TABLE V

CALCULATED RATE PARAMETERS IN THE HYDROLYSIS OF METAL ACETYLACETONATES

Complex	T, °K.	k_1, sec^{-1}	$k_1k_2K_1/k_{-1}$, sec^{-1} M^{-1}
Be(acac)$_2$ and Be(acac)$^+$	298.2	6.5 ± 1.5	126 ± 34
	308.2	10.4 ± 1.9	220 ± 51
	318.2	18.5 ± 2.5	472 ± 90
VO(acac)$_2$	298.2	...	360 ± 50
VO(acac)$^+$	298.2	...	2.37 ± 0.27

and Ni(acac)$_2$ are adding the nucleophile as a ligand in place of water before dissociation of the chelate occurs.

The rates of reaction of Ni^{2+}, VO^{2+}, and Be^{2+} with sulfate are characterized by interchange rate constants, k_{int}, of 10^4, 10^3, and 10^2 sec^{-1}, respectively.[16] These correlate reasonably well with the composite constant,

$$\text{M(H}_2\text{O)}_n{}^{2+},\text{SO}_4{}^{2-} \xrightarrow{k_{\text{int}}} \text{MSO}_4\text{(H}_2\text{O)}_{n-1},\text{H}_2\text{O} \qquad (8)$$

$k_1k_2K_1/k_{-1}$, which has the values 8×10^5, 3.6×10^2, and 1.3×10^2 M^{-1} sec^{-1} for Ni(acac)$_2$, VO(acac)$_2$, and Be(acac)$_2$, respectively. The same ratios of constants for the mono complexes are 3.4×10^3, 2, and 1.3×10^2 for Ni(acac)$^+$, VO(acac)$^+$, and Be(acac)$^+$, respectively. The rate of hydrolysis of VO(acac)$^+$ is seen to be anomalously slow, or else Be(acac)$^+$ is anomalously fast. The successive stability constants do not show any large anomaly,[12] though the first and second constants are more nearly equal for Be^{2+} than for the other two ions.

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Perfluoromethylphosphine–Nickel Compounds, Including a New Volatile Heterocycle[1]

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The displacement of 3CO from Ni(CO)$_4$ by (CF$_3$)$_2$PF occurs as readily as the displacement of 2CO by CF$_3$PF$_2$, but this method arrives at pure (CF$_3$PF$_2$)$_4$Ni (mp −84°, bp estd 160°) far more easily than pure [(CF$_3$)$_2$PF]$_4$Ni (air-stable, mp 57.8°, bp estd 218°), for steric reasons such as prevent third-stage action by (CF$_3$)$_3$P. The infrared spectra suggest a slight increase of C–O bond strength as CF$_3$ replaces F in PF$_3$–Ni–CO compounds, and the effect is ascribed to minor differences in π bonding. The action of PF$_3$ upon (CF$_3$PF$_2$)$_4$Ni relates to the hypothesis that compounds of the type Li$_2$NiL'$_2$ often will be more stable than others having different proportions of the same ligands. The new chelate compound (CF$_3$)$_2$PC$_2$F$_4$P(CF$_3$)$_2$-Ni(CO)$_2$ (mp 30°, bp estd 179°) is more volatile but less stable than the similar C$_2$H$_4$-connected compound: complete displacement of the ligand (CF$_3$)$_2$PC$_2$F$_4$P(CF$_3$)$_2$ and one CO leads to the product [(CF$_3$)$_2$PC$_2$H$_4$P(CF$_3$)$_2$]$_2$NiCO with one bisphosphine unit acting unifunctionally.

The displacement of 4CO from Ni(CO)$_4$ by 4PF$_3$ has been verified,[2] but the more voluminous ligand (CF$_3$)$_3$P displaces only 2CO.[3,4] We now have found that repetitively used CF$_3$PF$_2$ can replace 4CO from Ni(CO)$_4$, making possible a quantitative synthesis of the new volatile compound (CF$_3$PF$_2$)$_4$Ni. The like action of (CF$_3$)$_2$PF occurs more easily for the first three CO, but the fourth-stage replacement is extremely difficult to complete. Thus steric interference is important for the third ligand in the series PF$_3$, CF$_3$PF$_2$, (CF$_3$)$_2$PF, (CF$_3$)$_3$P and becomes governing for the fourth.

However, the varying character of Ni–P bonding also may be significant. The P–F bond should have a small but not quite negligible $F_{2p} \rightarrow P_{3d}$ π component, enhanced by the high polarity of the P–F σ bond—itself improved by the reverse polarity of the π bond. The F→P π bond also inductively aids the σ-dative P→Ni bond, but tends to suppress the $Ni_{3d} \rightarrow P_{3d}$ π bonding. But let CF$_3$ replace F on P, and the less occupied P_{3d} system will more effectively receive Ni_{3d} π electrons. Thus, although PF$_3$ is a stronger π acceptor than most other phosphines,[5,6] CF$_3$PF$_2$ should be appreciably stronger.

