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Structures of the Isomeric Forms of Tris(triphenylphosphine)copper(I) Tetrachloroferrate(III), $(PPh_3)_3CuFeCl_4$: Examples of the Weakly Coordination and Uncoordinated Tris(triphenylphosphine)copper(I) Cation

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Introduction

Earlier, complexes of the formula $(Ph_3P)_3CuFeCl_3X$ (**I**, X = Cl; **II**, X = Br) were reported.[1] On the basis of spectroscopic evidence, one crystalline form of the complex was proposed as ionic $[(Ph_3P)_3Cu]^+[FeCl_3X]^-$ (**Ia**, X = Cl; **IIa**, X = Br) while a distinctly different crystalline form was proposed as having a coordinated $FeCl_3X$ unit to the copper, thus $[(Ph_3P)_3Cu–X–FeCl_3]$ (**Ib**, X = Cl; **IIb**, X = Br). Reported herein are the structures of **Ia** and **Ib** which verify and further clarify the structural formulations of these complexes. Of the numerous previously reported[2–4] structures of phosphine-ligated copper(I) complexes, none have been isolated in two isomeric forms. Moreover, single X-ray determinations of tris(triphenylphosphine)copper(I) complexes has not thus far detected the presence of the three-coordinate $(Ph_3P)_3Cu^+$ cation.

Ib converts irreversibly to **Ia** upon heating in the solid state. The greater stability of **Ia** over **Ib** may seem unusual in light of the common tendency of tris(triphenylphosphine)copper(I) to coordinate certain anions either strongly[2c,4] or weakly.[5,6]

Experimental Section

Materials. All reagents are commercially available in reagent grade quality. USP grade absolute alcohol was used. All were used without further purification.

Preparation of Ia and Ib. **Ia** originally prepared[1] by reaction of tris(triphenylphosphine)copper(I) chloride with iron(III) chloride is prepared by a different method. To a solution of copper(II) chloride dihydrate (0.375 g, 2.20 mmol) in 30 mL of absolute ethanol was added iron(II) chloride tetrahydrate (0.436 g, 2.19 mmol) in 15.0 mL of absolute ethanol. The olive green solution changed to dark brown after stirring for 30 min. Triphenylphosphine (2.152 g, 8.19 mmol) in 45 mL of CH_2Cl_2 was added. The reaction mixture changed immediately to a darker brown color and then gradually to a golden yellow color. After a total reaction time of 1 h, 400 mL of petroleum ether was added with stirring, which caused precipitation of well-defined golden yellow crystals of **Ia**. The vacuum-filtered product was washed with petroleum ether and dried under vacuum. Yield: 1.86 g (81.1%). The observed melting point, the electronic spectrum in methylene chloride, and the reversion to $(Ph_3P)_3CuCl$ and $FeCl_3$ with ethanol were identical to that reported previously.[1] Crystals of the dark brown **Ib** form were isolated as in the original report by dissolving **Ia** and a small amount of Ph_3P in methylene chloride and precipitating using petroleum ether.

Table I. Crystallographic Data

	complex	
	Ia	**Ib**
formula	$C_{54}H_{45}P_3CuFeCl_4$	$C_{54}H_{45}P_3CuFeCl_4$
fw	1048.08	1048.08
space group	$P2_1/n$	$P\bar{1}$
a, Å	19.146(2)	13.233(4)
b, z	23.388(2)	18.108(5)
c, Å	11.452(1)	12.669(4)
α, deg	90.00	101.13(2)
β, deg	98.683(3)	117.29(2)
γ, deg	90.00	94.29(2)
V, Å^3	5069.3	2600.4
Z	4.0	2.0
T, °C	20	20
λ, Å	0.710 73	0.710 73
ρ_{calc}, g cm^{-3}	1.373	1.338
μ, cm^{-1}	10.468	10.203
R/R_w[a]	0.0579/0.0628	0.0578/0.0663

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

X-ray Structures. Quality single crystals of **Ia** were grown from a 1:1 mixture of ethanol and methylene chloride with added pentane at 5 °C overnight. Suitable crystals of **Ib** were obtained by vapor diffusion equilibration of pentane with a methylene chloride solution of **Ib** over several days slightly below room temperature.

