showed a broad singlet at 2.95 ppm (2 protons) and a singlet at 2.65 ppm (1 proton).

Chloro[bis(2-(dimethylamino)ethyl)][2-(dimethylaminium)ethyl-amine]palladium(2+) Perchlorate, [PdCl(trenMe₆H)](ClO₄)₂. This complex was prepared and purified in an analogous manner to that used for the tetrafluoroborate analogue. The limited solubility of the perchlorate derivative precluded the recording of its proton NMR spectrum.

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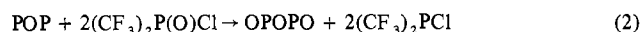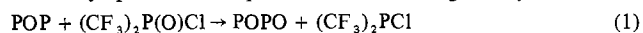(7) T. J. Lotz and T. A. Kaden, *J. Chem. Soc., Chem. Commun.*, 15 (1977).

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Bis(trifluoromethyl)phosphoryl-μ-oxo-bis(trifluoromethyl)phosphine. The Mixed Anhydride of a Phosphinous and Phosphinic Acid

Anton B. Burg

In a review publication some years ago,[1] it was implied that the unknown compound (CF₃)₂POP(O)(CF₃)₂ (hereinafter written as "POPO") would be stable against disproportionation into (CF₃)₂POP(CF₃)₂ and [(CF₃)₂PO]₂O (hereinafter, "POP" and "OPOPO"). The basis of this prediction was the ROQ rule: if R and Q differ enough in regard to π-acceptor bonding strength, ROQ will be formed irreversibly from ROR and QOQ. In fact, POPO now has been made by the following virtually quantitative processes, occurring easily at 25 °C.

$$\text{POP} + (\text{CF}_3)_2\text{P(O)Cl} \rightarrow \text{POPO} + (\text{CF}_3)_2\text{PCl} \quad (1)$$

$$\text{POP} + 2(\text{CF}_3)_2\text{P(O)Cl} \rightarrow \text{OPOPO} + 2(\text{CF}_3)_2\text{PCl} \quad (2)$$

$$\text{POP} + \text{OPOPO} \rightarrow 2\text{POPO} \quad (3)$$

These processes represent an extension of an earlier series of quantitative reactions whereby (CF₃)₃P was NO₂ oxidized to (CF₃)₃PO, convertible to (CH₃)₂NP(O)(CF₃)₂ and finally to (CF₃)₂P(O)Cl.[2] Reaction 2 represents a new way to make OPOPO, but more direct is an improved procedure for NO oxidation of P₂(CF₃)₄;[3] attack by NO upon the slowly warming liquid leads to a high yield of pure OPOPO. In contrast, P₂(CF₃)₄ vapor (50 °C) is converted by NO to pure POPO in high yield. In reactions 1, 2, and 3, P₂(CF₃)₄ (an impurity in POP) remains inert.

Almost simultaneously with the prediction of a stable POPO came reports of the analogous F₂POP(O)F₂,[4-6] F₂PSP(S)PF₂,[6] and (CF₃)₂PSP(S)(CF₃)₂.[6] In F₂POP(O)F₂ it was expected that F→P π bonding would weaken the O→P π bonding, making the ROQ rule less applicable. However, the decomposition of F₂POP(O)F₂ was complicated, making it difficult to demonstrate disproportionation, although F₂POPF₂ was one observed product.[5]

Table I. Relevant NMR Parameters[a]

	¹⁹F		³¹P	
	δ	J_{FCP}	δ	J_{PCF}
POPO	65.6	93.1	−91.4	92.9
	72.5	131.9	+0.3	131.8
POP	66.5	"98.8"[b]	−99.3	Complex
OPOPO[c]	72.03	137.5	+5.4	137.5
P₂(CF₃)₄	47	"84.9"[b]	+9.0	Complex
(CF₃)₂PCl	63.3	85.1	−50.2	85.0
(CF₃)₂P(=O)Cl	72.3	129.8	−10.8	129.4

[a] The chemical shifts, δ, are measured from Cl₃CF or H₃PO₄, with the upfield direction positive. [b] Second-order spectra; cf. ref 7. [c] Simple ¹⁹F doublet and ³¹P septet; no second-order pattern; cf. ref 3.

Experimental Methods

A modified Stock-type high-vacuum manifold (including mercury float-valves) was used for quantitative work with the volatile compounds here studied. For accurate ¹⁹F and ³¹P NMR spectra, the Varian XL-100-FT instrument was employed, with (CD₃)₂CO as the lock standard in 4.2 mm i.d. tubes and the samples in smaller sealed glass inserts. For rapid monitoring of a reaction, the ¹⁹F spectrum was observed by the Varian T-60 instrument.