Now if the Ni→P π electrons are more effectively moved toward P, those directed toward Ni→C π bonding in a Ni–C–O pattern in the same molecule will be less effective. Hence the O_{2p}–C_{2p} π bond would be strengthened by using CF$_3$PF$_2$ as a ligand instead of PF$_3$. The resulting increase in the C=O stretching frequency is apparent as one compares the first two monocarbonyls in Table I.

[1] It is a pleasure to acknowledge the support of this research by Grants GP-199 and GP-3812 from the National Science Foundation, which contributed also through Grant G-14665 toward the purchase of the Beckman IR7 instrument.

[2] M. Bigorgne, *Bull. Soc. Chim. France*, 1986 (1961).

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[4] A. B. Burg and W. Mahler, *J. Am. Chem. Soc.*, **80**, 2334 (1958)

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[6] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

TABLE I

C=O STRETCHING FREQUENCIES IN P—Ni—CO COMPOUNDS

$(PF_3)_3NiCO$	2085	$(PF_3)_2Ni(CO)_2$	2101, 2064
$(CF_3PF_2)_3NiCO$	2092	$(CF_3PF_2)_2Ni(CO)_2$	2106, 2071
$[(CF_3)_2PF]_3NiCO$	2092	$[(CF_3)_2PF]_2Ni(CO)_2$	2106, 2072
		$[(CF_3)_3P]_2Ni(CO)_2$	2106, 2071
		Chelate $(CF_3)_2PC_2H_4P(CF_3)_2Ni(CO)_2$[a]	2092, 2060
		Chelate $(CF_3)_2PC_2F_4P(CF_3)_2Ni(CO)_2$	2103, 2071

[a] A. B. Burg and G. B. Street, *J. Am. Chem. Soc.*, **85**, 3522 (1963); the higher values here came from a new calibration of the Beckman IR7 instrument, to an absolute error <1 cm^{-1}.

The use of $(CF_3)_2PF$ instead of CF_3PF_2 does not further increase the C=O frequency, presumably for two reasons: (1) the double $F \rightarrow P$ π bond in $(CF_3)_2PF$ should be not much less effective than the two $F \rightarrow P$ π systems in CF_3PF_2; (2) the larger reduced mass of the oscillating system lowers the C=O stretching frequency enough to balance a small inductive effect. Similar arguments would apply with less force to the dicarbonyls.

In the second chelate compound (here reported as new), the connecting C_2F_4 unit would be more effective than C_2H_4 for induction of $Ni_{3d} \rightarrow P_{3d}$ π-bond strength, permitting the C=O bonding to be stronger. Also, induced electronegativity would enhance the C—O σ bonding.

Substitution of CF_3 for F in $Ni(PF_3)_4$ should enhance both the σ and the π Ni–P bonding, as well as adding mass to the oscillating system. For both reasons the reduced mass of the P–F oscillator is greater; moreover, the F_{2p} to P_{3d} π bonding adds very little more to the force constant (whereas the P–F σ bond might actually be weaker) when there are fewer P–F connections. Accordingly, it is not really surprising that the P–F frequencies trend downward: 903.5 and 865 cm^{-1} for $(PF_3)_4Ni$, 894 and 862 cm^{-1} for $(CF_3PF_2)_4Ni$, and 857 cm^{-1} for $[(CF_3)_2PF]_4Ni$. However, the multiplicity of cause and effect makes it difficult to demonstrate a true correlation between the spectra and subtle differences of bond order. Other measures of Ni–P bond order might be more useful.

Another approach would be the study of ligand-substitution equilibria, preferably in the vapor phase. Such a comparison of the ligands $(CF_3)_nPF_{3-n}$ should be feasible, for our exploratory studies indicate easy reversibility. Pertinent to the subject is our observation that $(CF_3)_2PF$ displaced more CO from $Ni(CO)_4$ than CF_3PF_2 did under similar conditions, indicating that $(CF_3)_2PF$ is the stronger ligand except for steric interference at the fourth stage.

Another experiment has shown that $(CF_3)_2PC_2H_4P(CF_3)_2$ completely displaces the analogous C_2F_4-connected diligand from the new chelate $(CF_3)_2PC_2F_4P(CF_3)_2Ni(CO)_2$; and indeed a second molecule of the PC_2H_4P diligand acts unifunctionally to replace one CO as well. Thus the C_2H_4 connector improves the $P \rightarrow Ni$ σ-dative bond much more than C_2F_4 enhances the $Ni \rightarrow P$ π-dative bond.

