction vessel using a General Electric 360 w. Uviarc lamp. The metal carbonyls were either purchased or were prepared by methods already described in the literature.¹² Tetrakis(trifluoromethyl)diarsine was prepared by the method of Brandt, *et al.*¹³

Preparation of the Complexes. π -Cyclopentadienylbis(trifluoromethyl)arsenidodicarbonylmolybdenum.— $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2]_2$ (0.70 g., 1.43 mmoles), $\text{As}_2(\text{CF}_3)_4$ (0.61 g., 1.43 mmoles), and toluene (50 ml.) were refluxed together for 4 hr. to give an orange solution, which was then filtered and evaporated at 15 mm. The residual brown oil crystallized at -78° and the resulting solid was sublimed at 75° (0.2 mm.). Oily crystals were obtained at first and finally the pure complex sublimed at 85° as yellow-orange crystals (m.p. 111–117°; yield, 64%).

Anal. Calcd. for $\text{C}_{10}\text{H}_5\text{AsF}_6\text{MoO}_2$: C, 26.2; H, 1.1; F, 24.9; Mo, 20.95; mol. wt., 458. Found: C, 25.5; H, 0.9; F, 25.5; Mo, 21.2; mol. wt. (C_6H_6), 444.

The ¹H n.m.r. spectrum shows a singlet due to the cyclopentadienyl protons at 4.52 τ and the ¹⁹F spectrum a singlet at 40.45 ϕ .

π -Cyclopentadienylbis(trifluoromethyl)arsenidodicarbonyliron.— $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ (0.66 g., 1.87 mmoles), $\text{As}_2(\text{CF}_3)_4$ (0.80 g., 1.87 mmoles), and toluene (50 ml.) were refluxed together for 16 hr. to give an orange solution containing some black solid. After filtration, the solvent was evaporated at 15 mm., leaving a red oil which solidified to yellow crystals at -78° . These were dissolved in hexane and chromatographed. A faint yellow band was eluted by 10% benzene-hexane and the main band by 50% benzene-hexane. Evaporation of the yellow-orange eluate gave a brown oil which crystallized at -78° . Two sublimations at 55° (0.2 mm.) gave the pure complex as orange crystals (m.p. 48–50°; yield, 65%).

Anal. Calcd. for $\text{C}_9\text{H}_5\text{AsF}_6\text{FeO}_2$: C, 27.7; H, 1.3; F, 29.2; Fe, 14.3; mol. wt., 390. Found: C, 27.0, 27.5; H, 1.2, 1.25; F, 28.25, 31.2; Fe, 14.4, 14.9; mol. wt. (C_6H_6), 376, 340.

The ¹H n.m.r. spectrum shows a singlet due to the cyclopentadienyl protons at 5.08 τ and the ¹⁹F spectrum a singlet at 42.16 ϕ .

Di- μ -(bis(trifluoromethyl)arsenido)-di- π -cyclopentadienyl-tetracarbonyldimolybdenum.—A solution of $[\text{C}_5\text{H}_5\text{Mo}\{\text{As}(\text{CF}_3)_2\}(\text{CO})_2]$ (0.69 g.) in methylcyclohexane (30 ml.) was stirred and irradiated with ultraviolet light for 16 hr. The solution changed from yellow to black and deposited black crystals. These were

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filtered and crystallized from methylcyclohexane to give a dark green solution and, on cooling, brown crystals, with a yellow-green streak (m.p. 320–330° dec., with darkening and sublimation above 280°; yield, 46%).

Anal. Calcd. for $C_{18}H_{10}As_2F_{12}Mo_2O_4$: C, 25.15; H, 1.2; F, 26.5; Mo, 22.3; mol. wt., 860. Found: C, 25.0; H, 1.8; F, 26.3; Mo, 24.6, 24.9; mol. wt. (C_8H_8), 828.

The 1H spectrum shows a singlet at 4.44 τ due to the cyclopentadienyl protons and the ^{19}F spectrum a singlet at 46.29 ϕ .

