Spectra were run at −30° for GeH_3SiF_2H and at 0° for $GeH_3Si_2F_4H$. The ^{19}F spectrum of GeH_3SiF_2H was obtained on a Varian HR-100 spectrometer at 94.1 Mc.

Physical Properties.—The melting points of the GeH_3SiF_2H and $GeH_3Si_2F_4H$ fractions were measured by the Stock ring method at −77 and −4°, respectively. Vapor pressure measurements on the GeH_3SiF_2H fraction over the temperature range −70 to −10° and on the $GeH_3Si_2F_4H$ fraction over the temperature range −40 to −4° gave log p *vs.* $1/T$ plots which could be fitted approximately to the equations $\log p_{\mathrm{mm}} = 6.93 - (1162/T)$ and $\log p_{\mathrm{mm}} = 10.10 - (2365/T)$. From the vapor pressure equation of the liquid GeH_3SiF_2H fraction, the boiling point of the compound is estimated to be 13°.

The Reaction with KOH.—A sample of the GeH_3SiF_2H fraction, corresponding to 0.30 mmol, was condensed on top of 5 ml of 10% KOH solution frozen in an ampoule. The ampoule was sealed, warmed to room temperature to allow reaction to occur, and then reopened on the vacuum line. The gas pumped out contained 0.28 mmol of germane, 94% of the theoretical yield.

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Further Knowledge of Ligand–Nickel Sesquicarbonyls[1]

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An earlier publication described new binuclear nickel–carbonyl derivatives of the type $L_2Ni_2(CO)_3$, where L is a bis-phosphine ligand.[2] The synthesis of another compound in this class, namely, $Lhn_2Ni_2(CO)_3$, where Lhn = $(CF_3)_2P(NH)P(CF_3)_2$,[3] permits a fuller comparison of properties; for example, an infrared comparison with the compound previously designated as "$Ln_2Ni_2(CO)_3$," namely $[(CF_3)_2P(NCH_3)P(CF_3)_2]_2Ni_2(CO)_3$, leads to a possible explanation of the greater stability of $Lhn_2Ni_2(CO)_3$.

Synthesis and Formula.—A solution of the ligand Lhn and $Ni(CO)_4$ in isohexane (a clean mixture of 2- and 3-methylpentanes) was formed under high-vacuum conditions in a stopcocked filtering λ tube, which then stood at 25° with frequent pump-off of the evolved CO. During the first 3 hr it developed a pale yellow tinge, and after 6 hr (1.387 CO evolved per Ni) yellow crystals appeared. After 81 hr the yellow solid was collected on the filter, leaving only an unweighable trace in the yellow solution.

The quantitative results now could be expressed by the following equation with millimolar stoichiometry.

$$\begin{array}{ccccccc} 2\mathrm{Ni(CO)_4} & + & 2\mathrm{Lhn} & \longrightarrow & 5\mathrm{CO} & + & \mathrm{Lhn_2Ni_2(CO)_3} \\ 1.768 & & 2.105 & & 4.164 & & 0.878 \\ & & & & (>94\%) & & (99.2\% \text{ of Ni}) \end{array}$$

Although the measured CO was nearly 6% deficient, its further evolution during the subsequent work-up of the mixture would account for the difference. Also, although the amount of unused Lhn was not accurately determined, a rough estimate would agree well enough with the exact equation.

At 80–90° under high vacuum, the yellow solid $Lhn_2Ni_2(CO)_3$ sublimed completely except for a 0.36% residue (not included in the reported 0.878-mmol yield). Its volatility over a range of temperatures conformed well to the equation $\log P = 12.502 - (4820/T)$ (examples: 0.31 mm at 97.3°, 0.55 mm at 105.1°, 0.97 mm at 112.0°, and 1.36 mm at 116.5°), indicating a pure substance having a 22.07-kcal molar heat of sublimation. The molecular weight was determined tensiometrically in ether: 907 at 25° or 956 at 0° (calcd, 907.5). The virtually quantitative synthesis left no doubt of the identity of the new compound as a close analog of the earlier $Ln_2Ni_2(CO)_3$,[2] differing only in having NH rather than NCH_3 groups connecting P to P. The infrared spectra also confirmed the analogy.

Solubility and Stability Comparisons.—Many tests showed that the N-connected sesquicarbonyls dissolve only in media which might solvate them by electron-donor bonding. For example, $Ln_2Ni_2(CO)_3$ is not soluble enough in hexane to show color, while $Lhn_2Ni_2(CO)_3$ shows only the faintest yellow; but both dissolve fairly well in acetone. The solubility of $Lhn_2Ni_2(CO)_3$ in diethyl ether at 25° is at least 20%; that of $Ln_2Ni_2(CO)_3$ at 36°, about 8%. The far stronger base $(CH_3)_3N$ was absorbed (10 days at 25°) to form $Ln_2Ni_2(CO)_3 \cdot 2(CH_3)_3N$ without loss of CO. The purple, solid product in a Nujol mull showed infrared peaks at 2047, 2032, and 1832 cm^{-1}, *vs.* 2075, 2052, and 1913 cm^{-1} for the original $Ln_2Ni_2(CO)_3$.