Crystallographic data are given in Table I. X-ray data were collected using a Syntex $P\bar{1}$ diffractometer (reflections collected: **Ia**, 8629; **Ib**, 3267) for a golden yellow crystal of **Ia** (0.25 × 0.20 × 0.15 mm) and a dark brown crystal of **Ib** (0.24 × 0.21 × 0.16 mm). Intensity data were collected in the range $2 < 2\theta < 48°$ (**Ia**) and $3 < 2\theta < 46°$ (**Ib**). The data were empirically corrected for absorption effects. No decay correction was applied. As a check on crystal stability, two representative reflections were measured every 97 reflections. The structure was solved by direct methods and refined by full-matrix least-squares refinement on 568 (**Ia**) and 569 (**Ib**) parameters. All non-hydrogen atoms were refined anisotropically: Structure **Ia**, $R(F) = 5.79\%$ for 3689 observed reflections; structure **Ib**, $R(F) = 5.78\%$ for 3267 observed reflections ($F_o > 3\sigma(F_o)$). Scattering factors were taken from the literature.[7] The final atomic coordinates and displacement parameters are given in Tables II and III. All calculations were performed on a VAX 8300 computer with the SDP/VAX package.[8]

Conversion of Ib to Ia with Heat. **Ib** is stable indefinitely as a solid at room temperature. Upon heating, however, the dark-brown **Ib** form converts to the golden yellow **Ia** form in the solid state. The conversion readily takes place at 109.5–111.0 °C. The powder pattern X-ray of the converted **Ia** is the same as reported.[1]

Results and Discussion

Molecular Structure of Ia. The molecular structure of **Ia** is shown in Figure 1, and selected bond distances and angles are presented in Table IV. **Ia** shows no coordination between the $(Ph_3P)_3Cu^+$ cation and $FeCl_4^-$ anion; the ions are discrete entities. The closest atom of the anion to that of the copper in $(Ph_3P)_3Cu^+$ is that of Cl(2), which resides at a distance of 4.160(2) Å from the copper.

In the $(Ph_3P)_3Cu^+$ ion, the copper atom is in a mildly distorted trigonal environment with the copper atom at a distance of 0.1837(12) Å above the plane of the three phosphorus atoms. The Cu–P bond distances have a mean value of 2.295 Å. The mean

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Table II. Atomic Positional Parameters and Equivalent Displacement Parameters (Å^2) for **Ia**