Procedures and Results

Reaction 1. The reactants (0.339 mmol of POP and 0.321 mmol of the phosphinyl chloride) were condensed together in a 2.5 mm i.d. NMR tube insert, which then was sealed off from the vacuum line. The ¹⁹F spectrum (T-60), taken after 20 min at 25 °C, showed not only the (CF₃)₂P(O)Cl doublet and the known second-order pattern of POP[7] but also the incipient presence of (CF₃)₂PCl. Two other doublets represented POPO; one was almost perfectly superposed upon the (CF₃)₂P(O)Cl doublet, but made it seem ragged. After 16 h at 25 °C, the POP spectrum had almost disappeared. The final spectrum, recorded by the XL-100-FT instrument after 11 days, showed the barely detectable excess of POP and full and equal intensity for the (CF₃)₂PCl and the two POPO doublets. The upfield POPO doublet now had replaced that for (CF₃)₂P(O)Cl, with a slightly different chemical shift and a distinctly different coupling constant. The pertinent NMR parameters are compared in Table I.

The ³¹P NMR spectrum of this final mixture showed the known (CF₃)₂PCl septet,[8] between the two POPO septets, which differed in sharpness and saturability. Especially the downfield POPO septet showed tall, sharp peaks; P–O–P coupling was not detectable. In view of a simple septet for OPOPO, in contrast to a second-order spectrum for POP, it may be that the lack of P–O–P coupling in POPO relates to the bonding on the phosphorus(V) side. With the noise level at 0.5% of the highest peak, the spectrum failed to show either OPOPO or (CF₃)₂P(O)Cl.

Reaction 2. A mixture of 2.30 mmol of (CF₃)₂P(O)Cl and 1.00 mmol of POP, plus 0.025 mmol of P₂(CF₃)₄ impurity, was monitored by its ¹⁹F NMR spectrum (T-60 instrument), showing complete reaction after 18 h at 25 °C. The relative intensity of the small second-order P₂(CF₃)₄ spectrum[7] remained unchanged. It now was possible to remove 2.10 mmol of (CF₃)₂PCl and 0.20 mmol of unused (CF₃)₂P(O)Cl and to isolate 0.96 mmol of virtually pure OPOPO, having the previously described properties.[3] Since OPOPO condenses as clean white crystals melting near −42 °C, its vapor-pressure curve (log *P* vs. 1/*T*) is much steeper at lower temperatures, than that of P₂(CF₃)₄, POP, or other more volatile components, which are easily removed by slow passage through a U-trap in vacuo at −60 °C. The very clean NMR spectra of the final product (Table I) indicated its purity.

Reaction 3. The ¹⁹F NMR spectrum of a mixture of POP (0.428 mmol) and OPOPO (0.403 mmol) was observed at intervals, showing 18% conversion of POP to POPO after 20

min at 25 °C, 70% after 140 min, and 94% after 26 h–representing complete consumption of the OPOPO. The residual POP now could be removed by very slow high-vacuum fractional condensation through a trap at −60 °C, leaving very pure POPO as a crystalline condensate.

Physical Characterization of POPO. The melting range of pure POPO was visually observed as −41.7 to −41.4 °C, and its volatility was 8.2 mm at 0 °C—both results remarkably similar to those reported for OPOPO.[3] However, any conceivable confusion between POPO and OPOPO was eliminated by their very different infrared and NMR spectra. A fuller range of vapor-pressure data indicated the equation $\log P = 7.7805 + 1.75 \log T - 0.007T - 2518/T$ (bp 97 °C; Trouton constant 22.7 eu): found, 8.2 mm at 0 °C, 17.7 mm at 12.0 °C, 25.5 mm at 18.0 °C, and 40.0 mm at 26 °C; calcd, 8.2, 17.8, 25.5, and 40.0 mm.

For the molecular weight determination, a 100.1-mg sample of POPO was measured at 25 °C and 34 mm pressure, as 5.90 cm³ of gas at standard conditions, or 6.02 cm³ when measured at 25 °C and 24 mm. A reasonable extrapolation, to 6.12 cm³, would give a molecular weight value 1.0% lower than the calculated 370. This result, taken with the slight abnormality of the vapor-pressure data, would suggest a slight reversal of reaction 3.