The ostensibly analogous $[(CF_3)_2PSP(CF_3)_2]_2Ni_2(CO)_3$, which we have written as $Ls_2Ni_2(CO)_3$,[2] decomposes promptly in any medium capable of dissolving it. In ethers it turned brown, with liberation of volatiles showing C–F infrared spectra; and the original compound could not be recovered. The $(CH_3)_2O$ solution at 25° became permanently violet during 24 hr. The effects of methanol, acetone, acetylacetone, monoglyme, or acetonitrile were much like those of the ethers. The amines $(CH_3)_3N$ and $(C_2H_5)_3N$ liberated CO and $P_2(CF_3)_4$, and the infrared spectrum of the residue showed no CO-bridge mode.

This S-connected compound is very unstable in the vapor phase (so that only its strongest infrared peaks could be recorded, at 65°), whereas $Lhn_2Ni_2(CO)_3$ vapor remained stable during long infrared scans at 102°. Solid $Lhn_2Ni_2(CO)_3$ survived a 10-min heating at 157° but melted at 180° with loss of CO and Lhn. The de-

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[1] It is a pleasure to acknowledge the generous support of this research through Grants GP-3812 and GP-6751X from the National Science Foundation, which aided also toward making available the Beckman IR7 infrared spectrophotometer through Grant No. 14665.

[2] A. B. Burg and R. A. Sinclair, *J. Am. Chem. Soc.*, **88**, 5354 (1966).

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

TABLE I

COMPARISON OF INFRARED SPECTRA[a]

$Lhn_2Ni_2(CO)_3$				$Ln_2Ni_2(CO)_3$						$Lo_2Ni_2(CO)_4$			
Vapor	Ether soln	Mull	Lhn vapor	Vapor	CCl_4 soln	Mull	Ln vapor	$Ls_2Ni_2(CO)_3$ mull	Ls vapor	Vapor	n-C_5H_{12} soln	Mull	Lo vapor
2086 (26)	2068 vs	2085 vs		2084 (29)	2075 vs	2076 vs		2088 vs		2104 s	2100 vs	2130 s	
2076 (42)	2053 vs	2080 vs		2073 (39)	2062 vs	2052 vs		2075 vs		2095 vs	2095 s	2100 s	
		2065 vs				2019*					2090 vs		
		2033*				2018*		2033*		2077 s	2084 s		
		2025*								2069 vs	2065 vs		
											2056 vs		
1917 (10)	1897 s	1870 sh		1918 (8)	1906 m	1913 s		1894 vs			2043 s		
		1865 vs				1868*		1854*			2035 s		
		1825*									2026 s		
1268 (5)			1294 (22)										
			1290 sh										1278 (1.7)
			1208 sh		1217 s		1205 (29)						
1196 (50)			1200 (60)		1197 s			1200 ms	1203 (70)	1221 s		1220 vs	1231 (65)
1184 (19)			1180 (116)	1188 (94)	1185 vs	1180 vs	1187 (78)	1178 s	1174 (132)	1183 s		1170 vs	1178 (165)
1164 (36)			1161 (125)	1161 (79)	1155 vs	1143 vs	1159 (182)	1162 vs	1142 (114)	1154 m		1145 vs	1143 (77)
1126 (5)			1132 (55)	1132 (11)	1140 sh	1133 vs	1131 (53)	1145 s	1130 (64)	1145 m			
					1118 m	1115 vs		1131 vs	1110 (7)	1129 m			
						1056 s	1047 (0.7)	1120 vs				1070 sh	961 sh (5)
										948 s		942 s	944 (10)
905 (3)			925 (25)	865 (16)	865 s	863 s	923 (0.3)						924 (38)
							869 (33)						887 (3.5)
812 (4)			808 (5)	820 (5)			822 (0.2)						
						743 s						750 w	749 (1.0)
						654 s	647 (0.7)						715 (2.2)

[a] Frequencies marked with an asterisk represent sharp spikes on the edges of strong bands. The parenthetical numbers are calculated relative intensities. Abbreviations: sh, shoulder; v, very; s, strong; m, medium; w, weak.

composition of $Ln_2Ni_2(CO)_3$ was relatively fast at 150°. Decomposition spoiled vapor tension measurements above 110°, as well as slow infrared scans of the vapor at 100°. The 25° air stability of all three sesquicarbonyls may be due to surface films.

