agitation; hence the average initial state "stability" will decrease as the temperature increases—the greater the complexity of structural interactions, the more sensitive the solvent shell to temperature. It is such changes with temperature summed over a number of solvent interaction terms which we believe are observed when $\Delta C_p^{\ne}$ changes with composition. Were this the only factor involved in the activation process, it is a corollary that $\Delta H^{\ne}$ would increase through the concentration range where structural stability appears to increase. This does not happen, but it is significant that the maxima in $-\Delta C_p^{\ne}$ appear to lie at about the same ethanol–water concentration as that for maxima in Walden products and $d\eta/dx_2$.[11] Since the former reflects the effect of ions on the structure and the latter is related to structural stability, it is probably no coincidence that the breakdown of structure as a consequence of charge development in the activation process should show similar sensitivity to solvent change.

t-Butyl chloride had been purified for previous study[7] and was passed through Al_2O_3 prior to use. Alcohol–water mixtures were made up from purified solvents in sufficient quantity for a $\Delta C_p^{\ne}$ determination, and the final concentration was determined by density. Rate determinations were by the conductance method previously reported,[7] and calculation of constants followed previous work.

[15] National Research Council of Canada summer student, 1965.

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Nickel Carbonyl Complexes with Bifunctional Nonchelate Ligands[1]

Sir:

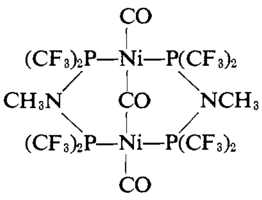
Bifunctional phosphines of the type represented by $(CF_3)_2POP(CF_3)_2$,[2] $(CF_3)_2PSP(CF_3)_2$,[3] and $(CF_3)_2P(NCH_3)P(CF_3)_2$[4] are not expected to be effective chelating ligands on account of unfavorable bond angles at O, S, or N. Accordingly, their reactions with nickel carbonyl lead to polynuclear complexes.

The Aminobisphosphine Product. Equimolar quantities of $Ni(CO)_4$ and $(CF_3)_2P(NCH_3)P(CF_3)_2$ (ligand Ln), in hexane at 25°, liberated one CO in 35 min, after which a bright yellow precipitate began to form as more CO was removed by the automatic Sprengel pump. More than 24 hr was required to approach the limit indicated by the following equation with millimole stoichiometry.

$$\begin{array}{lllll} 2\text{Ln} & + \ 2\text{Ni(CO)}_4 & \longrightarrow 5\text{CO} & + \ \text{Ln}_2\text{Ni}_2\text{(CO)}_3 \\ 1.678 & \quad 1.64 & \quad 3.957 & \quad 0.811 \\ \underline{-0.064} & & (2.45\times\text{Ln}) & \\ 1.614 & & & \end{array}$$

The air-stable yellow product (weighed after evaporation of the hexane) could be recrystallized from CCl_4, $HCCl_3$, acetone, or ether. It could be sublimed *in vacuo* at 90° without change but lost CO during melting near 150°. Its molecular weight in ether (by means of the differential tensimeter at 23.5°) was 922 *vs.* 935 calculated for the formula as written. Heated in a stream of CO, it liberated at least 82% of the original ligand, showing that this bisphosphine had not been disrupted in forming the complex.

The infrared spectrum of this sesquicarbonyl as a vapor at low pressure showed peaks at 2083, 2072, and 1917.5 cm^{-1} (or 2074.5, 2052, and 1912.5 cm^{-1} in Nujol *vs.* 2075.5, 2062, and 1905.5 cm^{-1} in CCl_4), clearly demonstrating both terminal and bridging C–O groups.[5] In view of its stability, it is reasonable to suggest a compact bicyclic structure such as



in which the hexatomic rings could well have the cyclohexane chair configuration.