A fuller study of equilibria among the various types $L_nNi(CO)_{4-n}$ (where L is a CF_3–P–F ligand) might be complicated by Ni–(CO)–Ni bridge formation. Evidence for such bridging appeared in our recent study of the slow or photochemically assisted decomposition of $[(CF_3)_3P]_2Ni(CO)_2$.[3,4,7] A thin film of the deep-red "neat" liquid mixture showed infrared peaks at 1878 and 1897 cm^{-1}, characteristic of metal-bridging CO groups. No such decomposition of our colorless Ni chelate $(CF_3)_2PC_2H_4P(CF_3)_2Ni(CO)_2$[8] ever has been observed, but the less stable $(CF_3)_2PC_2F_4P(CF_3)_2Ni(CO)_2$ develops a pink color on heating at 50°, suggesting incipient bridge formation.

The experimental work described in the following sections was performed by means of a high-vacuum manifold, with U traps and mercury float valves in series for separations by high-vacuum fractional condensation; thus most chemical processes involving volatile compounds could be monitored quantitatively. Numerous special devices could be attached through ground-glass joints. Where stopcocks were necessary, a chlorofluorocarbon grease was preferred.

The Reaction of Nickel Carbonyl with Trifluoromethyldifluorophosphine

Monitored Process.—The initial experiment on the displacement of CO from $Ni(CO)_4$ by CF_3PF_2 was done in stages for the observation of the intermediate P–Ni–CO compounds. Free CO appeared very soon; hence equilibrium may have been approached when 0.81 mmole of $Ni(CO)_4$ and 5.72 mmoles of CF_3PF_2 were left in a 60-ml closed tube for 18 days at 26°. The liberated CO now amounted to 2.32 per Ni and the consumed CF_3PF_2 was 2.36 per Ni. The major component of the product mixture showed strong, sharp vapor-phase infrared peaks at 2106 and 2071 cm^{-1}, representing the new dicarbonyl compound $(CF_3PF_2)_2Ni(CO)_2$. An apparently pure sample of this was made in another experiment, but its characterization was limited to a partial infrared spectrum. Another sharp peak at 2092 cm^{-1} represented $(CF_3PF_2)_3NiCO$. The average vapor-phase molecular weight of the mixture (428) agreed with calculation from the CO content (expected, 429), suggesting 0.55 mmole of dicarbonyl with 0.26 mmole of monocarbonyl. The absence of additional C=O stretching peaks argued against the presence of the tricarbonyl $CF_3PF_2Ni(CO)_3$, but superposition would have been possible. Certainly the dicarbonyl was predominant, even though the CF_3PF_2 was much in excess.

The unused CF_3PF_2 now was returned to the mixture of nickel compounds, and the displacement was continued for a further 15-day period. The infrared spectrum now showed none of the dicarbonyl; the only C=O stretching was at 2092 cm^{-1} (monocarbonyl). The displaced CO now totalled 3.75 per Ni, meaning that 75% of the nickel was in the form of $(CF_3PF_2)_4Ni$. Further action of the remaining CF_3PF_2 (single heating; 3 days at 100°) brought the monocarbonyl content down to less than 0.1%, for a 2092 cm^{-1} peak was barely

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(7) G. B. Street and A. B. Burg, *Inorg. Nucl. Chem. Letters*, **1**, 47 (1965).

(8) See footnote *a* to Table I.

detectable. Still further action of CF_3PF_2 eliminated it altogether. Thus the experiment arrived at pure $(CF_3PF_2)_4Ni$ without much difficulty, although losses in late-stage handling reduced the recovery to 77%.

Formula and Properties.—A more precise repetitive experiment, with frequent removal of CO, is summarized by the following equation with quantities in mmoles.

$$\begin{array}{cccc} \mathrm{Ni(CO)_4} + & \mathrm{4CF_3PF_2} \longrightarrow & \mathrm{(CF_3PF_2)_4Ni} + & \mathrm{4CO} \\ 0.718 & 8.15 & 0.711 & \ldots. \\ (122.5\ \mathrm{mg}) & \underline{-5.30} & (99\%; & \\ & 2.85 & 434.2\ \mathrm{mg}) & \end{array}$$

Confirmation of the indicated composition came from the reaction of 201.5 mg of the compound with iodine in excess (without solvent) to give 1.33 mmoles of CF_3PF_2 (calcd, 1.32). The vapor-phase molecular weight was determined as 614 (calcd, 610.7), confirming the molecular formula $(CF_3PF_2)_4Ni$. The white crystals melted to a colorless liquid in the range −88 to −84°. The equilibrium vapor pressure at 21.5° was 4.48 mm, suggesting a normal boiling point near 160°.

