2). The actual modes of this and other quenching phenomena are presently under more detailed investigation.

Acknowledgment. The authors gratefully acknowledge the Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No. *trans*-[Rh(cyclam)$(CN)_2$]ClO_4, 85436-84-6; $Cr(CN)_6^{3-}$, 14875-14-0.

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Received July 26, 1983

Bis(allyl)nickel and Bis(pentadienyl)iron as Precursors for the Synthesis of $Ni(PF_3)_4$, $Ni(PF_2H)_4$, and $Fe(PF_3)_5$

Sir:

The synthesis of PF_3 complexes of transition metals is known to be significantly more difficult than the synthesis of metal carbonyls,[1,2] although well-defined processes for preparations of compounds such as $Ni(PF_3)_4$, $Fe(PF_3)_5$, $Cr(PF_3)_6$, etc. have been reported.[2-4] Wilkinson[2] first fluorinated $Ni(PCl_3)_4$ with antimony trifluoride to get the PF_3 complex. Timms[4] used the metal atom reactor technique to prepare $Ni(PF_3)_4$ (85% yield). Clark and Brimm[5] allowed $Ni(CO)_4$ to react with PF_3 in a pressure vessel at 150 °C for 12 h and obtained 90% pure $Ni(PF_3)_4$ by displacement of CO. A number of other procedures based on the reaction of nickel metal and PF_3 at high temperatures (up to 100 °C) and high pressures (50–350 atm), with reaction times of up to 10 days, have been reported[6] to give good yields. Most procedures using nickel and PF_3 under milder conditions and short reaction times have given low yields,[7] although studies in this laboratory, with H_2S-activated nickel and $H_3B{\cdot}PF_3$ as a source of PF_3, have shown that yields of up to 98% can be obtained with use of low PF_3 pressures (2 atm H_3BPF_3) and temperatures of 50 °C for 46 h.[1] $Ni(PF_3)_4$ can also be prepared in ca. 20% yield from nickelocene and PF_3.[8]

While $Ni(PF_3)_4$ and related species can be prepared with some difficulty by the above procedures, the compound $Ni(PF_2H)_4$ has been successfully prepared only by utilizing the metal atom reactor.[9] Other methods, useful for preparing $Ni(PF_3)_4$, were not successful for the PF_2H analogue.

$Fe(PF_3)_5$ was first prepared by Kruck and Prasch by the direct reaction of FeI_2 and PF_3 over copper powder.[3] The iron–PF_3 complex has also been prepared in 25% yield with use of metal atom cocondensation techniques.[4] However, the synthesis of $Fe(PF_3)_5$ is usually carried out by the displacement of CO from $Fe(CO)_5$ by PF_3. High pressures of PF_3 give only partially substituted products: ultraviolet irradiation of $Fe(CO)_2(PF_3)_3$ and excess PF_3 is necessary to obtain $Fe(PF_3)_5$.[10] Separation procedures are quite involved.

Herein we report an effective synthetic route to tetrakis(trifluorophosphine)nickel and related species, to pentakis(trifluorophosphine)iron, and to the elusive tetrakis(difluorophosphine)nickel. The procedures represent modifications and extensions of the work of Wilke and Bogdanovic, which involved $Ni(allyl)_2$ and organophosphines.[11] We have thus prepared $Ni(PCl_3)_4$, $Ni(PF_3)_4$, $Ni(PF_2N(CH_3)_2)_4$, $Ni(PF_2Cl)_4$, and $Ni(PF_2H)_4$ through the reaction of $Ni(allyl)_2$ with the appropriate ligand. The experimental procedures are quite convenient; reactions are carried out at 25 °C, at pressures below 1 atm, and with reaction times of approximately 1 h. For all of the preparations, the pure nickel complexes can be isolated from the unidentified organic byproducts by vacuum line trap-to-trap distillation or by recrystallization. The synthesis of the iron–PF_3 complex was carried out with bis(pentadienyl)iron (an "open ferrocene") and PF_3. The displacement process goes smoothly, but the procedure is handicapped by present difficulties in preparing the bis(pentadienyl)iron starting material in large quantity.

Standard vacuum line procedures as described by Shriver[12] were used throughout. Bis(η^3-allyl)nickel was prepared from the reaction of allylmagnesium chloride with nickel bromide in ether as described by Wilke and Bogdanovic.[11] PF_2H was prepared by the method of Centofanti and Rudolph,[13] and PF_3 was a purified sample from Ozark-Mahoning. Bis(pentadienyl)iron was prepared as described by Wilson, Ernst, and Cymbaluk.[14]

Synthesis of $Ni(PF_3)_4$ and Related Species

In a trap with Teflon stopcocks, a 4.39-mmol sample of PF_3 (29% excess) was condensed onto a 0.85-mmol sample of $Ni(allyl)_2$. The reagents were then allowed to react without solvent at 25 °C. After 1.5 h, the reaction mixture was fractionated. A 0.49-mmol sample (58% yield) of $Ni(PF_3)_4$ was recovered in the −80 °C trap. IR, and ^{31}P and ^{19}F NMR spectra coincided with the reported literature values.[9]

In reactions similar to that described above, a 70% yield of $Ni(PF_2Cl)_4$ was isolated by fractionation under high vacuum; an excellent yield of $Ni(PCl_3)_4$ was easily obtained and crystallized, and a quantitative yield of white crystalline $Ni[PF_2N(CH_3)_2]_4$ was recovered. The products were identified by NMR spectroscopy and by their physical characteristics.[4,9,15,16] In addition to the previously reported data for $Ni(PF_2Cl)_4$ and $Ni[PF_2N(CH_3)_2]_4$, ^{31}P NMR shifts of +177.6 and +169 ppm respectively were observed (downfield from H_3PO_4).