atom	*x*	*y*	*z*	B^a
Cu	0.25837(6)	0.09337(5)	0.2165(1)	4.14(2)
Fe	0.17231(9)	–0.19625(7)	0.4983(2)	6.26(4)
Cl(1)	0.1400(2)	–0.1141(2)	0.4199(3)	9.1(1)
Cl(2)	0.2461(2)	–0.2378(2)	0.3988(3)	9.7(1)
Cl(3)	0.2209(4)	–0.1844(3)	0.6768(4)	19.8(2)
Cl(4)	0.0809(2)	–0.2499(2)	0.4798(6)	18.0(2)
P(1)	0.3621(1)	0.0516(1)	0.1812(2)	4.38(6)
P(2)	0.1557(1)	0.0604(1)	0.1083(2)	4.36(6)
P(3)	0.2611(1)	0.1468(1)	0.3844(2)	4.23(6)
C(1)	0.3691(5)	–0.0236(4)	0.2204(8)	4.5(2)
C(2)	0.3112(5)	–0.0523(4)	0.2498(8)	4.9(2)
C(3)	0.3148(6)	–0.1101(5)	0.279(1)	6.1(3)
C(4)	0.3781(7)	–0.1390(5)	0.278(1)	7.2(3)
C(5)	0.4357(6)	–0.1103(5)	0.249(1)	7.6(3)
C(6)	0.4318(6)	–0.0528(5)	0.220(1)	6.2(3)
C(7)	0.4479(5)	0.0802(4)	0.2506(8)	4.4(2)
C(8)	0.4705(6)	0.0679(5)	0.366(1)	6.5(3)
C(9)	0.5346(7)	0.0896(6)	0.424(1)	8.0(4)
C(10)	0.5748(6)	0.1239(5)	0.364(1)	7.2(3)
C(11)	0.5516(6)	0.1367(5)	0.249(1)	7.2(3)
C(12)	0.4883(5)	0.1151(5)	0.1908(9)	6.0(3)
C(13)	0.3669(5)	0.0554(4)	0.0231(7)	4.3(2)
C(14)	0.3386(5)	0.0111(5)	–0.0430(9)	5.5(3)
C(15)	0.3897(6)	0.0191(6)	–0.1615(9)	6.8(3)
C(16)	0.3715(7)	0.0710(6)	–0.2156(9)	7.2(3)
C(17)	0.3495(7)	0.1149(5)	–0.1481(9)	7.1(3)
C(18)	0.3456(6)	0.1076(5)	–0.0290(9)	5.9(3)
C(19)	0.1602(5)	–0.0130(4)	0.0542(8)	4.7(2)
C(20)	0.1279(6)	–0.0577(4)	0.105(1)	5.7(3)
C(21)	0.1386(6)	–0.1138(5)	0.066(1)	7.2(3)
C(22)	0.1822(7)	–0.1241(5)	–0.018(1)	7.6(3)