Ligand Displacement by Trifluorophosphine.—As a step toward determining the feasibility of equilibrium studies, the displacement of CF_3PF_2 from $(CF_3PF_2)_4Ni$ by PF_3 in excess was performed in a sealed 60-ml tube, heated for 3 weeks at 105°. The results are summarized by the following mmole stoichiometry.

$$\begin{array}{cccc} \mathrm{(CF_3PF_2)_4Ni} + & \mathrm{2PF_3} \longrightarrow & \mathrm{2CF_3PF_2} + & \mathrm{(CF_3PF_2)_2Ni(PF_3)_2} + \\ 0.148 & 2.96 & 0.228 & 0.129 \\ \underline{-0.004} & \underline{-2.73} & & \mathrm{CF_3PF_2Ni(PF_3)_3} \\ 0.144 & 0.23 & & \underline{0.014} \\ & & \text{total Ni:} & 0.143 \end{array}$$

Here the nickel and phosphorus balance well, but equally good accounting of the $P–CF_3$ and P–F bonds was prevented by difficulties of separation. The major product must have been the new compound $(CF_3PF_2)_2Ni(PF_3)_2$, for this fraction (passing a trap *in vacuo* at −25° but trapped out at −65°) had a uniform volatility suggestive of purity (*e.g.*, 15 mm at 21.5°; normal boiling point roughly estimated as 125°) and its vapor-phase molecular weight (519 *vs.* calcd 511) agreed with the formula as written. The persistence of this compound despite much excess PF_3 might have two causes: the greater ligand strength of CF_3PF_2 and an arguable tendency for the $L_2NiL'_2$ type to be intrinsically more stable than the L_3NiL' or L_4Ni types.

The minor product $CF_3PF_2Ni(PF_3)_3$ slowly passed the −65° trap and condensed at −75°. Its identity was indicated by a roughly determined vapor-phase molecular weight (445 *vs.* calcd 461). Its infrared group frequencies were virtually the same as for the major product, but with far lower intensities (*cf.* next section). There was no absorption extraneous to that expected for the presumed series of $CF_3PF_2–Ni–PF_3$ compounds.

No fraction corresponding to $(CF_3PF_2)_3NiPF_3$ could be found, but its strict absence is not proved because its infrared spectrum could be wholly covered by the very intense bands of $(CF_3PF_2)_2Ni(PF_3)_2$. An experiment employing only $0.28PF_3$ per $(CF_3PF_2)_4Ni$ yielded some CF_3PF_2 and a nickel fraction appreciably more volatile than the original compound, but the indicated $(CF_3PF_2)_3NiPF_3$ could not be isolated.

In sum, the $CF_3PF_2–Ni–PF_3$ system seems to offer an opportunity for equilibrium studies, with results governed by bonding conditions rather than steric effects. However, such studies must await the availability of perfected techniques more suitable than separative distillation or infrared intensity measurements, for estimating each component.

Infrared Spectra.—The frequencies (cm^{-1}) of the C–F and P–F stretching peaks in $(CF_3PF_2)_4Ni$ and three related compounds are compared in Table II. These were recorded by the Beckman IR7 instrument, for the vapors at pressures as low as 0.016 mm and as high as 1.92 mm, using a 10-cm path. The intensities of all peaks were calculated on an arbitrary scale defined by $k = (100/P) \log I_0/I$ for pressures P in mm at 25° and path 10 cm; these k values appear in parentheses after the frequencies.

TABLE II

C–F AND P–F STRETCHING FREQUENCIES OF FOUR CF_3PF_2–Ni COMPOUNDS[a]

L_4Ni	$L_2Ni(CO)_2$	$L_2Ni(PF_3)_2$	$LNi(PF_3)_3$
1214 (226)	1216 (34)	1217 (400)	1216 (27)
1174 (262)	1169 (107)	1170 (390)	1170 (34)
894 (140)	887 (60)	905 (400)	905 (130)
862 (150)	857 (58)	868 (370)	867 (77)

[a] Here L refers to CF_3PF_2.

In these compounds, the band for CF_3 symmetric deformation is so weak that it could be observed (at the available low pressures) only for $(CF_3PF_2)_2Ni(PF_3)_2$, at 758 (6). The low-frequency range was explored only for $(CF_3PF_2)_4Ni$: the PF_2 scissors-bending mode was recognized at 588 (13), the CF_3 asymmetric deformation at 562 (57), the PF_2 shear-bending at 509 (42), and the $P–CF_3$ stretching at 430 (9). A shoulder at 908 (28) was not assigned. For $CF_3PF_2Ni(PF_3)_3$, the peaks at 1030 (6), 943 (7), and 932 (6) also were unassigned. For the record of intensities, we repeat the C=O stretching bands of $(CF_3PF_2)_2Ni(CO)_2$: 2106 (112) and 2071 (59).

