Other workers have reported the preparation of variously $\beta$-substituted alkyl azides from olefins, and in several cases the initial step is thought to be the addition of the azido radical to the olefin.[12,14]

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**Walter S. Trahanovsky,***[15a] **M. Dwight Robbins**[15b]
*Department of Chemistry*
*Iowa State University of Science and Technology*
*Ames, Iowa 50010*

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## Lanthanide Shift Reagents. The X-Ray Structure of the Eight-Coordinate Bis(4-picoline) Adduct of 2,2,6,6-Tetramethylheptane-3,5-dionatoholmium, $Ho(dpm)_3(4\text{-}pic)_2$[1]

*Sir:*

Following the 1969 report by Hinckley,[2] there has been considerable interest shown[3-45] in paramagnetic lanthanide shift reagents. The mechanism of action of shift reagents is generally attributed to dipolar interactions[46] between the electronic magnetic moment and the nuclear spin moments which do not vanish for magnetically anisotropic complexes. Several authors have attempted to obtain information about the geometry of the substrate molecule with the assumption that the shifts should follow a $(3 \cos^2 \theta - 1)r^{-3}$ dependence.[47] This assumption is justified only for axially symmetric systems.[46e]

The dpm chelate of praeseodymium is known to be dimeric in the solid state with seven-coordination for each metal atom achieved by bridging oxygen atoms.[48] The X-ray structure of the seven-coordinate monohydrate, $Dy(dpm)_3H_2O$, has recently been reported.[49] In this structure the coordination polyhedron resembles a monocapped trigonal prism with the water molecule occupying a prism corner, a site of no real or approximate symmetry. While solid state and solution structures need by no means be identical, particularly in stereochemically nonrigid lanthanide complexes, it is of some interest to determine the X-ray structure of a shift reagent adduct as a focus for our thinking about its solution stereochemistry. Furthermore, in order to assess directly the dipolar shifts[46a] from single-crystal magnetic anisotropy[50] data,[51] the crystal structure of a shift reagent adduct is necessary. We report here the structure of the bis(4-picoline) adduct of $Ho(dpm)_3$.

The crystals, obtained by slow evaporation of a 4-picoline solution of $Ho(dpm)_3$,[52] are orthorhombic, space group $Pbcn$ ($D_{2h}^{14}$, no. 60). The cell dimensions are $a = 10.260\ (8)$, $b = 23.08\ (3)$, $c = 20.23\ (2)$ Å, $V = 4789\ (4)$ Å$^3$, $Z = 4$. Computer-controlled diffractometer data were obtained using Mo $K\bar{\alpha}$ radiation ($\lambda$ 0.71069 Å) and a $\theta$–$2\theta$ scan technique. The structure was solved by direct methods[53] using the program MAGIC[54] employing 1121 reflections with $I \geq 3\sigma(I)$. Least-squares refinement yielded an $R$ of 0.077 with isotropic temperature factors for all but the holmium and seven peripheral carbon atoms which were refined anisotropically.

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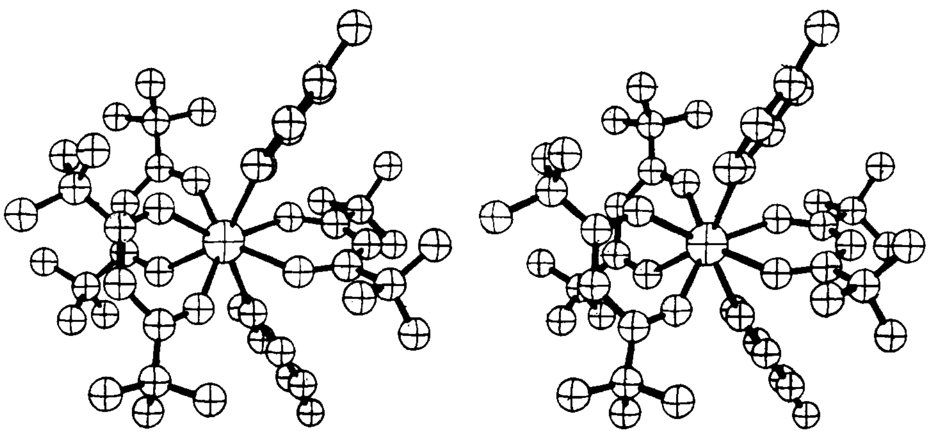