C(23)	0.2148(6)	–0.0793(5)	–0.064(1)	6.6(3)
C(24)	0.2047(5)	–0.0233(4)	–0.278(9)	5.4(3)
C(25)	0.1214(5)	0.0988(4)	–0.0269(8)	4.1(2)
C(26)	0.0702(5)	0.0758(4)	–0.1120(9)	5.1(2)
C(27)	0.0446(6)	0.1067(5)	–0.2131(9)	6.4(3)
C(28)	0.0707(6)	0.1597(5)	–0.229(1)	6.6(3)
C(29)	0.1220(7)	0.1832(5)	–0.146(1)	7.6(4)
C(30)	0.1479(6)	0.1522(5)	–0.043(1)	6.4(3)
C(31)	0.0838(5)	0.0601(4)	0.1958(8)	4.6(2)
C(32)	0.0199(5)	0.0869(5)	0.1593(9)	5.4(3)
C(33)	–0.0309(6)	0.0898(6)	0.236(1)	7.2(3)
C(34)	–0.0174(6)	0.0658(6)	0.346(1)	7.8(3)
C(35)	0.0462(6)	0.0380(5)	0.383(1)	7.0(3)
C(36)	0.0966(6)	0.0356(5)	0.3085(9)	6.0(3)
C(37)	0.3443(5)	0.1830(4)	0.4408(8)	4.1(2)
C(38)	0.3830(5)	0.2064(4)	0.3596(9)	5.7(3)
C(39)	0.4453(6)	0.2365(5)	0.399(1)	7.7(3)
C(40)	0.4643(6)	0.2429(5)	0.517(1)	8.4(4)
C(41)	0.4281(8)	0.2205(6)	0.598(1)	8.6(4)
C(42)	0.3663(6)	0.1889(5)	0.558(1)	7.1(3)
C(43)	0.1939(5)	0.1993(4)	0.4051(8)	4.7(2)
C(44)	0.2072(1)	0.2454(6)	0.477(1)	9.8(4)
C(45)	0.1540(7)	0.2809(6)	0.502(1)	11.1(4)
C(46)	0.0858(6)	0.2714(5)	0.450(1)	7.3(3)
C(47)	0.0724(6)	0.2254(5)	0.381(1)	7.3(3)
C(48)	0.1263(6)	0.1896(5)	0.354(1)	7.1(3)
C(49)	0.2499(5)	0.0924(4)	0.4940(7)	4.5(2)
C(50)	0.2049(5)	0.0979(5)	0.5768(8(	5.6(3)
C(51)	0.1926(6)	0.0507(5)	0.6474(9)	6.9(3)
C(52)	0.2245(6)	–0.0005(5)	0.634(1)	7.0(3)
C(53)	0.2695(6)	–0.0069(5)	0.552(1)	6.6(3)
C(54)	0.2822(6)	0.04033(4)	0.4819(8)	5.3(3)