Infrared Spectra.—Table I presents the data for a broad comparison of the infrared spectra of the sesquicarbonyls and the $(CF_3)_2POP(CF_3)_2$ compound written as $Lo_2Ni_2(CO)_4$,[2] under various conditions. For vapor-phase spectra at temperatures up to 110°, the cell (with NaCl windows and an 80-mm path) was mounted in an asbestos box with a heater–blower, all fitted into the cell chamber of the Beckman IR7 instrument. For $Lhn_2Ni_2(CO)_3$ it was possible to calculate the relative intensities by the defining equation $k = (100/PL) \log (I_0/I)$, where P is the pressure and L is the path length, both in centimeters. The same calculation for $Ln_2Ni_2(CO)_3$ was based upon the assumption of the same volatility as for $Lhn_2Ni_2(CO)_3$ and so may involve a systematic error. When samples of this compound were overheated, there was a fading-out of the terminal and bridging CO frequencies, with replacement by the fine-structure of free CO, suggesting that a kinetic study of the vapor-phase decomposition might be feasible.

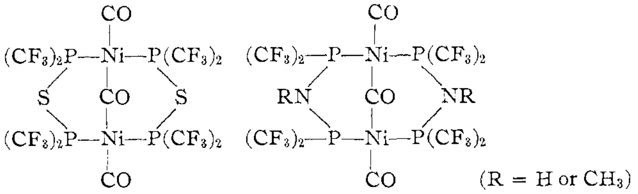
For the vapor over a sample of $Ls_2Ni_2(CO)_3$ at 65°, peaks were observable at 2097 and 2087 cm^{-1}, comparable to the very intense peaks for the CCl_4 solution at 2090 and 2075 cm^{-1}, but these changed in 20 min to 2110 and 2050 cm^{-1} while the fate of the medium peak at 1915 cm^{-1} (for the initial CCl_4 solution) was not determined. The altered CCl_4 solution showed C–F stretching at 1190 vs, 1174 s, 1150 m, and 1120 m cm^{-1}, inconsistent with the spectrum in a Nujol mull (see Table I).

Most of the Nujol mulls showed sharp spikes on the low-frequency sides of the CO bands. It is difficult to decide whether these are due to C^{13} isotope effects or to solid-phase interactions.

The terminal CO stretching frequencies for $Lhn_2Ni_2(CO)_3$ are slightly but definitely higher than those for $Ln_2Ni_2(CO)_3$. The reason might be only that the latter is a slightly heavier molecule, but we note also that the direction of the effect is as expected if the CH_3N group outdoes the NH group in π bonding to P_{3d}, causing certain Ni_{3d} electrons to occupy C_{2p} more effectively. The reason for that could be electronic pressure from the C–H bonds.

The vapor-phase peak for $Ln_2Ni_2(CO)_3$ at 865 cm^{-1} is assigned to P–N–P asymmetric stretching and differs little from the corresponding peak for the free ligand Ln at 869 cm^{-1}. On the other hand, this mode for $Lhn_2Ni_2(CO)_3$ is at 905 cm^{-1} *vs.* 925 cm^{-1} for free Lhn. The difference suggests that the P–N–P angle in Lhn undergoes a greater change by complex formation than occurs when Ln forms the complex. Such an effect would correspond to the general observation that hydrogen has no great power to govern the hybridization on an atom to which it is bonded, whereas carbon in the methyl group exerts a relatively strong influence, demanding just the right hybrid for the most energetic bonding. This argument would imply that the P–N–P angle is more flexible in Lhn than in Ln, so that the nickel complex can adjust the P–N–P angle to the value which is most nearly ideal for stability. There seems to be no better way to explain why $Lhn_2Ni_2(CO)_3$ has higher vapor-phase stability than $Ln_2Ni_2(CO)_3$.

Structural Discussion.—The previously suggested patterns[2]



(R = H or CH_3)

continue to seem most reasonable for the sesquicarbonyls in the vapor phase: smaller molecules are not allowed by the empirical formulas; larger molecules would mean lower volatility; and less compact structures should be less stable. The mass spectra (by the Varian M66 instrument) of the compounds seemed confirmatory: although the parent molecule ions were absent, there were mass numbers corresponding to loss of CO therefrom, with greater intensities for more CO removed.

However, the curious solubility behavior of the sulfur compound suggests that the solid may be a higher polymer, subject to depolymerization during vaporization or solution, and then lacking stability because the relatively wide PSP bond angle would lead to strain in the six-atomic rings.