The Thiobisphosphine Product. The action of $(CF_3)_2PSP(CF_3)_2$ (ligand Ls) upon $Ni(CO)_4$ was much like that of Ln, always forming a sesquicarbonyl despite a considerable variation of the reactant ratio. In this case, however, a volatile red product (very unstable) appeared in the early stages, and the final air-stable yellow product contained a nonvolatile red impurity, removable by washing with hexane. With equimolar reactants, the usual limit was represented by 2.5CO evolved.

Again the infrared spectrum of the yellow precipitate (Nujol mull) showed terminal and bridging C=O stretching, at 2088, 2075, and 1894 cm^{-1}. Analysis by iodine in CCl_4 gave 8.88% CO, 12.8% Ni, and (by difference) 78.3% Ls; calculated for $Ls_2Ni_2(CO)_3$, 8.92, 12.5, and 78.6%, respectively. However, the molecular weight remains unknown because of instability in any effective solvent. For example, in CCl_4 the C=O frequencies at 2090, 2075, and 1915 cm^{-1} lost intensity with time as new peaks at 2110 and 2050 cm^{-1} replaced them.

Thermal decomposition of pure $Ls_2Ni_2(CO)_3$ at 80° led to the recovery of 48% of the expected Ls, from the rest of which some $P_2(CF_3)_4$ was formed while the nickel ended as a black solid having the X-ray powder pattern of Ni_3S_2. However, on heating in a stream of CO, this sesquicarbonyl was dissociated and partly re-formed, giving the appearance of sublimation.

Possibly $Ls_2Ni_2(CO)_3$ is only a less stable example of the $Ln_2Ni_2(CO)_3$ structural type, but a decision will await the results of X-ray studies which have been initiated.

The Diphosphoxane Product. The action of $(CF_3)_2POP(CF_3)_2$ (ligand Lo) upon equimolar $Ni(CO)_4$ is different, forming a slightly volatile, hexane-soluble white solid having the molecular formula $Lo_2Ni_2(CO)_4$ and showing only terminal C=O stretching, at 2100

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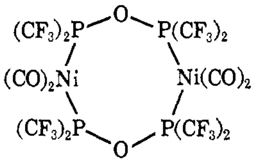
[2] J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **82**, 1507 (1960); **84**, 3442 (1962).

[3] (a) R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 5825 (1964); (b) A. B. Burg and K. Gosling, *J. Am. Chem. Soc.*, **87**, 2113 (1965).

[4] A. B. Burg and J. Heners, *ibid.*, **87**, 3092 (1965).

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

and 2060 cm^{-1}. It can be argued that a very wide P–O–P bond angle would make Ni–(CO)–Ni bridging impossible because the nickel atoms would be too far apart. We suggest an eight-membered ring structure such as



in which the $Ni(CO)_2$ units could be situated on either the same or opposite sides of the $(POP)_2$ plane. The argument for a very wide P–O–P bond angle relates to the known 144° Si–O–Si angle in $(SiH_3)_2O$.[6] In the present case the widening effect of O_{2p}–P_{3d} π bonding should be even more important. In contrast, a weaker S_{3p}–P_{3d} π bonding in $(CF_3)_2PSP(CF_3)_2$[3b] would permit a narrower P–S–P bond angle and allow CO bridging in $Ls_2Ni_2(CO)_3$.

A quantitative synthesis in hexane at 25° is described by the following equation with millimole stoichiometry.

$$\begin{array}{ccccccc} 2Lo & + & 2Ni(CO)_4 & \rightarrow & 4CO & + & Lo_2Ni_2(CO)_4 \\ 1.004 & & 1.002 & & 1.954 & & \text{(not detmd)} \end{array}$$

The molecular weight of a recrystallized sample (by differential tensimetry in *n*-pentane) was 964 or 966; calculated for the binuclear formula, 937. Analysis of a vacuum-sublimed sample by the iodine method gave 12.7% Ni (calcd, 12.5). The pure white crystals darkened with decomposition at 45°, or turned green during 24 hr in the open air. Whenever the synthesis was done with excess $Ni(CO)_4$, a red product began to form just as the CO displacement approached two per Lo. Obviously, some by-products are possible with all three of the bisphosphines here employed.