^{a} ${}^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table III. Atomic Positional Parameters and Equivalent Displacement Parameters (Å^2) for **Ib**

atom	*x*	*y*	*z*	B^a
Cu	0.6952(1)	0.24663(7)	0.3972(1)	3.93(3)
Fe	1.0946(2)	0.2796(1)	0.7439(2)	5.56(5)
Cl(1)	0.9232(3)	0.2955(2)	0.6117(4)	7.8(1)
Cl(2)	1.1911(3)	0.2579(2)	0.6444(4)	9.8(1)
Cl(3)	1.0795(4)	0.1837(2)	0.8188(4)	9.0(1)
Cl(4)	1.1872(4)	0.3824(2)	0.8922(4)	9.1(1)
P(1)	0.6271(3)	0.1430(2)	0.4416(2)	3.78(8)
P(2)	0.7519(2)	0.2337(2)	0.2501(2)	3.74(8)
P(3)	0.6224(3)	0.3550(2)	0.4398(3)	4.34(8)
C(1)	0.4786(8)	0.0950(5)	0.3251(8)	3.5(3)
C(2)	0.4454(9)	0.0956(6)	0.2057(9)	4.6(3)
C(3)	0.333(1)	0.0585(7)	0.114(1)	5.9(4)
C(4)	0.259(1)	0.0234(7)	0.145(1)	6.0(4)
C(5)	0.292(1)	0.0217(7)	0.263(1)	5.8(4)
C(6)	0.4034(9)	0.0582(6)	0.3542(9)	4.5(3)
C(7)	0.622(1)	0.1703(6)	0.5863(9)	4.8(3)
C(8)	0.528(1)	0.2014(6)	0.587(1)	5.4(4)
C(9)	0.529(1)	0.2294(8)	0.697(1)	7.4(4)
C(10)	0.622(1)	0.2264(8)	0.805(1)	8.7(5)
C(11)	0.715(1)	0.1971(8)	0.805(1)	8.6(5)
C(12)	0.717(1)	0.1680(7)	0.694(1)	6.2(4)
C(13)	0.7081(9)	0.0638(6)	0.4595(8)	4.1(3)
C(14)	0.828(1)	0.0821(6)	0.523(1)	5.6(4)
C(15)	0.105(1)	0.9739(7)	0.458(1)	6.7(4)
C(16)	0.840(1)	–0.0497(6)	0.496(1)	6.0(4)
C(17)	0.7227(9)	–0.0681(6)	0.432(1)	5.2(4)
C(18)	0.6522(9)	–0.0136(6)	0.4132(9)	4.4(3)
C(19)	0.6179(8)	0.2087(6)	0.1047(9)	4.0(3)
C(20)	0.5394(9)	0.2578(7)	0.0847(9)	5.5(4)
C(21)	0.430(1)	0.2392(8)	–0.018(1)	6.9(4)
C(22)	0.397(1)	0.1676(8)	–0.101(1)	6.9(4)
C(23)	0.474(1)	0.1191(7)	–0.082(1)	6.0(4)
C(24)	0.5848(9)	0.1378(6)	0.0179(9)	4.8(3)
C(25)	0.8331(9)	0.3188(6)	0.2482(9)	4.3(3)
C(26)	0.938(1)	0.3526(7)	0.357(1)	6.1(4)
C(27)	1.001(1)	0.4180(7)	0.360(1)	7.2(5)
C(28)	0.968(1)	0.4509(7)	0.266(1)	7.5(4)
C(29)	0.866(1)	0.4182(7)	0.159(1)	7.2(4)
C(30)	0.800(1)	0.3528(6)	0.1530(9)	5.4(3)
C(31)	0.8342(9)	0.1585(6)	0.2286(9)	4.2(3)
C(32)	0.8031(9)	0.0878(6)	0.2459(9)	5.0(3)
C(33)	0.859(1)	0.0277(7)	0.225(1)	5.9(4)
C(34)	0.942(1)	0.0396(7)	0.192(1)	6.3(4)
C(35)	0.9722(9)	0.1081(8)	0.175(1)	6.9(4)
C(36)	0.9160(9)	0.1694(7)	0.192(1)	5.7(4)
C(37)	0.6121(8)	0.4233(6)	0.3512(9)	4.4(3)
C(38)	0.7097(9)	0.4584(6)	0.355(1)	5.2(3)
C(39)	0.709(1)	0.5101(7)	0.288(1)	6.0(4)
C(40)	0.604(1)	0.5270(7)	0.212(1)	7.1(4)
C(41)	0.504(1)	0.4941(7)	0.204(1)	7.0(4)
C(42)	0.507(1)	0.4420(6)	0.273(1)	5.7(4)
C(43)	0.7011(9)	0.4126(6)	0.5980(9)	4.5(3)
C(44)	0.715(1)	0.4922(6)	0.628(1)	5.6(4)
C(45)	1.222(1)	0.4682(7)	0.247(1)	6.5(4)
C(46)	0.816(1)	0.4960(8)	0.840(1)	7.1(4)
C(47)	0.196(1)	0.5851(8)	0.185(1)	8.1(5)
C(48)	0.743(1)	0.3759(7)	0.690(1)	6.1(4)
C(49)	0.4774(9)	0.3290(6)	0.4128(9)	4.5(3)
C(50)	0.4381(9)	0.3564(6)	0.495(1)	5.4(3)
C(51)	0.3294(9)	0.3317(7)	0.473(1)	6.5(4)
C(52)	0.251(1)	0.2783(8)	0.366(1)	8.1(5)
C(53)	0.286(1)	0.2512(7)	0.279(1)	7.2(5)
C(54)	0.3954(9)	0.2746(6)	0.302(1)	5.8(4)

