ring makes an angle of 12.0° with the plane defined by the holmium and the two oxygen atoms.

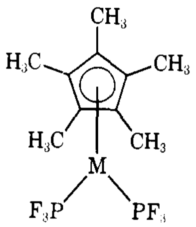
William DeW. Horrocks, Jr.,* James P. Sipe III, Joseph R. Luber
Whitmore and Chandlee Laboratories, Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802
Received June 14, 1971

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

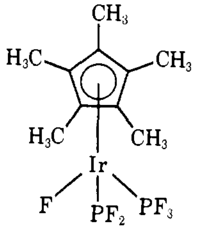
Sir:

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]

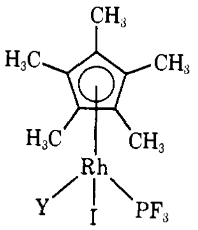
This new synthetic method was first used to prepare the compounds $(CH_3)_5C_5M(PF_3)_2$ (I, M = Rh and Ir) from the corresponding chlorides $[(CH_3)_5C_5MCl_2]_2$ (M = Rh[7,8] and Ir[8]). Thus the reaction of 8.40 g (13.6 mmol) of $[(CH_3)_5C_5RhCl_2]_2$ with excess (20 ml, ~36 g, 87.5 mmol) $Ni(PF_3)_4$ 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 ϕ 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 $^4J_{FF} \approx 0$.



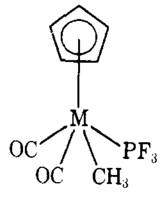
I



II



III



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 ϕ 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 ϕ 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 τ 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–

---

[1] J. F. Nixon, *Advan. Inorg. Nucl. Chem.*, **13**, 363 (1970).

[2] T. Kruck, *Angew. Chem., Int. Ed. Engl.*, **6**, 53 (1967).

[3] R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964); R. J. Clark and P. I. Hoberman, *ibid.*, **4**, 1771 (1965); R. J. Clark and E. O. Brimm, *ibid.*, **4**, 651 (1965).

[4] Ozark-Mahoning Company, Tulsa, Okla.

[5] A. N. Nesmeyanov, E. P. Mikheev, K. N. Anisimov, V. L. Volkov, and Z. P. Valueva, *Zh. Neorg. Khim.*, **4**, 402, 249 (1959); *Chem. Abstr.*, **53**, 21327*h*, 12907*c* (1959).

[6] B. L. Booth, M. J. Else, R. Fields, H. Goldwhite, and R. N. Haszeldine, *J. Organometal. Chem.*, **14**, 417 (1968).

[7] J. W. Kang and P. M. Maitlis, *J. Amer. Chem. Soc.*, **90**, 3259 (1968).

[8] J. W. Kang, K. Moseley, and P. M. Maitlis, *ibid.*, **91**, 5970 (1969).

[9] Fluorine nmr spectra are reported in parts per million upfield from internal $CFCl_3$ using the ϕ scale of G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

[10] R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

[11] R. K. Harris and C. M. Woodman, *Mol. Phys.*, **10**, 437 (1966).

[12] The notation used here is the same as that used by F. Ogilvie, R. J. Clark, and J. G. Verkade, *Inorg. Chem.*, **8**, 1904 (1969).

fluorine bond. The rhodium compound $(CH_3)_5C_5Rh(PF_3)_2$ (I, M = Rh) has also been found to undergo a variety of oxidative-addition reactions with iodine compounds of the type RI (R = I, CF_3, C_2F_5, n-C_3F_7, and n-C_7F_{15}) to give the oxidative-addition products of general structure III as listed in Table I. These reactions appear to be the first examples of oxidative-addition reactions of metal–trifluorophosphine complexes. Similar oxidative-addition reactions have been recently reported for the iridium carbonyl derivative $(CH_3)_5C_5Ir(CO)_2$.[13]

Table I. Oxidative-Addition Reactions of $(CH_3)_5C_5Rh(PF_3)_2$[a]

Reactant	Product[b]	Color	Mp, °C	Yield, %
I_2	$Me_5C_5Rh(PF_3)I_2$	Deep red	Dec >275	95
CF_3I	$Me_5C_5Rh(PF_3)(CF_3)I$	Orange-brown	Dec >200	72
C_2F_5I	$Me_5C_5Rh(PF_3)(C_2F_5)I$	Red-brown	230–231	76
n-C_3F_7I	$Me_5C_5Rh(PF_3)(n\text{-}C_3F_7)I$	Deep red	147–149	77
n-$C_7F_{15}I$	$Me_5C_5Rh(PF_3)(n\text{-}C_7F_{15})I$	Orange	86–88	62

[a] These reactions were all carried out at room temperature in benzene solution using a large excess of the iodine compound. [b] All of these products were characterized by correct analyses for five elements and infrared spectra and nmr spectra (proton and fluorine).

