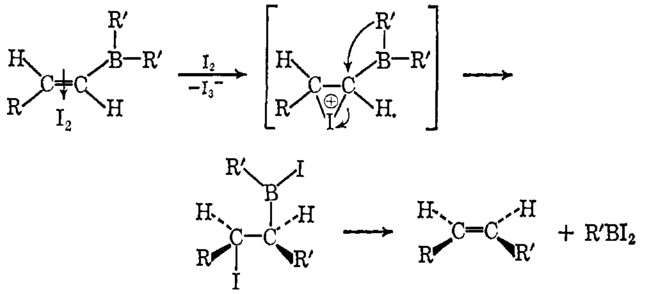
Although our efforts were mainly directed toward the practical application of this novel reaction, we have also carried out a brief mechanistic investigation of the reaction of iodine with *trans*-1-hex-1-enyl-bis(dicyclohexyl)borane[8] in tetrahydrofuran in the absence of base. Ultraviolet examination of the vinylborane–iodine solution indicated that the halogen reacted rapidly with the organoborane. Likewise the strong infrared absorption band of the *trans* double bond (1604 cm^{-1}) disappeared on adding a stoichiometric amount of iodine. Finally, examination of the organoborane–iodine solution by nmr revealed that 1-cyclohexyl-1-hexene (92% *cis* and 8% *trans*) is formed during the iodine-addition step, and not during the work-up. The formation of the olefin from the iodoorganoborane may be rationalized in terms of an initial fast base or solvent-assisted migration of a cyclohexyl group from boron to the adjacent carbon. The intermediate β-iodoorganoborane then undergoes deboronoiodination to give the *cis* olefin. It should be noted that all of the reactions leading to the *cis* olefins must be stereoselective.[9]



Migrations of alkyl substituents from boron to the α-carbon in α-haloorganoboranes[10] and deboronohalogenation of β-haloorganoboranes[2,3] are well documented.

[8] Derived from the hydroboration of 1-hexyne with dicyclohexylborane.

[9] Several possible mechanistic variations not explicitly considered herein will be discussed in the full paper.

[10] D. S. Matteson and R. W. H. Mah, *J. Am. Chem. Soc.*, **85**, 2599 (1963); G. Köbrich and M. R. Merkle, *Angew. Chem. Intern. Ed. Engl.*, **6**, 74 (1967).

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Mass Spectrometric Study of Tetrakis(trifluorophosphine)nickel(0)[1]

Sir:

Previous studies[2–4] of various transition metal carbonyls have indicated a consecutive unimolecular fragmentation of the parent-molecule ions formed upon electron impact. Because CO and PF_3 are rather different molecules, but yet bond to transition metals in similar fashion, we have initiated a mass spectrometric study of various PF_3-substituted metal carbonyls. We wish to report herein preliminary results of our studies of tetrakis(trifluorophosphine)nickel(0) that indicate several close similarities to the metal carbonyl systems and at least one significant difference.

Tetrakis(trifluorophosphine)nickel(0), $Ni(PF_3)_4$, was prepared approximately as described earlier.[5] About 2 g of $Ni(CO)_4$ was vacuum distilled into a 150-ml stainless-steel pressure vessel along with a quantity of purified[6] PF_3 adequate to yield a pressure of 300 psi at room temperature. The vessel was heated to 125–150° for 12 hr and then cooled to −195°, and the CO that was formed was removed by vacuum. This was continued through about four cycles until the amount of CO formed in the successive steps was approaching the point of diminishing return.

The product was a mixture of about 80% $Ni(PF_3)_4$ and 20% $Ni(CO)(PF_3)_3$ and no more than a trace of any of the other trifluorophosphinenickel carbonyl species. The tetraphosphine was isolated by preparative-scale gas–liquid chromatography using an Autoprep A-700 gas chromatograph. A 7.5 m × 0.25 in. column of 40% DC-702 silicone oil[7] on Kromat FB was used with helium as the carrier at a flow of about 60 cc/min. Temperatures of 25–40° were satisfactory using injections of about 30 μl. The product, which was trapped at −78°, was dried by vacuum distillation through a bed of 4A molecular sieves. The product was chromatographically pure when tested by glpc on an analytical scale and was found by low-voltage mass spectrometry to contain no discernible impurities.

The compound was introduced easily at room temperature to the ion source of the mass spectrometer. Operating pressures were about $2\text{–}5 \times 10^{-6}$ torr. The 70-ev mass spectrum, appearance potentials, clastogram, and metastable transitions were determined with a time-of-flight mass spectrometer described previously.[8] The modifications made to this instrument for metastable transition studies and the data interpretation are reported elsewhere.[9] No thermal decomposition was noted in these studies, and no contamination of the source or detector components was found.