^{a} *B* is defined in Table II.

P–Cu–P bond angle is 119.4°, which is close to the ideal value of 120°. The uncoordinated $[(Ph_3P)_3Cu^+]$ ion has been reported in $[(Ph_3P)_3Cu^+][B_9H_{12}S^-]$ on the basis of its isomorphism with the structurally characterized analogous gold complex.[9]

For the $FeCl_4^-$ anion in complex **Ia**, the iron atom is found in a distorted tetrahedral geometry. The values compare favorably with those reported[10] for the tetrachloroferrate(III) ion in $[Ph_4As^+][FeCl_4^-]$.

Molecular Structure of Ib. Figure 2 shows the structure, and Table V presents selected bond distances and bond angles for **Ib**.

An interaction between the $(Ph_3P)_3Cu^+$ and the $FeCl_4^-$ in complex **Ib** is evidenced by a small but significant elongation of the Fe–Cl(1) bond over the remaining Fe–Cl bonds. Three of the Fe–Cl bond lengths are similar in value while different from

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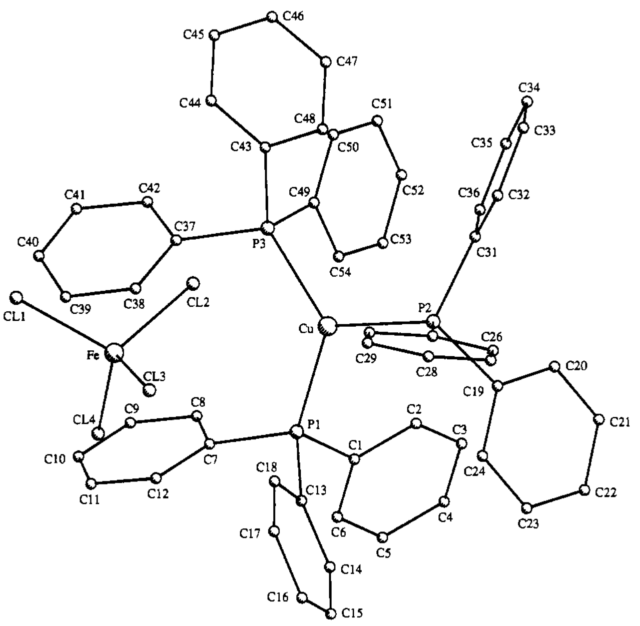

Figure 1. Molecular structure and numbering scheme for **Ia**.

Table IV. Selected Distances (Å) and Angles (deg) for **Ia**

Cu-P(1)	2.303(2)	Fe-Cl(3)	2.133(3)
Cu-P(2)	2.294(2)	Fe-Cl(4)	2.138(3)
Cu-P(3)	2.288(2)	P(1)-C(1)	1.815(5)
Fe-Cl(1)	2.171(2)	P(1)-C(7)	1.840(6)
Fe-Cl(2)	2.174(2)	P(1)-C(13)	1.830(5)
P(1)-Cu-P(2)	116.96(6)	Cl(3)-Fe-Cl(4)	113.8(2)
P(1)-Cu-P(3)	117.95(6)	Cu-P(1)-C(1)	113.7(2)
P(2)-Cu-P(3)	123.18(6)	Cu-P(1)-C(7)	120.5(2)
Cl(1)-Fe-Cl(2)	110.28(8)	Cu-P(1)-C(13)	109.1(2)
Cl(1)-Fe-Cl(3)	109.7(1)	C(1)-P(1)-C(7)	102.6(2)
Cl(1)-Fe-Cl(4)	107.5(1)	C(7)-P(1)-C(13)	103.6(2)
Cl(2)-Fe-Cl(3)	109.7(1)	C(1)-P(1)-C(13)	106.2(3)
Cl(2)-Fe-Cl(4)	105.9(1)		

Table V. Selected Distances (Å) and Bond Angles (deg) for **Ib**

Cu-P(1)	2.295(2)	Fe-Cl(2)	2.177(3)
Cu-P(2)	2.288(2)	Fe-Cl(3)	2.170(2)
Cu-P(3)	2.328(2)	Fe-Cl(4)	2.168(2)
Cu···Cl(1)	2.903(2)[a]	P(1)-C(1)	1.840(6)
Fe-Cl(1)	2.198(2)	P(1)-C(7)	1.838(7)
P(1)-Cu-P(2)	122.33(6)	Cl(2)-Fe-Cl(4)	108.2(1)
P(1)-Cu-P(3)	112.72(7)	Cl(3)-Fe-Cl(4)	109.6(1)
P(2)-Cu-P(3)	119.12(7)	Fe-Cl(1)···Cu	154.9(1)
Cl(1)-Cu-P(1)	99.83(7)	Cu-P(1)-C(1)	113.6(2)
Cl(1)-Cu-P(2)	97.94(7)	Cu-P(1)-C(7)	111.9(2)
Cl(1)-Cu-P(3)	96.38(6)	Cu-P(1)-C(13)	117.7(2)
Cl(1)-Fe-Cl(2)	106.7(1)	C(1)-P(1)-C(7)	105.1(3)
Cl(1)-Fe-Cl(3)	111.0(1)	C(1)-P(1)-C(13)	103.2(3)
Cl(1)-Fe-Cl(4)	111.0(1)	C(7)-P(1)-C(13)	104.0(3)
Cl(2)-Fe-Cl(3)	110.2(1)		