Di- μ -(bis(trifluoromethyl)arsenido)-di- π -cyclopentadienyl-dicarbonyliron.—Irradiation of $[C_5H_5Fe\{As(CF_3)_2\}(CO)_2]$ as described above gave a dark brown solution. After evaporation of solvent, the residual sticky solid was sublimed first at 60° and 0.2 mm. to remove a yellow oil and then at 95° (0.2 mm.) to give yellow-brown crystals (m.p. 260–262° dec.; yield, 60%).

Anal. Calcd. for $C_{18}H_{10}As_2F_{12}Fe_2O_2$: C, 26.55; H, 1.4; F, 31.5; Fe, 15.4; mol. wt., 724. Found: C, 26.8; H, 1.5; F, 31.35; Fe, 15.5; mol. wt. (C_8H_8), 771.

In the 1H n.m.r. spectrum absorption due to the cyclopentadienyl protons is observed at 5.43 τ . The absorption consists of two singlets separated by 0.7 c.p.s., the peak at higher field being the stronger by a factor of 1.65. The ^{19}F n.m.r. spectrum consists of a strong singlet at 48.57 ϕ flanked by two weak quartets at 46.15 and 51.38 ϕ , respectively, the coupling constant ($J_{FF'}$) being 6.65 c.p.s.

Di- μ -(bis(trifluoromethyl)arsenido)octacarbonyldimanganese.—Manganese carbonyl (0.465 g., 1.19 mmoles), tetrakis(trifluoromethyl)diarsine (0.506 g., 1.19 mmoles), and methylcyclohexane (50 ml.) were refluxed together for 16 hr. to give an orange-yellow solution. After evaporation of solvent at 15 mm., the residue was sublimed at 60–80° (0.1 mm.) to give an orange solid. This was dissolved in hexane and chromatographed. Hexane eluted a single yellow band and the eluate gave a yellow solid on evaporation. Crystallization from hexane gave the pure complex as pale yellow crystals (m.p. 111–120° dec.; yield, 25%).

Anal. Calcd. for $C_{12}As_2F_{12}Mn_2O_8$: C, 19.0; F, 30.0; Mn, 14.5; mol. wt., 760. Found: C, 19.3; F, 29.8; Mn, 14.7; mol. wt. (C_6H_6), 772.

The ^{19}F n.m.r. spectrum shows a single peak at 45.84 ϕ .

Di- μ -(bis(trifluoromethyl)arsenido)tetranitrosyldiiron.—Iron dicarbonylnitrosyl (0.53 g., 3.08 mmoles), $As_2(CF_3)_4$ (0.658 g., 1.54 mmoles), and methylcyclohexane (50 ml.) were refluxed together for 3 hr. to give a dark red solution. After filtration, the solvent was removed at 15 mm. leaving black crystals. Sublimation at 60° (0.2 mm.) gave initially a red oil and finally black cubic crystals of the pure complex (m.p. 120–125° dec.; yield, 38%).

Anal. Calcd. for $C_4As_2F_{12}Fe_2N_4O_4$: C, 7.3; As, 22.8; F, 34.7; Fe, 17.0; N, 8.5. Found: C, 7.35; As, 19.3; F, 31.1; Fe, 20.1; N, 8.5.

The ^{19}F n.m.r. spectrum shows a singlet at 43.52 ϕ .

Reaction between Iron Pentacarbonyl and $As_2(CF_3)_4$.— $Fe(CO)_5$ (0.61 g., 3.12 mmoles), $As_2(CF_3)_4$ (0.668 g., 1.56 mmoles), and ethylcyclohexane (50 ml.) were refluxed together for 16 hr. to give a red solution and some black solid. After filtration, the solvent was evaporated at 15 mm., leaving oily red crystals. After washing with a little hexane, the crystals were sublimed, first at 60° to remove a red oil and then at 85° (0.1 mm.) to give dark red crystals, two batches (A and B) being collected (m.p. (A or B) 160–165° dec.; total yield, 230 mg.).