The Reaction of Nickel Carbonyl with Bis(trifluoromethyl)fluorophosphine

Synthesis of the Monocarbonyl.—The initial experiment on the displacement of CO from $Ni(CO)_4$ by $(CF_3)_2PF$ (in excess) ran for 16 days in a closed tube at 26°, with results shown by the following rough stoichiometry in mmoles.

$$\begin{array}{ccccc} \mathrm{Ni(CO)_4} + & \mathrm{(CF_3)_2PF} \longrightarrow & \mathrm{CO} + & \mathrm{[(CF_3)_2PF]_3NiCO} + & \\ 1.61 & 10.78 & 5.26 & \text{“1.18”} & \\ & \underline{-5.27?} & & & \mathrm{[(CF_3)_2PF]_4Ni} \\ & 5.51? & & & \text{“0.39”} \end{array}$$

The yields of the main products could not be estimated directly because neither could be completely isolated from the other; hence the stoichiometry is based upon the sum of their weights and the accurate measurement of 3.26CO per Ni. The expected dicarbonyl was scarcely present: a very slight fraction passing a −5° trap *in vacuo* showed two C=O stretching peaks in the infrared spectrum.

Thus from an initial ratio of 6.7$(CF_3)_2PF$ per $Ni(CO)_4$, the reaction went one step farther than the CF_3PF_2–$Ni(CO)_4$ reaction had gone, during a longer time at the same temperature, from the higher initial ratio 7.06. Clearly, $(CF_3)_2PF$ is more effective than CF_3PF_2 for displacement of at least 75% of the CO from nickel carbonyl.

Characterization of the Monocarbonyl.—Repeated high-vacuum fractional condensation gave monocarbonyl samples for which the highest melting range was −29.5 to −28.5°. A fresh middle fraction from a 0° high-vacuum reflux column was measured as a vapor (13 mm at 79°), giving the molecular weight as 656 (calcd, 651). A 93-mg sample, heated with iodine in excess, gave 0.431 mmole of $(CF_3)_2PF$ (identity confirmed by its 15-mm vapor tension at −78°) and 0.142 mmole of CO; ratio, 3.035 *vs.* calcd 3.000.

Despite such evidences of purity and identity, a normal volatility–temperature relationship could not be demonstrated for $[(CF_3)_2PF]_3NiCO$. From 0° (0.12 mm) to 24.3° (1.18 mm) the equation was $\log P = 10.834 - 3200/T$ (Trouton constant, 36.4 eu); and from 24.3 to 52.1°, $\log P = 9.455 - 2791/T$ (Trouton constant, 30.1 eu). Such behavior seems best explained by a steady increase of more and less volatile disproportionation products with rising temperature; indeed, after the measurements a low average molecular weight value (631) was found after distillation had left behind a trace of the slightly volatile product $[(CF_3)_2PF]_4Ni$. An infrared scan of the saturated vapor (at 36°) of a purified sample showed about 2% of the more volatile product $[(CF_3)_2PF]_2Ni(CO)_2$, apparently forming before the scan could be completed.

The Dicarbonyl.—A nearly pure sample of the monocarbonyl remained in a sealed tube for 3 months at 25° and then was subjected to high-vacuum fractional condensation. The fraction passing a trap at −20° but condensing at −45° was measured as a vapor and weighed: 0.0648 mmole and 31.6 mg; molecular weight, 487 ± 5; calcd for $[(CF_3)_2PF]_2Ni(CO)_2$, 491. Analysis by reaction with iodine gave 1.004CO per $(CF_3)_2PF$ (identity of the latter was checked by volatility, infrared spectrum, and basic hydrolysis to $2HCF_3$). Before the analysis, the equilibrium vapor pressures of this sample were measured in mm as 1.61 at 0°, 3.18 at 10.4°, 4.36 at 15.4°, and 5.74 at 20.1°, all correlated within 0.02 mm by $\log P = 8.258 - 2199/T$. The corresponding value for the Trouton constant, 24.6 eu, is normal when the Clapeyron–Clausius equation is used for liquids in a low range. The same sample was employed for the infrared spectrum, shown in Table IV.

Tetrakis[bis(trifluoromethyl)fluorophosphine]nickel.—The synthesis of $[(CF_3)_2PF]_4Ni$ was accomplished quantitatively, proving its composition; then the vapor-phase molecular weight (820 *vs.* calcd 811), taken with physical evidences of purity (sharp melting point, correct volatility behavior, and infrared spectrum) established the molecular formula.