[a] Interactive distance.

the fourth; the latter [Fe-Cl(1)] being directed toward the cation is 0.026 Å larger than the mean value of the terminal Fe-Cl bonds. Distortion of the CuP_3 configuration is noted for **Ib** with the further displacement of the copper atom to a distance of 0.3232(14) Å above the plane of the three phosphorus atoms. As expected for interaction, the increased displacement of Cu is in the direction of the Cl(1) atom of the anion. Accompanying the displacement of the copper toward Cl(1) is the decrease of the mean P-Cu-P bond angle from a value of 119.4° in **Ia** to a value of 118.1° in **Ib**. The Cu-Cl(I) interaction distance in **Ib** is 2.903(2) Å. In sharp contrast, the $(Ph_3P)_3CuX$ (X = Cl, Br, I) complexes show shorter Cu-X distances (Cl, 2.335 Å; Br, 2.481 Å; I, 2.669 Å) and nearly regular tetrahedral P-Cu-P and P-Cu-X bond angles.[2c,4]

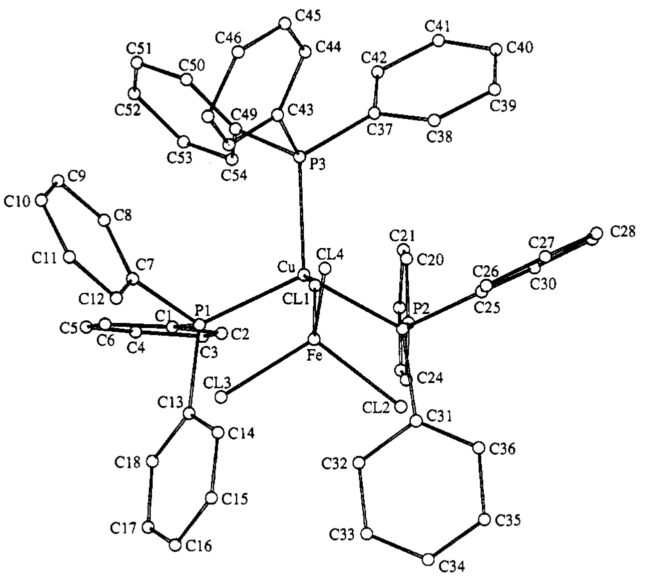

Figure 2. Molecular structure and numbering scheme for **Ib**.

The solid-state interaction between the P_3Cu cationic moiety and the tetrahloroferrate(III) anion of **Ib** appears to be much weaker than that in the corresponding BF_4^- and ClO_4^- complexes as evidenced[5,6] by a larger mean P-Cu-P bond angle (BF_4, 115.6°; ClO_4, 114.8°) and a smaller P-Cu-X mean bond angle (BF_4, 102.2°; ClO_4, 103.4°) in **Ib**. Also indicative of weaker coordination is the decreased distance of Cu from the plane of the three phosphorus atoms in **Ib**. The Cu-P_3 plane distance in **Ib** is 0.3232(14) Å, while the corresponding distance reported[5] for $(Ph_3P)_3CuBF_4$ is 0.487 Å. Experimentally, one finds that **Ib** undergoes a readily broken interaction by exposure to certain vapors[1] or heat to form **Ia** which is not noted for the related complexes.

The mean Cu-P bond length in **Ib** of 2.304 Å which is not significantly larger than the mean Cu-P distance in **Ia** (2.295 Å) does compare favorably to those values found for the weakly coordinated $(Ph_3P)_3CuBF_4$[5] (2.298 Å) and $(Ph_3P)_3CuClO_4$[6] (2.315 Å).