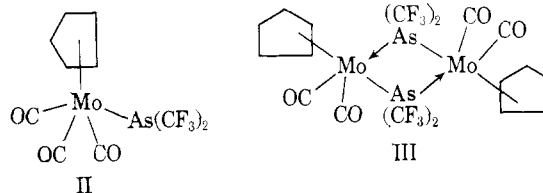
Anal. Calcd. for $C_{10}As_2F_{12}Fe_2O_8$: C, 17.0; As, 21.2; F, 32.3; Fe, 15.8. Calcd. for $C_{17}As_4F_{24}Fe_3O_9$: C, 16.1; As, 23.6; F, 36.0; Fe, 13.2. Found (A): C, 16.6; As, 22.1, F, 38.0, 37.6; Fe, 13.5, 13.3. Found (B): C, 15.3; F, 39.8; Fe, 10.9, 11.2.

The ^{19}F n.m.r. spectrum of B shows a pair of equal intensity singlets at 40.91 and 41.17 ϕ , respectively. No fine structure was observed, even under high resolution. The spectrum of A was complex and showed, in addition to the singlets present in B, two additional pairs of similar singlets.

Discussion

Cyclopentadienyl Metal Derivatives.— $[C_5H_5Fe(CO)_2]$ and $[C_5H_5Mo(CO)_3]$ react with tetrakis(trifluoromethyl)diarsine to give the mononuclear complexes, $[C_5H_5Fe\{As(CF_3)_2\}(CO)_2]$ and $[C_5H_5Mo\{As(CF_3)_2\}(CO)_3]$ (II), respectively. Under similar conditions tetramethyldiarsine reacts to give the arsenic-bridged complexes $[C_5H_5M\{As(CH_3)_2\}(CO)_n]_2$ ($n = 1, M = Fe$; $n = 2, M = Mo$).^{3,12b} This difference is probably due to the weakening of the electron-donating power of the arsenic atom effected by the strongly electronegative trifluoromethyl groups. Dimerization with expulsion of carbon monoxide therefore does not take

place under the usual conditions. The resulting mononuclear complexes are analogous to the halogeno and organo derivatives, $[C_5H_5Fe(CO)_2X]$ and $[C_5H_5Mo(CO)_3X]$ ($X =$ halogen, alkyl, or aryl).¹⁴ The properties of the compounds are consistent with this; they are volatile, low-melting, very soluble compounds which decompose slowly in air in the solid state. The infrared spectra show only terminal carbonyl absorption, two bands being found for the iron compound and three for the molybdenum. These are the same number of bands as are found for the corresponding halogeno complexes, the frequencies being almost identical with those of the iodo analogs.¹⁴



The n.m.r. spectra of both mononuclear arsine complexes show a singlet due to the cyclopentadienyl protons and a singlet due to the equivalent fluorine nuclei of the trifluoromethyl groups. The spectra are thus consistent with the proposed structures, there being no reason to expect isomerism or nonequivalence of either type of resonant nucleus.

On irradiation with ultraviolet light both $[C_5H_5Fe\{As(CF_3)_2\}(CO)_2]$ and $[C_5H_5Mo\{As(CF_3)_2\}(CO)_3]$ undergo dimerization with loss of carbon monoxide to give $[C_5H_5Fe\{As(CF_3)_2\}(CO)_2]_2$ and $[C_5H_5Mo\{As(CF_3)_2\}(CO)_2]_2$ (III), respectively. These compounds have spectral properties very similar to those previously observed for the analogous compounds derived from $As_2(CH_3)_4$,^{3,12b} and hence undoubtedly also have arsenic-bridged structures. The iron complex appears to exhibit *cis-trans* isomerism (as does $[C_5H_5Fe\{As(CH_3)_2\}(CO)_2]_2$)³ although no attempt was made here to separate the isomers owing to the limited amount of material available. However, the n.m.r. spectra in particular clearly indicate the presence of both isomers. The symmetrical *trans* isomer appears to be present in the greater quantity (ca. 60%) and gives rise to the stronger higher-field singlet in the proton spectrum and to the central singlet in the fluorine spectrum. The *cis* isomer accounts for the weaker cyclopentadienyl resonance and for the two quartets in the ^{19}F spectrum. In the *cis* isomer, the two trifluoromethyl groups attached to each bridging arsenic are in different environments and hence have different chemical shifts. In *cis*- $[C_5H_5Fe\{As(CH_3)_2\}(CO)_2]_2$, each type of methyl group gave rise to a singlet absorption,³ but here quartets are observed due to coupling between the trifluoromethyl groups attached to each arsenic atom. $J_{FF'}$ (6.65 c.p.s.) is of the same order of magnitude as that observed in $(CF_3)_2AsCl$ (7.85 c.p.s.) from ^{13}C satellite spectra.¹⁵ The carbonyl region of the infrared spectrum also contains more bands than expected for a single isomer and is thus consistent with a mixture of isomers.