Reversibility of Reaction 3. These slight indications of a disproportionation of POPO were amplified by three-times equilibration of the sample at 60–70 °C, with isolation of POP each time. The combined effluent was further purified by slow passage through a high-vacuum trap at −70 °C (repeatedly for maximum yield and purity), and the yield of POP was measured with correction for a trace of unremoved POPO (determined by the intensity of its 959-cm⁻¹ infrared peak), as 0.011 mmol from the 0.270 mmol POPO sample. This would represent 8% reversal of reaction 3, influenced not only by the elevated temperature and the triple equilibration but also by some escape of POP into the vapor phase. The recovered POP was remixed with the main POPO sample, in the same 38-mL tube, and the vapor pressure at 0 °C was measured: 10.0 mm, diminishing to 9.0 mm during 23 h at 0 °C. Now it was possible to isolate only 0.004 mmol of POP, indicating a definite reversal in the sense of reaction 3. At a rough estimate, reaction 3 at equilibrium might be about 98–99% complete at 25 °C, implying that ΔG_{298} is not far from −5 kcal (−12 kJ) mol⁻¹, or ΔH close to −0.3 eV. This could be a rough lower limit for the bonding advantage of the three-atom P–O–P heterobonding in POPO vs. a mixture of POP and OPOPO.

Infrared Spectra. Table II compares the pertinent infrared spectra, showing that POPO is quite distinct from POP, OPOPO, or the possible $P_2(CF_3)_4$ impurity, my own spectrum for which is included for comparison. The spectra were recorded by the Beckman IR7 or IR20A instrument, each carefully calibrated to a probable error near 1 cm⁻¹. The results for POPO and OPOPO were obtained by the use of silver chloride windows (avoiding the alkali–halide reaction[3]) or 0.75 mm thick polyethylene windows for the low-frequency range. The relative intensities (shown in parentheses after each frequency in Table II) were calculated by the equation $k = (100/PL) \log (I_0/I)$ for pressures and path lengths in centimeters and I representing minimum transmission for each frequency.

NO Oxidation of the Diphosphine. The optimum conditions for making OPOPO by NO oxidation of $P_5(CF_3)_4$[3] remain unknown. Table III summarizes a mostly vapor-phase reaction which proved to be efficient for POPO but not OPOPO. The NO and $P_2(CF_3)_4$ were brought together in a 1-L bulb and vaporized as quickly as possible at 50 °C, with good mixing. The final main product was 3.45 mmol of POPO (84%), with

Table II. Comparison of Infrared Spectra (cm⁻¹)

POPO	POP	OPOPO	$P_2(CF_3)_4$
1340 (13)		1360 (14)	
1221 (63)	1231 (69)	1342 (24)	
1202 (73)		1204 (164)	1207 sh (40)
1182 (95)	1179 (17)		1193 (74)
		1161 (11)	1169 (151)
1154 (25)			1154 (64)
1138 (46)	1143 (80)		1141 (84)
			1120 (70)
		993 sh (9)	
959 (44)	961 sh (5)	965 (39)	
	944 (10)		
921 (7)	924 (38)		
764 (0.3)	887 (3.5)	769 (1.4)	
750 (1.7)	748 (0.9)	752 (1.6)	749 (6)
	715 (2.1)		
697 (0.9)			
582 (13)	566 (2.0)	584 (30)	560 (1.2)
	544 (0.9)	555 (5)	535 (0.2)
503 (6)		508 (7)	
443 (5)	461 (11)	454 (7)	442 (6)
			403 (0.4)
380 (6)	368 (3.2)	385 (4)	363 (0.4)
			342 (0.6)
			260 (0.2)
			240 (0.3)

Table III. Vapor-Phase NO Oxidation of $P_2(CF_3)_4$ (4.102 mmol)

time intervals, h	T, °C	high volatiles, total mmol			remarks
		N_2	N_2O^a	NO	
0	50			26.77	minor fog; white solid soon gone
2	50				at −196 °C, deep red solid; fades on slight warming
8	25	2.23	1.67	19.54	colorless liquid and vapor
40	?	3.11	2.96	16.19	heat by 100 °C blower at bulb bottom
15	?	3.11	3.24	13.31	same; all colorless

^{a} N_2O is an inert by-product failing to react with $P_2(CF_3)_4$ during 26 h at 110 °C, at 16 atm pressure.

no NMR-detectable trace of OPOPO. The unidentified more volatile products (with neither CF_3NO nor COF_2) amounted to 0.20 mmol.

Further NO oxidation of POPO was relatively difficult: the reaction of 0.683 mmol of POPO with 1.410 mmol of NO, in a 6 mL sealed bomb-tube, progressed only 10% during 64 h at 25 °C but was virtually complete after 65 h at 113 °C. The yield of OPOPO now was 0.565 mmol (83%), with most of the loss accounted for by a light brown residue. The recovery of NO was 0.223 mmol. The yield of N_2O was 0.491 mmol and of N_2, 0.036 mmol.