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The Formolysis of *exo*-2-*t*-2-Norbornyl Brosylate[1]

Sir:

The problem of 3,2 hydride shifts during solvolysis of norbornyl derivatives can be investigated with a singly labeled substrate, and the results from such a study on the acetolysis of *exo*- and *endo*-2-*t*-2-norbornyl brosylates (*exo*- and *endo*-I-2-*t*) have been reported.[2] In a well-known review, Berson[3] has discussed 3,2 hydride shifts and has referred to the analysis of Dill[4] on the data of Roberts and co-workers[5] obtained from solvolyses of norbornyl brosylates labeled with ^{14}C at both C-2 and C-3. It may be of interest to point out that the contributions of various processes, including 3,2 (and 7,1) hydride shifts, assigned by Dill,[4] as quoted by Berson,[3] for the acetolysis of *exo*-I-2,3-$^{14}C_2$ at 45° do not fit the more recent data obtained with *exo*-I-2-*t*.[2] Reference to Dill's work has again been made in a very recent review by Sargent[6] in regard to the necessity of postulating 3,2 hydride shifts during formolysis. In order to provide some clarification on the rearrangement processes involved in formolysis, we now report the results from the formolysis of *exo*-I-2-*t*.

Roberts and co-workers[5] were unable to explain the isotopic distribution in the product obtained from formolysis, at reflux temperature, of a mixture of *exo*- and *endo*-I-2,3-$^{14}C_2$. We believe that one of the chief factors responsible for this difficulty resulted from complications arising from the subsequent ionization and rearrangement of the *exo*-2-norbornyl formate in the reaction mixture at reflux temperature.[5] In order to minimize these complications, the present work was carried out at 25°.

exo-I-2-*t*[2] was solvolyzed in anhydrous formic acid in the presence of sodium formate at 25° for 20 hr. The resulting product was degraded and the tritium distribution determined as described in the analogous acetolysis studies.[2] The results are given in Table I. The presence of about 6% of the activity at C-3 indicates a substantial involvement of 3,2 hydride shifts during the formolysis of *exo*-I-2-*t*. Since the rates of the Wagner–Meerwein rearrangement and the 6,2 (and 6,1) hydride shift are very much faster than the rate of the 3,2 hydride shift in the norbornyl cation in a highly acidic medium,[7] it is also likely that the 3,2 shift is the slowest rearrangement under solvolytic conditions. Thus 3,2 shifts together with the Wagner–Meerwein rearrangement and 6,2 (and 6,1) hydride shifts will result in the complete equivalence of all seven carbon positions of the norbornyl cation.[5]

Table I. Tritium Distribution in the Product from Formolysis of *exo*-I-2-*t* at 25°

	Tritium content, %[a]			
	C-2	C-3	C-1,4,7	C-5,6
Run 1	31.0	6.5	39.1	23.3
Run 2	30.8	6.2	39.2	23.8

[a] Activities were measured by a liquid scintillation counter; 100% corresponded to specific activities of 29,587 and 31,125 counts/min mmole, respectively, for runs 1 and 2.

As discussed previously for the acetolysis of *exo*-I-2-*t*,[2] the isotopic distribution shown in Table I can be attributed to three processes, namely (1) complete equivalence of all carbon positions resulting from 3,2 hydride shifts together with Wagner–Meerwein and 6,2 (and 6,1) hydride shifts; (2) equivalence of C-1 and C-2 from reaction with the initially formed norbornonium ion; and (3) equivalence of C-1, C-2, and C-6 from the equilibration of norbornonium ions *via* 6,2 and 6,1 hydride shifts. If the contributions of these processes were as shown in Table II, the calcu-

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