Also for the nitrogen compounds it is not certain that the suggested pattern represents the crystals, for good efforts at X-ray structure determination so far have failed, and change could occur on solution or vaporization. Indeed, the ^{19}F nmr spectra of their ether or acetone solutions (Figure 1) clearly show two environments for fluorine, as though the basic solvent were influencing one nickel or two phosphorus atoms differently from the others—still without destroying the Ni–(CO)–Ni bridge which the infrared spectra show for the solutions.

In summary, then, the suggested bicyclononane pattern seems supportable only for these complexes in the vapor phase and remains uncertain for other conditions.

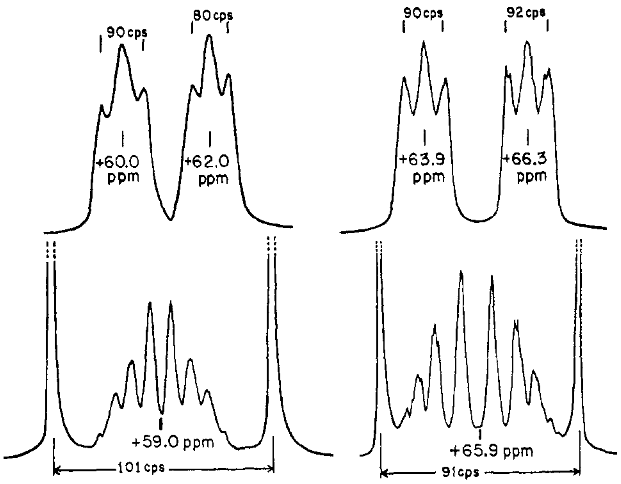


Figure 1.—Fluorine nmr spectra (at 94.1 Mc) of Ln (lower left), Lhn (lower right), and ether solutions of $Ln_2Ni_2(CO)_3$ (upper left) and $Lhn_2Ni_2(CO)_3$ (upper right). At far lower resolution, the Ln and Lhn bands have the appearance of 1:2:1 triplets. The upper figures represent the same "triplets," blurred by a larger number of nearby magnetic nuclei and doubled by a differential effect of the solvent. The different shapes and widths of these bands are quite real and repeatable. The chemical shifts are measured upfield from Cl_3CF.

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Nuclear Magnetic Resonance Study of the Exchange of Hexamethylphosphoramide with Dihalobis(hexamethylphosphoramide)cobalt(II)[1]

By Steven S. Zumdahl and Russell S. Drago

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In two previous studies[2,3] of the exchange kinetics of pseudo-tetrahedral complexes of Co(II) the reactions were found to proceed by a mechanism giving purely second-order kinetics. In order to further explore the exchange reactions of the CoL_2X_2 complexes, we have studied $Co(HMPA)_2X_2$ complexes (where HMPA is hexamethylphosphoramide and X^- is Br^- or Cl^-) in deuteriochloroform with various concentrations of excess HMPA. The $Co(HMPA)_2X_2$ complexes enable us to study a very bulky ligand which is a poorer coordinating ligand than those previously investigated. These complexes have been previously prepared and characterized.[4]

Experimental Section

Complexes.—The $Co(HMPA)_2X_2$ complexes were prepared as previously described.[4] *Anal.* Calcd for $Co(HMPA)_2Cl_2$: C, 29.52; H, 7.46; N, 17.22. Found: C, 29.31; H, 7.64; N, 16.74. Calcd for $Co(HMPA)_2Br_2$: C, 24.97; H, 6.30; N, 14.56. Found: C, 25.18; H, 6.53; N, 14.58.

Nmr Spectra.—The proton spectra were obtained in deuteriochloroform which was distilled from potassium carbonate just prior to use. A Varian Model A-60 nuclear magnetic resonance spectrometer equipped with a Model V-6040 temperature controller was used to record the spectra. The temperature was monitored by means of a YSI Model 42SL thermistor thermometer.

Results

The present experiments were carried out on deuteriochloroform solutions of the $Co(HMPA)_2X_2$ complexes containing various concentrations of free HMPA. Preliminary studies on this system[5] have shown that below $-25°$ separate pmr signals are observed for the free and complexed HMPA. At $-61°$ the paramagnetic isotropic shift ($\Delta\nu_M$) between the signals due to protons in the coordinated and free ligand sites is -203 cps for $Co(HMPA)_2Cl_2$ and -621 cps for $Co(HMPA)_2Br_2$.

In order to study the ligand-exchange kinetics of the $Co(HMPA)_2X_2$ complexes, the slow-exchange line-width technique, which is applicable in the temperature region where $1/\tau_M \ll \Delta\nu_M$, was used. In the slow-exchange temperature region the line width of the signal due to protons in the coordinated ligand site is given by the expression[6,7]

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