In extreme contrast to this experiment, 0.329 mmol of $P_2(CF_3)_4$ and 1.66 mmol of NO, in a 4-mL NMR microtube, reacted completely during a 5-min warm-up from −78 to +25 °C (with the tube horizontal for maximal liquid–vapor contact), forming 0.296 mmol of OPOPO (90%) with no trace of POPO nor any nonvolatiles. The loss could be ascribed to unidentified products slightly volatile at −78 °C.

It would appear that the close liquid-phase contact of the reactants allowed multiple-body reactions, faster than quenching of activated intermediates, so that oxidation to OPOPO was fast and complete.

POPO Cleavage Reactions. Like OPOPO,[3] POPO is rapidly cleaved by HCl at 25 °C; with millimole coefficients:

0.48POPO + (0.68 − 0.23)HCl →

   0.42(CF₃)₂PCl + 0.44(CF₃)₂POOH
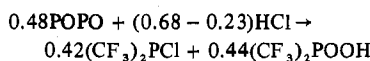
The OPOPO impurity here produced 0.015 mmol of (C-F$_3$)$_2$P(O)Cl.

Similarly, 0.163 mmol of POPO and 0.183 mmol of HCl, in an NMR microtube, quickly showed the known ^{19}F doublet for (CF$_3$)$_2$PCl at full intensity. The ^{19}F doublet for (CF$_3$)$_2$POOH appeared at δ = 73.7 ppm upfield of Cl$_3$CF (J = 130.1 s^{-1}), and for ^{31}P, δ = −0.3 (downfield of H$_3$PO$_4$) with J = 129.8 s^{-1} (septet not split by the proton). The proton spectrum of (CF$_3$)$_2$POOH was a sharp singlet at δ = 13.63 ppm (downfield of Me$_4$Si), probably not appreciably affected by the slight excess of HCl in the vapor phase. The HCl cleavage of either POPO or OPOPO is a relatively easy way to make a clean sample of this extremely strong acid.[9]

Potassium chloride also cleaves POPO, rapidly at 25 °C:

$$POPO + KCl \rightarrow KO_2P(CF_3)_2 + (CF_3)_2PCl \ (98\%)$$

This reaction was performed with excess KCl, finely powdered and vacuum-baked. The 2% by-product (CF$_3$)$_2$P(O)Cl was due to OPOPO.

POPO as a Chelating Ligand. It was considered that the phosphine part of POPO might replace CO in nickel carbonyl, also perhaps liberating a second CO by chelation to form
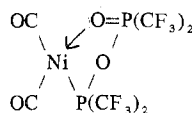
The experiment employed 0.647 mmol each of Ni(CO)$_4$ and POPO, in a 25-mL reaction tube. Tiny bubbles appeared immediately at 25 °C. After 16 h, the CO was pumped off at −196 °C and measured to confirm the reaction

$$Ni(CO)_4 + POPO \rightarrow POPO \cdot Ni(CO)_3 + CO$$
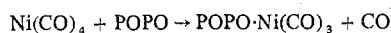
The ^{19}F spectrum of the colorless liquid product showed the (CF$_3$)$_2$P=O unit unchanged (δ = 72.6 ppm and J = 130.6 s^{-1}), whereas the doublet for the (CF$_3$)$_2$P unit had moved upfield to δ = 70.0 ppm with J increased to 101.3 s^{-1}, as a result of bonding P to Ni. During vacuum distillation, some CO was lost and the liquid turned green and then purple. Its ^{19}F NMR spectrum now showed (additionally) two overlapping second-order patterns, at δ = 53.2 ppm with $J_1 + J_2$ = 83.5 s^{-1} and δ = 53.9 with $J_1 + J_2$ = 84.3 s^{-1}. It seemed that POPO had been reduced to POP (second-order spectra) in complexes wherein the transferred oxygen had either gone exclusively to nickel or oxidized some of the CO to formate. The whole reaction merits further study, including X-ray crystallography of the final purple solid.

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Registry No. POPO, 66792-50-5; POP, 2728-67-8; POPOPO, 34043-22-6; P$_2$(CF$_3$)$_4$, 2714-60-5; (CF$_3$)$_2$PCl, 650-52-2; (CF$_3$)$_2$P(O)Cl, 646-71-9; NO, 10102-43-9; Ni(CO)$_4$, 13463-39-3; (CF$_3$)$_2$POOH, 422-94-6; POPO·Ni(CO)$_3$, 66792-56-1.