The n.m.r. spectra of $[C_5H_5Mo\{As(CF_3)_2\}(CO)_2]_2$ indicate the presence of only one isomeric form, a symmetrical one, since only one fluorine and one proton resonance are observed. The infrared spectrum, however, shows the presence of one broad band in the carbonyl region rather than the two sharp bands expected by analogy with $[C_5H_5Mo\{As(CH_3)_2\}(CO)_2]_2$.^{12b}

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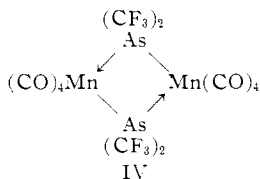
TABLE I
 INFRARED SPECTRA

	Absorption bands in the carbonyl region (cm. ⁻¹)		Other absorption bands (cm. ⁻¹) ^{a, b}
	Solution in carbon disulfide	Halocarbon mull	
[C ₅ H ₅ Mo{As(CF ₃) ₂ }(CO) ₃]	2040, 1974, 1956 (all vs)	2040 (s), 1972 (s), 1964 (s), 1940 (s), 1920 (sh)	3125 (w), 1432 (w), 1422 (w), 1139 (vs), 1110 (sh), 1101 (vs), 1084 (vs), 1058 (s), 1012 (w), 1002 (w), 939 (w), 871 (w), 837 (s), 722 (m), 573 (m), 549 (s), 490 (sh), 482 (s), 460 (m), 442 (m), 435 (m)
[C ₅ H ₅ Fe{As(CF ₃) ₂ }(CO) ₂]	2038 (vs), 1995 (vs)	2044 (s), 2000 (s)	1257 (w), 1248 (w), 1142 (vs), 1100 (vs), 1084 (vs), 1058 (vs), 1015 (s), 1002 (s), 888 (m), 868 (m), 856 (s), 836 (m), 720 (s), 618 (s), 603 (m), 583 (vs), 566 (vs), 503 (m), 452 (m)
[C ₅ H ₅ Mo{As(CF ₃) ₂ }(CO) ₂] ₂	1928 (br)	1915 (br)	3018 (w), 1420 (m), 1258 (s), 1255 (s), 1195 (s), 1158 (vs), 1150 (vs), 1122 (vs), 1102 (sh), 1037 (m), 1004 (m), 971 (s), 924 (m), 919 (m), 899 (m), 873 (s), 850 (s), 840 (s), 831 (s), 820 (s), 804 (sh), 788 (m), 749 (w), 715 (m), 705 (s), 670 (m), 646 (m), 602 (m), 515 (s), 508 (s), 463 (s)
[C ₅ H ₅ Fe{As(CF ₃) ₂ }(CO)] ₂	1998 (vs), 1985 (s), 1973 (s)	2000 (s), 1970 (vs), 1924 (w)	1432 (m), 1422 (m), 1369 (w), 1254 (w), 1149 (vs), 1130 (sh), 1113 (vs), 1091 (m), 1060 (m), 1012 (m), 1002 (m), 880 (w), 860 (m), 843 (m), 836 (m), 725 (m), 600 (m), 546 (s), 530 (m)
[Mn{As(CF ₃) ₂ }(CO) ₄] ₂	2084 (m), 2044 (vs), 2026 (s), 2011 (vs), 1979 (s)	2092 (m), 2052 (s), 2032 (sh), 2020 (vs), 1987 (m)	1157 (s), 1128 (sh), 1116 (s), 1107 (s), 732 (m), 646 (vs), 625 (vs), 496 (m), 472 (m)
[Fe{As(CF ₃) ₂ }(NO) ₂] ₂	...	1883 (sh), 1822 (vs), 1798 (vs) ^c	1157 (vs), 1134 (vs), 1118 (vs), 1100 (vs), 736 (s), 725 (sh), 648 (m), 642 (m), 571 (s)
Products from Fe(CO) ₅ reaction	A	2092 (m), 2065 (vs), 2058 (vs), 2036 (s) ^d	1170 (sh), 1152 (vs), 1120 (vs), 1094 (vs), 1087 (sh), 1060 (sh), 734 (s), 726 (s), 608 (sh), 598 (vs), 590 (sh), 533 (w), 520 (m), 505 (m)
	B	2101 (s), 2061 (vs), 2051 (s) ^e	1178 (vs), 1150 (vs), 1116 (vs), 1093 (vs), 1083 (vs), 1056 (sh), 733 (s), 725 (s), 598 (vs), 590 (sh), 538 (w), 531 (w), 504 (m), 463 (w)