Figure 1. Stereoscopic pair showing $Ho(dpm)_3(4\text{-pic})_2$ viewed down the *c* crystallographic axis, roughly perpendicular to the square faces of the square antiprism coordination polyhedron. The *a* axis is vertical.

The asymmetric unit consists of half of the discrete, monomeric, eight-coordinate complex moieties, $Ho(dpm)_3(4\text{-pic})_2$. The coordination polyhedron (six O's and two N's) conforms closely to a square antiprism according to the criteria of Lippard and Russ.[55] A stereoview of the complex, from a vantage point perpendicular to the centers of the square faces, is shown in Figure 1. The square edges of the antiprism *s* range in length from 2.68 to 2.82 Å, while the lateral edges *l* range from 2.71 (constrained by the chelate bite) to 3.14 Å, $s_{av}$ = 2.74 Å, $l_{av}$ = 2.96 Å. The average $l/s$ ratio of 1.08 compares well with the "most favorable" value of 1.06 of Hoard and Silverton.[56] The atoms defining a square face all deviate from a best plane through themselves by $d_s$ = 0.06 Å; the square faces are nearly parallel, making an angle of 3.2° with each other. A description based on a dodecahedron is much less satisfactory, with distances from the "best" trapezoidal planes ranging from $d_T$ = 0.29 to 0.47 Å, with the trapezoidal "planes" making an angle of 85.8° with each other.

The complex has $C_2$ crystallographic symmetry, with the twofold axis passing through the holmium atom and bisecting one of the chelate rings. This symmetry operation takes the picoline and the other chelate ligand into their symmetry related partners. There are *no* real or approximate axes of threefold or higher order. The picoline ligands are *not* coaxial; the two Ho-N bonds make an angle of 139.1 (8)° with each other (see Figure 1). In the solid state the complex is not even approximately axially symmetric. The present structure, while not necessarily the only one present in solution, is a likely contributor in the solution state for complexes of this type. Our results suggest that the assumption of axial symmetry for shift-reagent adducts in solution may not be strictly valid and structural inferences made on this basis must be accepted with reservation.

Only two X-ray structures of complexes in the same stoichiometric class have been reported, namely $Ln(acac)_3(H_2O)_2$ in $Y(acac)_3(H_2O)_2 \cdot H_2O$[57] and $La(acac)_3(H_2O)_2$.[58] Both of these structures were described by their authors as square antiprisms; however, it has been pointed out[55] that the former structure is highly distorted toward a dodecahedron. It is noteworthy that while the water molecules in the diaquo species[57,58] occupy adjacent positions on the *same* square face, the picoline ligands of the present structure are situated at apices of *opposite* square faces as far removed from one another as possible. In the diaquo species, the chelate rings all span the sides of square faces, while in the present structure one chelate ring connects the opposite square faces.

On the basis of the difference between the diaquo and bis(picoline) structures, we offer the following tentative explanation of the fact that lanthanide chelate complexes with less bulky substituents,[18] as well as certain complexes involving mondentate ligands,[4] are inefficient as shift reagents. It may be that the presence of strong *intracomplex*, *interligand* interactions when bulky substituents are present limits the complex to a single (or perhaps a few) stable configuration. If a variety of different stereoisomers are present in solution, each with its own susceptibility tensor, the dipolar shifts, when averaged over all species, will tend toward zero. This is less likely to occur if one or at most a few isomers are present. For instance there is no *a priori* reason why the diaquo complex could not adopt the present structure in solution, while the presence of bulky substituents renders the converse not necessarily true.