The quantitative experiment began with 6.18 mmoles of $(CF_3)_2PF$ and 0.596 mmole of $Ni(CO)_4$ (molar ratio, 10.40). The container was a 70-ml U tube between mercury float valves. The early stages of CO displacement were fairly rapid; for example, after 16 hr at −15 to −6° the molar ratio of free CO to total Ni was 1.12, rising during a further 3 hr at 25° to 1.55; then during a further 19 hr at 35° it reached 2.73. To arrive at 3CO removed per Ni required a further 3 hr at 45°, but to liberate 0.3 more CO per Ni required a further 3 hr at 45°. As the process became more difficult, the temperature was raised and the CO was frequently removed from the actual site of reaction by condensing the $(CF_3)_2PF$ at −196° and reevaporating it so as to push the CO away from the slightly volatile product at the bottom of the tube. Even so, to raise the ratio from 3.83 to 3.93 required 5 hr at 75°; and to reach 3.975 required yet a further 24 hr at 90°. At this point, the monocarbonyl impurity was concentrated by crystallizing 90% of the product from hexane in a filtering Λ tube at −60°, and the part recovered from the mother liquor was treated with the remaining $(CF_3)_2PF$ for 10 hr at 100°, liberating only 0.0022CO per original $Ni(CO)_4$. Thus the displacement process had reached a practical limit at 3.977 free CO per Ni; and at this point a less accurate measurement of the gas volume of the unused $(CF_3)_2PF$ showed consumption of 3.94 $(CF_3)_2PF$ per Ni. The identity of the liberated carbon monoxide was confirmed by CuO combustion to form the same volume of carbon dioxide; and the identity of the recovered pure $(CF_3)_2PF$ was confirmed by its unchanged 15-mm vapor tension at −78°. Thus the composition represented by the formula $[(CF_3)_2PF]_4Ni$ was securely established.

However, the product still showed a weak record of the very intense 2092 cm^{-1} infrared peak of $[(CF_3)_2PF]_3NiCO$. This could be minimized by crystallization from hexane (a clean mixture of 2-methylpentane and 3-methylpentane) or by a repetitive process of fractional sublimation such that the crystals were evaporated by a heat gun and recondensed (hundreds of times) along an evacuated tube leading through traps at −5 and −196° to the high-vacuum pump. The infrared spectrum of the best sample showed less than 0.2% monocarbonyl impurity.

This sample melted in the range 57.73–57.76° (warming rate, 0.05°/min). Each vapor-tension datum in Table III represents averages of $\log P$ and $1/T$ for at least three observations in the same small region.

The compound $[(CF_3)_2PF]_4Ni$ failed to react with moist air at 85° and could not be analyzed by the iodine method because it would not react at temperatures low enough to avoid destruction of the ligand $(CF_3)_2PF$. The Ni–P bonds seem to be well protected by the F and CF_3, which should occupy the faces of the nickel tetrahedron in such a way that each face is covered by one F and two CF_3, all from different ligand units. The resulting asymmetric structure leads to a very large

TABLE III

VOLATILITY OF $[(CF_3)_2PF]_4Ni$

Solid: $\log P = 10.7009 - 3479/T$; $\Delta H_{fus} = 2225$ cal/mole

Temp, °C	31.7	36.4	44.3	56.2	57.75
P_{obsd}, mm	0.19	0.29	0.56	1.37	1.54
P_{calcd}, mm	0.195	0.29	0.55	1.37	1.54

Liquid: $\log P = 8.4155 + 1.75 \log T - 0.0064T - 3481/T$; $t_{760} = 218°$; Trouton constant = 21.6 eu.

Temp, °C	57.75	69.55	79.30	91.30
P_{obsd}, mm	1.54	3.17	5.51	10.34
P_{calcd}, mm	1.54	3.17	5.51	10.34

crystal-unit-cell, as demonstrated by an exploratory X-ray study of a single crystal by Howard Einspahr, under the direction of Professor J. Donohue.

Infrared Spectra.—The frequencies (cm^{-1}) of the important infrared peaks of the three $(CF_3)_2PF$–Ni compounds are shown in Table IV, with relative intensities (defined as for Table II) in parentheses. Most of these intensities are only roughly estimated, for lack of accurate knowledge of the pressure of each vapor.

TABLE IV

INFRARED SPECTRA OF THREE $(CF_3)_2PF$–Ni COMPOUNDS

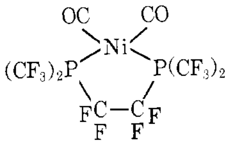
[L = $(CF_3)_2PF$; sh = shoulder]

Probable assignment	$L_2Ni(CO)_2$	L_3NiCO	L_4Ni
C═O stretching	2106 (57)	2092 (190)	. . .
	2072 (98)		
C—F stretching	1215 (107)	1215 (320)	1213 (300)
	1182 (72)	1186 (130)	1199 (250)
			1173 (100)
	1155 (33)	1163 (77)	1161 (97)
	1138 (23)	1143 (35)	1145 (43)
Fermi overtone	1096 (3)	. . .	. . .
P—F stretching	sh 869 (13)	869 (19)	871 (10)
	850 (17)	855 (42)	857 (80)
Uncertain	795 (5)	. . .	. . .
CF_3 sym deform	750 (2.5)	754 (2.0)	755 (2.2)
CF_3 asym deform	570 (18)	595 (5.6)	571.5 (65)
(and P–F bending?)	545 (0.7)	572 (46)	
		546 (4.4)	
P–CF_3 stretching	490 (18)	489 (46)	491.5 (92)
Ni–C–O deform	461 (1)		
	440 (2.5)	434 (1.8)	. . .
Ni–CO stretching	429 (3)	412 (1.9)	. . .