^a Nujol mull 400–1300 cm.⁻¹, halocarbon mull 1300–4000 cm.⁻¹. ^b Bands in the range 1050–1160 cm.⁻¹ are due to C–F vibrations. ^c Bands due to ν_{NO} vibrations. ^d 1,2-Dichloroethane solution. ^e Chloroform solution.

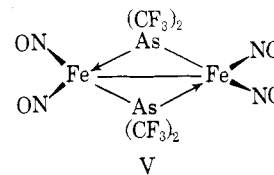
This is probably due to the accidental superposition of the two anticipated bands.

Metal Carbonyl Derivatives.—As₂(CF₃)₄ reacts with manganese carbonyl to give a volatile, yellow, crystalline complex, [Mn{As(CF₃)₂}(CO)₄]₂. This compound shows terminal carbonyl absorption only and a single fluorine resonance in its n.m.r. spectrum, indicating the symmetrical arsenic-bridged structure (IV). A number of complexes of this general type have recently



been characterized.¹

[Fe(CO)₂(NO)₂]₂ reacts with tetrakis(trifluoromethyl)diarsine to give a volatile, dark red complex, [Fe{As(CF₃)₂}(NO)₂]_n. The compound was insufficiently soluble for a molecular weight determination, but its volatility and diamagnetism (from the evidence of a sharp n.m.r. spectrum) indicates that *n* = 2. The complex therefore probably has structure V and is thus analogous to other sulfur¹⁶ and arsenic¹⁷-bridged



iron dinitrosyl complexes. The single resonance in the ¹⁹F n.m.r. spectrum is consistent with a planar four-membered ring, and the iron atoms are probably tetrahedrally coordinated.¹⁶

Iron pentacarbonyl reacts with As₂(CF₃)₄ to give a dark red crystalline product which was sublimed in two batches, A and B. A analyzed reasonably well for the composition [Fe₃{As(CF₃)₂}(CO)₉], but the infrared and n.m.r. spectra showed it to be a mixture of B and at least one other complex. B was apparently pure and its n.m.r. spectrum showed two equal singlets, as would be expected for [Fe{As(CF₃)₂}(CO)₃]₂, by analogy with [Fe{As(CH₃)₂}(CO)₃]₂.¹⁸ However, elemental analysis did not fit this or any other reasonable formulation. The relatively low yield from this reaction has prevented our investigating these products in further detail.

Chromium carbonyl reacted with As₂(CF₃)₄ in boiling ethylcyclohexane to give a pale yellow solution, but no crystalline complex could be isolated.

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