A Binuclear Nickel(0) Compound with Trifluorophosphine Ligands†

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DATA have been obtained that indicate a binuclear nickel compound containing a novel trifluorophosphine bridging unit has been prepared. During recent mass-spectrometric studies of $Ni(PF_3)_4$‡ at 70 ev, several low-intensity positive ions not ascribable to singly- or doubly-charged ions from the tetrakis(trifluorophosphine)nickel(0) compound were detected. The nominal masses and isotopic patterns for these low-intensity ions correspond to those expected of the series $Ni_2(PF_3)_n^+$, where $n = 2$, 3, 4, 5, and 6, and $Ni_2(PF_3)_nPF_2^+$, where $n = 2$, 3, and 4. In both series the ion intensities decrease with increasing value of n. Other ions, with the exception of $Ni_2(PF_3)_2F^+$, were not sufficiently intense for detection at the low concentrations available, or have m/q values identical to ions observed from the main component of the mixture, $Ni(PF_3)_4$. Attempts to observe negative ions of the Ni_2 series in the negative-ion spectra of $Ni(PF_3)_4$ have not been successful, possibly due to the severe decrease in ion current normally encountered for negative ions; negative ions formed from $Ni(PF_3)_4$ were observed.§

The observed binuclear fragments provide evidence for a compound $Ni_2(PF_3)_n$ where $n \geqslant 6$. For a consideration of possible structures, we may refer to the analogous systems of carbonyl compounds. The binuclear carbonyl compounds of Mn, Fe, and Co contain a metal–metal bond and 10, 9, and 8 ligands,[1] respectively. In the binuclear carbonyl compounds both atoms are bonded to an equal number of non-bridging ligands. For a binuclear nickel compound having six ligands with equal distribution, only structures without a metal–metal bond have no unpaired electrons. But none of the structures satisfy the "noble-gas formalism" frequently observed for carbonyl-type compounds. Possible structures for the heptaligand compound with one or three bridging PF_3 units and a metal–metal bond are "symmetrical" and satisfy the "noble-gas formalism." Regardless of the number of trifluorophosphine ligands, any proposed structure for $Ni_2(PF_3)_n$ containing no unpaired electrons and not more than one metal bond will contain a bridging PF_3 unit.¶

The observation of the dinickel compound reported certainly causes speculation about the existence of similar iron compounds. The mass spectrum of $Fe(PF_3)_5$ has recently been reported[2] with no mention of any polynuclear impurities.

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‡ Metastable transitions for the series $Ni(PF_3)_n^+ \rightarrow Ni(PF_3)_{n-1}^+ + PF_3$ where $n = 1, 2, 3, 4$ were observed in the present work, confirming the results of Kiser, Krassoi, and Clark.[4] Additional transitions noted in the present study were $Ni(PF_3)_nPF_2^+ \rightarrow Ni(PF_3)_{n-1}PF_2^+ + PF_3$ where $n = 1$ or 2 and $NiPF_4^+ \rightarrow NiF^+ + PF_3$.

§ A metastable transition due to $Ni(PF_3)_3^- \rightarrow Ni(PF_3)_2^- + PF_3$ was observed analogous to transitions observed in the metal carbonyl spectra (R. E. Sullivan and R. W. Kiser, *J. Chem. Phys.*, **1968**, in the press).

¶ *Added in proof:* It has been brought to our attention that a PE_2 bridging unit has been reported in $(PF_3)_6Co_2(PF_2)_2$ (T. Kruck and W. Lang, *Angew. Chem. Internat. Edn.*, **1967**, **6**, 454).

This may be due to a difference in preparative techniques, the low concentration expected of such impurities, or the non-existence of the compounds.

All data were obtained with an Hitachi RMU-6E double-focussing mass spectrometer. Ion-source temperatures were $\leqslant 45°$, and the glass inlet system was kept at room temperature. Sample pressures of $< 2 \times 10^{-6}$ torr were maintained in the analyzer regions and trap currents of $\leqslant 25\,\mu\text{A}$ were employed. The $Ni(PF_3)_4$ samples were kindly supplied by Dr. R. J. Clark of Florida State University and were prepared by a previously described technique.[3] The samples were stored in sealed Pyrex tubes in a deep-freeze maintained at $-10°$ for approximately nine months after receipt. Mass spectra, taken shortly after arrival of the samples, showed the polynuclear nickel impurity to be present in essentially the same concentration ($\leqslant 0{\cdot}1\%$) as in samples studied after 6, 9, and 10 months of storage. Previously published mass spectrometric studies of $Ni(PF_3)_4$[4] were made with a Bendix time-of-flight mass spectrometer which apparently lacked the sensitivity to detect this important impurity, present in such small concentration.

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[1] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1966, p. 724.

[2] T. Kruck and A. Prasch, *Z. anorg. Chem.*, 1968, **356**, 118.

[3] R. J. Clark and E. D. Brimm, *Inorg. Chem.*, 1965, **4**, 651.

[4] R. W. Kiser, M. A. Krassoi, and R. J. Clark, *J. Amer. Chem. Soc.*, 1967, **89**, 3653.