For these spectra, a wedge-shaped glass cell with thin KBr windows was employed, providing alternate paths of 11.7 or 113 mm length. The important bands for the monocarbonyl (L_3NiCO) are so intense that it was quite appropriate to employ pressures as low as 2 mm. Its disproportionation products $L_2Ni(CO)_2$ and L_4Ni showed some bands at closely similar frequencies, but could not have interfered appreciably with the record for the monocarbonyl. For $[(CF_3)_2PF]_4Ni$ (L_4Ni), a pressure of 0.29 mm (saturated at the cell-chamber temperature of 36°) was adequate for recording the expected bands, but some weak features might have been missed.

The New Perfluorinated Volatile Chelate

The bis-phosphine $(CF_3)_2PC_2F_4P(CF_3)_2$, first made by Dr. Louis R. Grant in our laboratories,[9] was used to displace 2CO from $Ni(CO)_4$, forming a new chelated-nickel dicarbonyl presumed to have the structure



This product seemed to be very similar to the previously described C_2H_4-connected chelate,[8] but appreciably less stable and about three times as volatile.

Synthesis.—A 50-ml ether solution containing 0.43 mmole each of $Ni(CO)_4$ and the bis phosphine showed a fairly fast evolution of CO, but was allowed 2 weeks at 25° for progress to a practical limit. The yield of the new chelate compound was 70%. A second experiment, similarly employing 0.73 mmole of $Ni(CO)_4$ and 0.60 mmole of the bis phosphine in 75 ml of ether, gave a yield representing 64% of the bis phosphine. Both samples were purified by high-vacuum fractional condensation, using traps at 0 and −20°.

Properties and Formula.—The colorless crystals of $(CF_3)_2PC_2F_4P(CF_3)_2Ni(CO)_2$ melted in the range 29.5–30.0°. The molecular weight in the vapor phase was determined as 545; calcd, 553. The equilibrium vapor pressures of the solid and the liquid are shown with equations in Table V.

TABLE V

VOLATILITY OF $(CF_3)_2PC_2F_4P(CF_3)_2Ni(CO)_2$

Solid: $\log P = 8.561 - 2463/T$; $\Delta H_{fus} = 770$ cal/mole

Temp, °C	19.95	21.90	25.45	27.07	29.30
P_{obsd}, mm	1.45	1.61	2.07	2.33	2.60
P_{calcd}, mm	1.44	1.64	2.06	2.28	2.62

Liquid: $\log P = 5.446 + 1.75 \log T - 0.00373T - 2495/T$; $t_{760} = 178.9$; Trouton constant = 20.95 eu

Temp, °C	31.33	35.90	40.95	45.35	47.15
P_{obsd}, mm	2.90	3.78	5.04	6.42	7.01
P_{calcd}, mm	2.90	3.78	5.03	6.39	7.01

Volatility measurements above 48° deviated upward from the calculated values, because of a slight decomposition which was indicated also by a pink coloration.

For analysis, 35.7 mg (0.0646 mmole) of the product, heated to 55° with excess iodine, yielded 0.0655 mmole of the free ligand and 0.129 mmole of CO (calcd, 0.0646 and 0.1292). The free ligand $(CF_3)_2PC_2F_4P(CF_3)_2$ could be identified by the following infrared peaks (listed as cm^{-1} frequencies with relative intensities in parentheses as in Tables II and IV): C–F stretching, 1212 (33), 1178 (33), 1154 (48), and 1120 (24); C–F bending, 782 (5.7). These were recorded for the vapor at 1.0 mm pressure.

Similarly, the infrared peaks recorded for the chelate $(CF_3)_2PC_2F_4P(CF_3)_2Ni(CO)_2$ (also in the vapor phase) were at 2103 (70), 2071 (86), 2035 (2.5), 1251 (29), 1216 (37), 1191 (24), 1177 (34), 1161 (51), 1144 (9), 1129 (16), 1108 (4), 1013 (6), 901 (4), and 753 (0.9) cm^{-1}.