The Ho-O bond distances range from 2.24 (2) to 2.30 (2) Å and average 2.27 (2) Å, in good agreement with the average Ho-O distance (2.29 (4) Å) in seven-coordinate $Ho(C_6H_5COCHCOC_6H_5)_3H_2O$.[59] The Ho-N distance of 2.53 (3) Å is reasonable compared with the La-N distance (2.65 (2) Å) in $La(NO_3)_3bipy$[60] when the lanthanide contraction is considered. The picoline and dpm geometries are normal. The holmium atom lies quite accurately in the plane of the chelate ring bisected by the $C_2$ axis, while the other β-diketonate ligand exhibits the often-noted[61] folding about the O-O internuclear axis, such that the plane of the chelate

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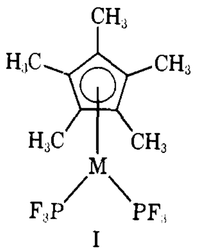
**William DeW. Horrocks, Jr.,* James P. Sipe III, Joseph R. Luber**
*Whitmore and Chandlee Laboratories, Department of Chemistry*
*The Pennsylvania State University*
*University Park, Pennsylvania 16802*
*Received June 14, 1971*

## Use of Tetrakis(trifluorophosphine)nickel as a Source of Trifluorophosphine in the Synthesis of Metal–Trifluorophosphine Complexes

*Sir:*

Metal complexes of trifluorophosphine (phosphorus trifluoride) have been prepared by the following two general methods: (1) reactions of the free metal, metal halide, metal–olefin complexes, or other carbonyl-free metal derivatives with phosphorus trifluoride under pressure, often in the presence of copper metal as an added reducing agent;[1,2] (2) reactions of metal carbonyls with phosphorus trifluoride under relatively mild conditions, often in the presence of ultraviolet irradiation.[1,3] This communication reports a third general method for the synthesis of metal–trifluorophosphine complexes. This new method uses thermal reactions of various transition metal derivatives with an excess of the commercially available[4] tetrakis(trifluorophosphine)nickel, $Ni(PF_3)_4$, as the source of the trifluorophosphine ligands. These reactions result in transfer of the trifluorophosphine ligands from nickel to the other transition metal. This new synthetic method resembles the use of pentacarbonyliron, $Fe(CO)_5$, as a source of carbonyl groups in reported syntheses of $W(CO)_6$[5] and $Rh_6(CO)_{16}$.[6]

This new synthetic method was first used to prepare the compounds $(CH_3)_5C_5M(PF_3)_2$ (I, M = Rh and Ir) from the corresponding chlorides $[(CH_3)_5C_5MCl_2]_2$ (M = Rh[7,8] and Ir[8]). Thus the reaction of 8.40 g (13.6 mmol) of $[(CH_3)_5C_5RhCl_2]_2$ with excess (20 ml, ~36 g, 87.5 mmol) $Ni(PF_3)_4$ in 250 ml of boiling toluene for 40 hr gave 6.5 g (58% yield) of deep orange volatile $(CH_3)_5C_5Rh(PF_3)_2$ (I, M = Rh), mp 88–89°, after sublimation at 30° (0.01 mm). [*Anal.* Calcd for $C_{10}H_{15}F_6P_2Rh$: C, 29.0; H, 3.6; F, 27.5; P, 15.0; Rh, 24.8; mol wt, 414. Found: C, 29.5; H, 3.6; F, 27.4; P, 14.9; Rh, 24.7; mol wt, 414 (mass spectrum)]. In this reaction the nickel(0) derivative $Ni(PF_3)_4$ functions both as a trifluorophosphinating and a dehalogenating agent. The $^{19}F$ nmr spectrum[9] of $(CH_3)_5C_5Rh(PF_3)_2$ exhibits a 12-line pattern centered at $\phi$ 10.8, consistent with a doubled $X_3AA'X'_3$ pattern,[10,11] and coupling constants[12] (Hz) $^1J_{PF}$ = 1334, $^2J_{PP}$ = 178, $^2J_{RhF} \approx 30$, $^3J_{PF} \approx 6$, and $^4J_{FF} \approx 0$.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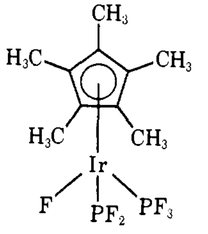
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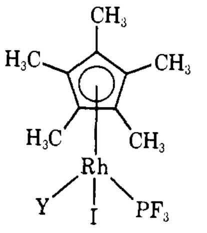
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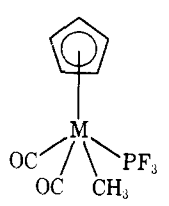
IV