Various metal carbonyl halides also react with $Ni(PF_3)_4$ in boiling toluene to form metal–trifluorophosphine complexes,[14] sometimes with dehalogenation. Thus $Mn(CO)_5Br$ reacts with $Ni(PF_3)_4$ to give a mixture of $Mn_2(CO)_{10-x}(PF_3)_x$ (x = 0, 1, or 2) derivatives with removal of the bromine atom. Under appropriate conditions a reasonably pure sample of the known[15] compound $Mn_2(CO)_8(PF_3)_2$ could be isolated. Reaction of the rhenium analog $Re(CO)_5Br$ with excess $Ni(PF_3)_4$ gives a 25% yield of white $Re(CO)_3(PF_3)_2Br$, mp 40–41°, with retention of the bromine atom. Reaction of $C_5H_5Fe(CO)_2I$ with excess $Ni(PF_3)_4$ gives a 77% yield of brown $C_5H_5Fe(CO)(PF_3)I$, mp 102–103°. Reaction of $C_5H_5Mo(CO)_3Cl$ with $Ni(PF_3)_4$ results in dechlorination to give either dark red $(C_5H_5)_2Mo_2(CO)_5PF_3$, mp 159–160° dec, or dark red $[C_5H_5Mo(CO)_2PF_3]_2$, decomposing at $\sim$175°, depending upon the reaction conditions.

The nickel compound $Ni(PF_3)_4$ can also be used as a source of trifluorophosphine in reactions with halogen-free metal complexes. Thus, the σ-methylmetal derivatives $CH_3M(CO)_3C_5H_5$ (M = Mo and W) react with $Ni(PF_3)_4$ in boiling toluene to give the yellow derivatives $CH_3M(CO)_2(PF_3)C_5H_5$ (IV, M = Mo and W).[14]

Further details on the compounds described here and closely related ones will be described in future publications.

Acknowledgment. The authors are indebted to the National Institute of Medical Sciences for partial support of this work under Grant No. GM-14664-03.

---

(13) R. B. King and A. Efraty, *J. Organometal. Chem.*, 27, 409 (1971).

(14) New compounds prepared in this work were characterized by elemental analyses. Infrared spectra and, when obtainable, nmr (proton and fluorine) and mass spectra were consistent with the proposed formulations.

(15) R. J. Clark, J. P. Hargaden, H. Haas, and R. K. Sheline, *Inorg. Chem.*, 7, 673 (1968).

(16) Postdoctoral research associate, 1968–1971.

R. B. King,* A. Efraty[16]
Department of Chemistry, University of Georgia
Athens, Georgia 30601

Received June 21, 1971

Stereochemical Nonrigidity in an Eight-Coordinate Complex

Sir:

We wish to report the first characterization of stereochemical nonrigidity in an eight-coordinate complex. Magnetic equivalence of ligand nuclei in eight-coordinate complexes has been a general observation.[1–6] In some instances, the magnetic equivalence has been ascribed to a rapid intramolecular rearrangement, and various stylized mechanisms have been considered.[1–3] However, in no case has the limiting, slow-exchange nmr spectrum been detected.

In the present communication we give data for the limiting fast- and slow-exchange ^1H and ^{31}P nmr spectra for complexes of the form $MoH_4(PR_3)_4$.[7] Figure 1 shows the 90-MHz ^1H nmr spectrum for the hydride protons of $MoH_4[P(C_6H_5)_2CH_3]_4$[7] at three temperatures. Figure 2 shows the 36.4-MHz ^{31}P nmr spectrum (with selective decoupling of the ligand protons) for the same complex at two temperatures; it is a 1:4:6:4:1 quintet in the high-temperature limit, confirming the presence of four hydride hydrogens in the molecule. Similar ^1H nmr spectra were obtained for the complex $MoH_4[P(C_6H_5)_2C_2H_5]_4$.[7] For both complexes, the ^1H hydride spectral patterns are independent of the spectrometer frequency in the low-temperature limit, as shown by experiments at 220 MHz. Thus the hydride hydrogens are chemically equivalent in the "rigid" state of the molecules.

Figure 1 illustrates the broadening of the central three lines of the high-temperature quintet as the temperature is lowered; similar behavior was observed in the ^{31}P spectrum, and in both cases the two outer lines remain sharp down to the low-temperature limit, a feature characteristic of intramolecular rearrangements in systems of this type.[8,9]

Preliminary work has been done on the analysis of the low-temperature limit spectra assuming a T_d model of two interpenetrating H_4 and P_4 tetrahedra. The model has an AA′A″A‴XX′X″X‴ spin system with two independent P–H coupling constants, a P–P coupling constant, and an H–H coupling constant. From the high-temperature limit spectrum, the sum

---

(1) E. L. Muetterties, *Inorg. Chem.*, 4, 769 (1965).

(2) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, 21, 109 (1967).

(3) E. L. Muetterties, *Accounts Chem. Res.*, 3, 266 (1970); *Rec. Chem. Progr.*, 31, 51 (1970).

(4) J. Chatt and R. S. Coffey, *J. Chem. Soc. A*, 1963 (1969).

(5) P. G. Douglas and B. L. Shaw, *ibid.*, *A*, 334 (1970).

(6) M. Freni, R. Demichelis, and D. Giusto, *J. Inorg. Nucl. Chem.*, 29, 1433 (1967).

(7) F. Pennella, *Chem. Commun.*, 158 (1971).

(8) F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 92, 1068 (1970).

(9) P. Meakin, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, L. J. Guggenberger, W. G. Peet, and E. L. Muetterties, *ibid.*, 92, 3482 (1970).