Synthesis of $Ni(PF_2H)_4$

A 1.25-mmol sample of PF_2H (0.8% excess) was condensed onto 0.31 mmol of $Ni(allyl)_2$ in a 9-mm NMR reaction tube, equipped with a gas expansion bulb and a stopcock. The reaction, carried out at a temperature of −80 to −90 °C for about 1 h, was monitored by ^{31}P, ^{19}F, and ^{1}H NMR. ^{19}F and ^{31}P spectra agree with those obtained previously in this laboratory.[9] The ^{31}P spectrum indicated a 50% yield of Ni(P-

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$F_2H)_4$. According to the NMR data, all of the PF_2H was consumed, which is reasonable considering that side reactions involving PF_2H are seen at −80 °C. $Ni(PF_2H)_4$ can be isolated from the various byproducts by vacuum manipulation if desired. In our hands, the bis(allyl)nickel route to $Ni(PF_2H)_4$ is superior to the metal atom reactor route described earlier.

Synthesis of $Fe(PF_3)_5$

A 2-mmol sample of $Fe(C_5H_7)_2$ was placed in the reaction tube and dissolved in about 25 mL of hexane. The reaction tube consisted of a 100-mL heavy-walled Pyrex tube fitted with a stainless steel cap and valve (Fischer & Porter Co.). The solution was degassed and frozen at −196 °C under vacuum. Approximately 20 mmol of PF_3 was then condensed into the tube. This would generate a pressure of approximately 5 atm in 100 mL at room temperature. After the tube was removed from the liquid-nitrogen bath, it was placed in a wire mesh pouch and placed behind a safety shield. The mixture was then heated to approximately 60 °C and stirred for 1 day. The reaction mixture was sampled, and $Fe(PF_3)_5$ was identified as the only observable product by ^{31}P NMR.[17]

Acknowledgment. Support of this work by the National Science Foundation through Grant Nos. CHE 7920313 and CHE 8120683 and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. $Ni(PF_3)_4$, 13859-65-9; $Fe(PF_3)_5$, 13815-34-4; $Ni(PF_2H)_4$, 69814-91-1; $Ni(PCl_3)_4$, 36421-86-0; $Ni(PF_2N(CH_3)_2)_4$, 15053-92-6; $Ni(PF_2Cl)_4$, 15024-22-3; NiB_2 (B = allyl), 12077-85-9; bis(pentadienyl)iron, 74910-62-6.

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Articles

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Silver Clusters in Zeolites: Fenske–Hall Self-Consistent Field Molecular Orbital Calculations

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Received March 25, 1983

The Fenske–Hall SCF–MO calculation was applied to Ag, Ag_2, and Ag_3 and the same clusters in a zeolitic environment. The spectroscopic properties of the naked clusters were calculated by using variable 5s and 5p exponents in the Slater-type 5s and 5p orbitals. For the calculation of the spectra of these clusters in the zeolites it is necessary to use Ag^+ functions. It is shown that the 5s–5p transition of Ag^0 in site I of zeolites X and Y occurs at almost the same position as in the gas phase. The yellow color of fully Ag-exchanged zeolites X and Y is due to a charge-transfer transition from Ag^0 on sites I′ to Ag^+ on site I. The calculations do not allow one to distinguish between dinuclear and trinuclear clusters. The most probable charge on the clusters is 1+. The yellow color of zeolite A is due to a charge transfer from the central Ag to the external Ag in the cluster $Ag^+–Ag^0–Ag^+$.

Introduction

Ag^+-exchanged zeolites form Ag clusters upon dehydration (zeolite A) or upon dehydration and oxidation (faujasite-type zeolites). Three types of clusters have been proposed on the basis of X-ray diffraction data.[2-4] In zeolite A Ag atoms form a linear cluster with a nuclearity of 3 inside the cubooctahedron.[3] The two external Ag atoms are coordinated to the three O_3 oxygens of the hexagonal ring with an interatomic distance of 0.223 nm. The central Ag occupies a site opposite the four-membered framework ring at a distance of 0.270 nm. The Ag–Ag distance is 0.285–0.300 nm, to be compared to the 0.289 nm in Ag metal.[5] Because of these interatomic distances the cluster is formally written as $Ag^+–Ag^0–Ag^+$. A maximum number of four Ag_3^{2+} clusters can be accommodated in one cubooctahedron, giving a cluster $(Ag_4^0Ag_8^{8+})$ very similar to the $(Ag_6^0)(Ag_8^{8+})$ cluster proposed by Seff.[2] In faujasite-type zeolites simultaneous occpancy of sites I and I′[6] by Ag was detected by X-ray diffraction.[4] The Ag–Ag distance is then 0.312 nm. Thus, cluster formation may be proposed. The charge of these clusters and their nuclearity are, however, ill-defined.[4] For Y-type zeolite, the excess occupancy of sites I and I′ can, in principle, be explained by dinuclear clusters. In X-type zeolites, trinuclear clusters must be assumed.[4]

The formation of these clusters is accompanied by a yellow coloration of the zeolites, and for interacting clusters in zeolite A, a brick red color is developed. These colors are due to visible absorption band at 25 000 cm^{-1} (3.10 eV) (yellow faujasite-type zeolites), at 23 000 cm^{-1} (2.85 eV) (yellow zeolite A) and at 20 000 cm^{-1} (2.48 eV) (brick red zeolite A).[3,7] For the faujasite-type zeolites bands at 30 100 ± 600 cm^{-1} (3.73 eV) and at 29 400 cm^{-1} (3.65 eV) of 27 800 cm^{-1} (3.45 eV)

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