An analogous reaction of the iridium compound $[(CH_3)_5C_5IrCl_2]_2$ with excess $Ni(PF_3)_4$ in boiling toluene gave a mixture of two isomeric compounds of composition $(CH_3)_5C_5IrP_2F_6$. [*Anal.* Calcd for $C_{10}H_{15}F_6IrP_2$: C, 23.8; H, 3.0; F, 22.6; Ir, 38.1; P, 12.3; O, 0.0; mol wt, 503. Found for isomer A: C, 24.0; H, 3.2; F, 22.6; Ir, 38.1; P, 12.4; O, 0.0; mol wt, 494 (osmometer in chloroform). Found for isomer B: C, 23.8; H, 3.2; F, 22.6; Ir, 38.1; P, 12.4; O, 0.0; mol wt, 517 (osmometer in chloroform)]. Isomer A is a pale yellow solid, mp 90–92°, which sublimes readily at 25° (0.01 mm). Its $^{19}F$ nmr spectrum exhibits a six-line pattern centered at $\phi$ 16.6, consistent with a $X_3AA'X'_3$ system,[10,11] and coupling constants[12] (Hz) $^1J_{PF}$ = 1250, $^2J_{PP}$ = 90, $^3J_{PF} \approx 2$, and $^4J_{FF} \approx 0$. Isomer A is therefore formulated as $(CH_3)_5C_5Ir(PF_3)_2$ (I, M = Ir). Isomer B is a pale yellow solid, mp ~140°, which sublimes only at 75–80° (0.05 mm) and hence can be separated from isomer A by this volatility difference. The $^{19}F$ nmr spectrum of isomer B exhibits two overlapping doublets centered at $\phi$ 4.4 ($J$ = 1177 Hz) and 20.5 ($J$ = 1280 Hz) of approximate relative intensity 2:3. The methyl proton nmr resonance of isomer B was an apparent quartet, separation ~4 Hz, centered at $\tau$ 7.83. This indicates that the methyl protons are split approximately equally by three spin $^1/_2$ nuclei, suggesting formulation of isomer B as $(CH_3)_5C_5IrF(PF_2)(PF_3)$ (II). The failure to observe in the $^{19}F$ nmr spectrum a resonance due to the single fluorine atom attached to the iridium atom may arise from excessive broadening of this resonance by coupling of this fluorine atom with two nonequivalent phosphorus atoms in addition to the apparent ~4-Hz coupling of this fluorine atom with the 15 equivalent protons of the pentamethylcyclopentadienyl ring.

The formation of $(CH_3)_5C_5IrF(PF_2)(PF_3)$ (II) by trifluorophosphination of $[(CH_3)_5C_5IrCl_2]_2$ with $Ni(PF_3)_4$ represents a novel example of an oxidative addition on a $(CH_3)_5C_5M(PF_3)_2$ derivative (I, M = Rh and Ir), where one of the $PF_3$ ligands acts as an oxidative-addition reagent with rupture of a phosphorus-

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