Chelate Ligand Replacement.—In the first of two

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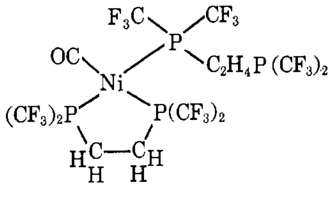
(9) L. R. Grant, Ph.D. Dissertation, University of Southern California Libraries, 1961, pp 44–49.

experiments on the subject, 0.12 mmole of the perfluoro chelate and 0.36 mmole of $(CF_3)_2PC_2H_4P(CF_3)_2$ were heated in a 10-ml sealed tube for 2 weeks at 36°. The displaced CO was measured as 0.13 mmole—essentially one per molecule of the original chelate compound, none of which could be recovered. The volatile material was a mixture of the two bis phosphines. The 96-mg weight of this mixture indicated 0.12 mmole of each bis phosphine (calcd weight, 96.5 mg), meaning that the nonvolatile product was 0.12 mmole of the compound



The second experiment, employing 0.1284 mmole of $(CF_3)_2PC_2H_4P(CF_3)_2$ and 0.0639 mmole of $(CF_3)_2PC_2F_4P(CF_3)_2Ni(CO)_2$, during 12 hr at 25° produced 0.017 mmole of CO, rising to 0.0547 during a further 25 hr at 40°. Now the free-ligand mixture amounted to 0.0655 mmole, with an infrared spectrum showing roughly an equimolar proportion of the two bis phosphines; thus the displacement was less advanced than in the first experiment. At this stage it was possible to isolate 0.006 mmole of a chelate–nickel dicarbonyl fraction, the infrared spectrum of which showed C═O stretching only at 2092 and 2060 cm^{-1}, identifying pure $(CF_3)_2PC_2H_4P(CF_3)_2Ni(CO)_2$. Thus it appears that the displacement of one chelating ligand by the other can precede the displacement of CO, although we cannot exclude a parallel mechanism whereby one CO is displaced before $(CF_3)_2PC_2F_4P(CF_3)_2$ is detached.

Nuclear Magnetic Resonance Results

The F^{19} magnetic resonance spectra of the two NiP_4 compounds were explored by Dr. S. L. Manatt at the Jet Propulsion Laboratory in Pasadena, Calif. The number and arrangement of the peaks agreed with the assumed tetrahedral structures, with some subtle distortions which might be ascribed either to nonbonding contacts within each molecule or to intermolecular contacts in the "neat" liquid samples. With Cl_3CF as an internal standard, the following parameters were measured.

For $(CF_3PF_2)_4Ni$ the chemical shifts were +82.14 ppm for F in CF_3 and +60.59 ppm for F on P; coupling constants, $J_{P-F} = 1190$ cps, $J_{F-C-P} = 119$ cps, and $J_{P-P-F} = 38$ cps.

For $[(CF_3)_2PF]_4Ni$ the chemical shifts were +68.53 ppm for F in CF_3 and +158.95 ppm for F on P; coupling constants, $J_{P-F} = 998$ cps, $J_{F-C-P} = 106$ cps, and $J_{P-P-F} = 40$ cps.

Attempts to relate these preliminary results to bond character would be premature. A more thorough study, including P^{31} spectra and the effects of temperature and dilution, is planned for the future.

CONTRIBUTION FROM THE MOBIL OIL CORPORATION, RESEARCH DEPARTMENT,
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Chemistry of Crystalline Aluminosilicates.
II. The Synthesis and Properties of Zeolite ZK-4[1]

BY GEORGE T. KERR

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A new zeolite, designated zeolite ZK-4, has been synthesized using aqueous solutions of sodium aluminate and tetramethylammonium silicate as reagents. For ZK-4, sodium and tetramethylammonium ions occupy cation sites in the zeolite lattice. This zeolite is isostructural with zeolite A. Unlike zeolite A, however, it has a ratio of silicon to aluminum occupying tetrahedral positions in the crystal lattice that exceeds 1.0, and ratios as high as 1.7 have been obtained. This increased silicon content of the new zeolite results in a smaller unit cell parameter than that of zeolite A. Because the sodium form of zeolite ZK-4 contains fewer sodium ions per unit cell than does sodium zeolite A, it is capable of adsorbing straight-chain hydrocarbons; sodium zeolite A is not.

Introduction

The work reported in the present study is concerned with the use of tetramethylammonium and sodium ions to produce a new crystalline aluminosilicate, designated zeolite ZK-4,[2] which is isostructural with zeolite A.[3] A substance similar to zeolite ZK-4 was probably synthesized by Barrer and Denny when they prepared a variety of zeolites in which only nitrogenous bases were used for crystallizing silica–alumina gels.[4] The use of quaternary ammonium ions in conjunction with ions of group I-A in the synthesis of zeolite was suggested by an earlier study,[1] which showed that zeolite growth probably proceeds from

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[1] Part I: G. T. Kerr, *J. Phys. Chem.*, **70**, 1047 (1966).

[2] G. T. Kerr and G. T. Kokotailo, *J. Am. Chem. Soc.*, **83**, 4675 (1961).

[3] D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed, and T. L. Thomas, *ibid.*, **78**, 5963 (1956).

[4] R. M. Barrer and P. J. Denny, *J. Chem. Soc.*, 971 (1961).