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Small-Ring Metallocycles Derived from Disiloxanes, Digermoxanes, or Bis(silyl)methanes and Transition-Metal Carbonyls

John Greene and M. David Curtis*

Polymer-supported catalysts have been demonstrated to have many of the advantages possessed by both homogeneous and heterogeneous catalysts.[1-5] Cross-linked polystyrene beads, the most investigated support, are subjected to multistep modifications in order to bind transition-metal complexes to the polymer backbone.

Polymeric silicon hydrides, e.g., the commercially available Dow Corning 1107 Fluid, are potential polymer supports to which metal centers could be attached in a simple one-step reaction due to the reactivity of Si–H bonds toward low-valent metal complexes.[6-9] Furthermore, the hydridosilicone polymers may be cross-linked with, e.g., polybutadiene, to give a range of physical properties from solvent-swellable gums to brittle resins.

In order to better characterize the types of transition-metal compounds which might form with polymeric silicon hydrides, we investigated several reactions of tetramethyldisiloxane, (Me$_2$SiH)$_2$O (TMDS), with transition-metal complexes since the HSiOSiH group is the simplest difunctional unit characteristic of the poly(hydridosiloxane). This work was expanded to include the behavior of tetramethyldigermoxane and bis(dimethylsilyl)methane toward metal carbonyl complexes.

Experimental Section

All air-sensitive materials were handled by standard Schlenk and/or high-vacuum techniques. Melting points were taken in sealed, evacuated capillaries. ^{1}H NMR spectra were recorded on a Varian A-60 spectrometer, mass spectra on an AEI 901 spectrometer, and IR spectra on a Perkin-Elmer 457 spectrometer. Photolyses were performed with a medium-pressure, 450-W Hanovia lamp. Tetramethyldisiloxane was a gift of the Dow Corning Corp.

Mass spectra were obtained on all new complexes. In all cases, the parent ion was observed, and the metallocycles had a fragmentation pattern showing Me$_4$E$_2$XM$_2$(CO)$_{8-n}^+$ ions. In addition, the germanium-containing complexes showed the correct isotope distributions.

1,3-Bis(tetracarbonylcobaltio)tetramethyldisiloxane, [Me$_2$SiCo-(CO)$_4$]$_2$O. Tetramethyldisiloxane (0.75 g, 5.0 mmol) was added by syringe to 1.7 g (5.0 mmol) of dicobalt octacarbonyl dissolved in a minimum amount of petroleum ether (bp 30–60 °C). Gas evolution was immediate, and the solution was then allowed to stir at room temperature for 1 h, after which time the solvent was pumped away to give a brown oil. Repeated crystallization from petroleum ether at −78 °C gave the product as extremely thermolabile white crystals: ν(CO) 2080, 2020, 2000, 1960 (vw) cm^{-1}; NMR δ 0.6. Anal. Calcd for C$_{12}$H$_{12}$Co$_2$O$_9$Si$_2$: Si, 11.85; Co, 24.86. Found: Si, 11.42; Co, 24.08.

1,3-Bis(tetracarbonylcobaltio)tetramethyldigermoxane. This complex was prepared in the manner described for the disiloxane analogue above. Thus, 0.85 g (2.5 mmol) of Co$_2$(CO)$_8$ reacted with 0.56 g (2.4 mmol) of (Me$_2$GeH)$_2$O to give the white crystalline product after low-temperature recrystallization. This compound is also extremely air-sensitive and thermolabile: ν(CO) 2090, 2040, 2020, 1985 (vw) cm^{-1}; ^{1}H NMR δ 1.0.

***cyclo*-1,3-(1,1,3,3-Tetramethyldisiloxanyl)octacarbonyldiiron-(*Fe–Fe*).** A solution consisting of 1.96 g (10.0 mmol) of iron pentacarbonyl and 0.67 g (5.0 mmol) of tetramethyldisiloxane in about 100 mL of pentane was photolyzed for 45 min in a jacketed, well-type reactor. The volatile material was then pumped away leaving a brown oil which was crystallized from a minimum volume of pentane at −20 °C to give the brown crystalline product, mp 84 °C in 55% yield: ν(CO) (in hexane) 2080, 2040, 2020, 1980, 1960, 1950, 1940 cm^{-1}; ^{1}H NMR δ 0.55. Anal. Calcd for C$_{12}$H$_{12}$Fe$_2$O$_9$Si$_2$: C, 30.80; H, 2.59. Found: C, 30.59; H, 2.64.