The 70-ev mass spectrum (monoisotopic) is given in Table I. This table also contains the appearance potentials determined by the energy compensation technique[10] with mercury (IP = 10.43 ev) as the calibrant. In these measurements, the nickel-58 isotope was used throughout.

A comparison of the relative abundances in Table I for the ions formed from tetrakis(trifluorophosphine)-nickel(0) and those produced from $Ni(CO)_4$[2] indicates a significant similarity of these two molecules, although the $Ni(PF_3)_3^+$ and $Ni(PF_3)_4^+$ ions are much less abun-

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[1] Taken in part from the M.S. thesis submitted by M. A. Krassoi to the Graduate School of Kansas State University, Manhattan, Kan.

[2] R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **3**, 699 (1964); **4**, 157 (1965); *J. Phys. Chem.*, **69**, 1618, 3198 (1965); *J. Organometal. Chem.* (Amsterdam), **4**, 190 (1965); *J. Chem. Phys.*, **44**, 1964 (1966).

[3] R. E. Winters and J. H. Collins, *J. Phys. Chem.*, **70**, 2057 (1966).

[4] A. Foffani, S. Pignataro, B. Cantone, and F. Grasso, *Z. Physik. Chem.* (Frankfurt), **45**, 79 (1965); S. Pignataro, A. Foffani, F. Grasso, and B. Cantone, *ibid.*, **47**, 106 (1965); B. Cantone, F. Grasso, and S. Pignataro, *J. Chem. Phys.*, **44**, 3115 (1966); S. M. Schildcrout, G. A. Pressley, Jr., and F. E. Stafford, *J. Am. Chem. Soc.*, **89**, 1617 (1967); and D. R. Bidinosti, and N. S. McIntyre, *Can. J. Chem.*, **45**, 641 (1967).

[5] R. J. Clark and E. O. Brimm, *Inorg. Chem.*, **4**, 651 (1965).

[6] R. J. Clark and P. I. Hoberman, *ibid.*, **4**, 1771 (1965).

[7] The high oil loading (calculated on the basis of dry support) is important. In contrast to the normal behavior, the resolution for many of these metal carbonyl–trifluorophosphine species decreases on going to loading lower than this.

[8] E. J. Gallegos and R. W. Kiser, *J. Am. Chem. Soc.*, **83**, 773 (1961); *J. Phys. Chem.*, **65**, 1177 (1961).

[9] D. L. Dugger and R. W. Kiser, submitted for publication.

[10] R. W. Kiser and E. J. Gallegos, *J. Phys. Chem.*, **66**, 947 (1962).

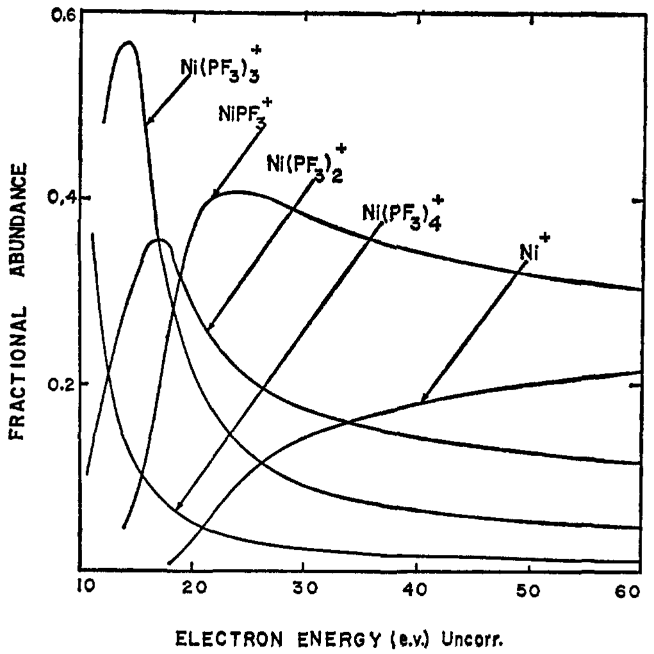

Figure 1. Clastogram for the nickel-containing ions from tetrakis(trifluorophosphine)nickel(0).

dant than the corresponding ions in the carbonyl compound. Additionally, no metal-containing ions possessing two positive charges were observed in the mass spectrum of $Ni(PF_3)_4$; this is in sharp contrast to the rather intense $Ni(CO)^{2+}$ (1.7% of the base peak) and $Ni(CO)_2^{2+}$ (4.5% of the base peak) ions formed from $Ni(CO)_4$. In $Ni(CO)_4$ the highest occupied molecular orbital (e) arises principally from the 3d orbitals of the metal (*i.e.*, are localized) and both the first and the second ionization potentials determined for the nickel-containing ions from $Ni(CO)_4$ support this. However, the absence of doubly charged ions in the $Ni(PF_3)_4$ mass spectrum suggests that the Ni–PF_3 bonding in $Ni(PF_3)_4$ is different to some extent from the analogous bonding encountered in $Ni(CO)_4$, but the low ionization potential of 8.7 ev for $Ni(PF_3)_4$ (see Table I) does indicate that the highest occupied molecular orbital in this compound also arises principally from the 3d orbitals of the nickel atom.