The $FeCl_4^-$ unit contains iron surrounded by four chlorine atoms in a mildly distorted tetrahedral geometry. The Fe-Cl bond angles range from 106.7 to 110.0° with a mean value of 109.5°. With weak anion coordination found in **Ib**, the Fe-Cl bond distances on average are lengthened from 2.154 Å in **Ia** to that of 2.178 Å in **Ib**.

A weighted best least-squares plane[11] was calculated through the atoms P(3), Cu, Cl(1), Fe, and Cl(4). Distances (Å) of these atoms from the plane are as follows: P(3), -0.042(3); Cu, 0.029(1); Cl(1), 0.064(4); Fe, -0.084(2); Cl(4), 0.034(5). Atoms P(1) and P(2) are equidistant from the plane with values of -2.006(3) and 2.007(3) Å, respectively, while atoms Cl(2) and Cl(3) are almost equidistant with values of 1.627(5) and -1.932(5) Å, respectively. $P_3CuClFeCl_3$ shows a Cu-Cl(1)-Fe angle of 154.9°. The mean Cl(1)-Cu-P angle is 98.0°.

Solid-State Conversion of Ib to Ia. Both **Ia** and **Ib** are stable indefinitely at room temperature in the solid state. Upon heating of **Ib** at 109.5-111.0 °C, a rapid conversion of **Ib** to **Ia** takes place in the solid state. The solid-state reverse conversion of **Ia** to **Ib** has not been observed upon cooling **Ia** to -196 °C for several hours.

Steric factors and electronic factors both enter into understanding the greater stability of **Ia** over **Ib**. That steric constraints are important in tris(triphenylphosphine)copper(I) complexes is well established. The Tolman cone angle[12] of 145° for triphen-

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(11) Orthonormal equation of plane: $0.6415x + 0.5661y - 0.5177z - 3.8117 = 0$. Crystallographic equation of plane: $8.4485x + 9.3541y - 10.9946z - 3.8117 = 0$.

(12) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

ylphosphine has been used to explain, for example, the behavior of some (triphenylphosphine)copper(I) complexes in solution.[13,14] Steric crowding has been described as a major determining factor in the partially staggered conformation of P_3CuFBF_3 in $(Ph_3P)_3CuBF_4$.[5]

$FeCl_3$ has strong affinity for halide ion.[15] The competition for the chloride ion between the $(Ph_3P)_3Cu^+$ cation and $FeCl_3$ favors the $FeCl_3$ as indicated by a large Cu–Cl(1) distance and only a minor distortion of the $FeCl_4^-$ anion in **Ib**. As $FeCl_3$ is a strong Lewis acid toward chloride ion, so too is BF_3 toward fluoride ion. The more weakly coordinating ability of the $FeCl_4^-$ to the $(Ph_3P)_3Cu^+$ in **Ib** over that of BF_4^- to the $(Ph_3P)_3Cu^+$ in $(Ph_3P)_3CuBF_4$ is most probably caused by the larger steric bulk of the $FeCl_4^-$ anion which is limited in reaching the sterically crowded copper atom. As with the case for BF_4^-, the smaller relative size of the ClO_4^- anion compared to $FeCl_4^-$ may be the overridding factor in the preference for ClO_4^- attaching to the tris(triphenylphosphine)copper(I) cation. Upon gentle heating of $[(CH_3CN)(PPh_3)_3Cu]ClO_4$,[16] the CH_3CN escapes and conversion to the weakly coordinated $(PPh_3)_3CuClO_4$ results.

The described structural features of **Ia** and **Ib** and the instability of **Ib** relative to **Ia** are consistent with proposing **Ib** as an isolable intermediate in the formation of **Ia** from the reaction of $(Ph_3P)_3CuCl$ and $FeCl_3$.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, hydrogen atom locations, and least-square planes and packing diagrams for **Ia** and **Ib** (44 pages). Ordering information is given on any current masthead page.

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