Table I. 70-ev Monoisotopic Mass Spectrum and Appearance Potentials of the Principal Ions Formed from Tetrakis(trifluorophosphine)nickel(0)

Ion	70-ev relative abundance	Appearance potential,[a] ev	Probable neutral products	ΔH_f(ion), kcal/mole
P^+	1.3			
PF^+	5.1			
PF_2^+	27.3			
PF_3^+	7.4			
Ni^+	77.4	17.3	$4PF_3$	(−948)[b]
NiF^+	9.9			
NiP^+	4.0			
$NiPF^+$	3.0			
$NiPF_2^+$	8.4			
$NiPF_3^+$	100.0	14.0	$3PF_3$	+35
$NiPF_4^+$	10.4			
$NiP_2F_4^+$	2.0			
$NiP_2F_5^+$	10.4			
$NiP_2F_6^+$	38.4	11.4	$2PF_3$	−245
$NiP_2F_7^+$	0.5			
$NiP_3F_8^+$	12.8			
$NiP_3F_9^+$	14.5	9.7	PF_3	−505
$NiP_4F_{11}^+$	0.7		F	
$NiP_4F_{12}^+$	3.4	8.7		−747

[a] Determined by the energy compensation method.[10] [b] Based on $\Delta H_f(Ni^+)$ = 330 kcal/mole[2] and $\Delta H_f(PF_3)$ = −219.6 kcal/mole (D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schuman, "Selected Values of Chemical Thermodynamic Properties. Part 1," National Bureau of Standards Technical Note 270-1, U. S. Government Printing Office, Washington, D. C., 1965); $\Delta H_f[Ni(PF_3)_4]$ = −948 kcal/mole.

The clastogram determined for the five $Ni(PF_3)_n^+$ ions, where $n = 0, 1, \ldots, 4$, is shown in Figure 1. The same interpretation[11] is applied to this study as that employed previously[2] to indicate the consecutive unimolecular decomposition of $Ni(PF_3)_4$ in the main (and is supported also by the energetics presented in Table I).

$$Ni(PF_3)_4^+ \longrightarrow Ni(PF_3)_3^+ \longrightarrow Ni(PF_3)_2^+ \longrightarrow NiPF_3^+ \longrightarrow Ni^+ \quad (1)$$

However, other processes indicated by the complete clastogram study are: (i) $NiP_3F_9^+ \rightarrow NiP_3F_8^+ + F$, and (ii) $NiP_2F_6^+ \rightarrow NiP_2F_5^+ + F$.

Winters and Collins[3] have shown that the appropriate metastable transitions are observed in $Fe(CO)_5$ to substantiate the consecutive decomposition scheme. By using a retarding field on the multiplier stack[9,12] in our time-of-flight instrument, we have observed the metastable transitions for all of the steps in eq 1 except $NiPF_3^+ \rightarrow Ni^+$. In addition, we observed a "metastable transition" for $NiP_4F_{11}^+ \rightarrow NiP_4F_{12}^+$; this is interpreted as a collision phenomenon, *i.e.*

$$NiP_4F_{11}^+ + Ni(PF_3)_4 \longrightarrow Ni(PF_3)_4^+ + NiP_4F_{11} \quad (2)$$

In order to determine the ΔH_f of $Ni(PF_3)_4$ from the energetic data, we choose the process

$$Ni(PF_3)_4 \longrightarrow Ni^+ + 4PF_3 \quad (3)$$

Assuming that the same excess energy is involved in the formation of Ni^+ in this process as in the formation of Ni^+ from $Ni(CO)_4$, we calculate $\Delta H_f[Ni(PF_3)_4]$ = −948 kcal/mole. This value is within 20 kcal/mole of the value we estimated using Franklin's method.[13] Using this value of $\Delta H_f[Ni(PF_3)_4]$ and the processes indicated in Table I, we have calculated also the heats of formation of the other $Ni(PF_3)_n^+$ species.

(11) R. W. Kiser and R. E. Winters, presented before the Division of Physical Chemistry, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 12–16, 1966, Abstract V006.

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(13) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

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