

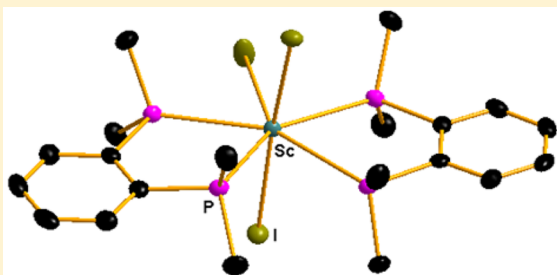
1 Rare Neutral Diphosphine Complexes of Scandium(III) and 2 Yttrium(III) Halides

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5 **S** Supporting Information

6 **ABSTRACT:** Reaction of $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ or $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$
7 (L–L) with a suspension of ScI_3 or YI_3 in MeCN solution under
8 rigorously anhydrous and oxygen-free conditions produced the highly
9 unusual complexes $[\text{ScI}_3(\text{L–L})_2]$, $[\text{YI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$, and
10 $[\text{YI}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2\text{MeCN}]$. X-ray crystal structures reveal that the
11 scandium complexes adopt seven-coordinate, pentagonal-bipyramidal
12 geometries with chelating diphosphines, while the eight-coordinate
13 $[\text{YI}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2\text{MeCN}]$ is dodecahedral. The complexes were
14 characterized by microanalysis and IR and multinuclear NMR
15 spectroscopy. Solid-state NMR data (^{45}Sc , ^{89}Y , ^{31}P) and variable-
16 temperature solution NMR data (^1H , $^{31}\text{P}\{^1\text{H}\}$, ^{45}Sc) are presented and
17 compared, leading to the conclusion that the same species are present in both the solid state and CH_2Cl_2 solution. Attempts to
18 prepare complexes with other scandium halides and with aryl diphosphines and $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$ are briefly described.



19 INTRODUCTION

20 Neutral phosphine ligands have played a key role in the
21 development of mid- and late-transition-metal coordination and
22 organometallic chemistry for the last 80 years or so.¹ More
23 recent work has shown that most p-block metals and metalloids
24 also form phosphine complexes, and there are examples with
25 nonmetal halides, including those of boron, silicon, and
26 arsenic.² As phosphines are soft σ -donor ligands, their ability
27 to complex with the hard, oxophilic metal ions of groups 1–3
28 or the lanthanides is expected to be small. Structurally
29 authenticated complexes are limited to a very small number
30 of examples: $[\text{BeCl}_2(\kappa^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2]$ ^{3a} and $[\text{Be}_2\text{Cl}_2(\mu\text{-}$
31 $\text{Cl})_2(\text{PCy}_3)_2]$ ^{3b} and our recently reported homoleptic diphos-
32 phine cations of lithium and sodium, $[\text{Li}(\text{L–L})_3][\text{Al}\{\text{OC-}$
33 $(\text{CF}_3)_3\}_4]$ and $[\text{Na}(\text{L–L})_3][\text{B}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_4]$ ($\text{L–L} =$
34 $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$, $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$).⁴ The only report of
35 complexes with scandium halides is of $[\text{ScCl}_3\text{-}$
36 $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ and $[\text{Sc}_2\text{Br}_6(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_3]$,
37 characterized only by microanalysis and IR spectroscopy,⁵
38 and there are no reports of phosphine complexes of yttrium
39 halides. The organometallic complexes $[\{(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2(\eta^1\text{-}$
40 $\text{NCMe}_3)\}(\text{PMe}_3)\text{Sc}(\mu\text{-H})]_2$ and $\{(\text{CH}_3)_2\text{Si}[(t\text{-C}_4\text{H}_9)\text{-}$
41 $\text{C}_3\text{H}_3]_2\text{Sc}(\text{PMe}_3)_2\}(\mu\text{-Te})\cdot\text{C}_6\text{H}_6$ represent extremely rare ex-
42 amples of neutral phosphine coordination to scandium.⁶ The
43 Ce(III) complex $[\text{Ce}(\text{MeC}_5\text{H}_4)_3(\text{PMe}_3)]$, obtained by reaction
44 of the thf adduct with PMe_3 in diethyl ether, has been
45 structurally characterized.^{6d}

46 Neutral phosphino groups coordinated to Sc or Y are present
47 in complexes containing anionic PNP ligands, including
48 $\{\text{N}(\text{SiMe}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2\}^-$, $\{\text{pyrrole-2,5-(CH}_2\text{PCy}_2)_2\}^-$, and $\{\text{bis-}$
49 $(2\text{-diisopropylphosphino-4-tolylamide})\}^-$ as well as related
50 P_2N_2 -donor dianionic macrocycles,⁷ and in complexes bearing

51 pendant phosphino groups on a Cp^- ring.⁸ In these cases the
52 anionic N or C centers significantly contribute to the stability of
53 the Sc/Y–P linkage. Here we report the synthesis and the first
54 detailed structural and spectroscopic data on complexes of ScI_3
55 and YI_3 with the neutral diphosphines $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ and
56 $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$ and explore whether complexes with related
57 ligands or other scandium halides are accessible.

58 EXPERIMENTAL SECTION

59 All reactions were carried out using standard Schlenk and vacuum line
60 techniques. Samples were manipulated and stored in a glovebox and
61 under a dry dinitrogen atmosphere. Dichloromethane and acetonitrile
62 were distilled over CaH_2 and diethyl ether and n -pentane from sodium
63 benzophenone ketyl. Anhydrous ScI_3 was obtained from Sigma-
64 Aldrich and YI_3 from Alfa, $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$,
65 and $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ were obtained from Strem, and all were used as
66 received. $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$ and $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$ were made by the
67 literature routes.⁹

68 IR spectra were obtained as Nujol mulls on a PerkinElmer Spectrum
69 100 spectrometer. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded in
70 solution in anhydrous CD_2Cl_2 on a Bruker AV 400 spectrometer and
71 referenced to residual solvent and external H_3PO_4 , respectively. ^{45}Sc
72 and ^{89}Y solution spectra were also recorded in the same solvent on a
73 Bruker AV 400 spectrometer.

74 Solid-state NMR experiments were performed at 14.1 T using an
75 Agilent DD2 600 MHz narrow-bore spectrometer, using 3.2 and 1.6
76 mm T3 triple-resonance probes. In all cases, samples were handled and
77 transferred into 1.6 or 3.2 mm zirconium oxide rotors using a
78 dinitrogen-filled glovebox. Unless otherwise specified, all measure-
79 ments were performed with magic-angle spinning (MAS) NMR
80 measurements under nitrogen, obtained from the boil-off of 80

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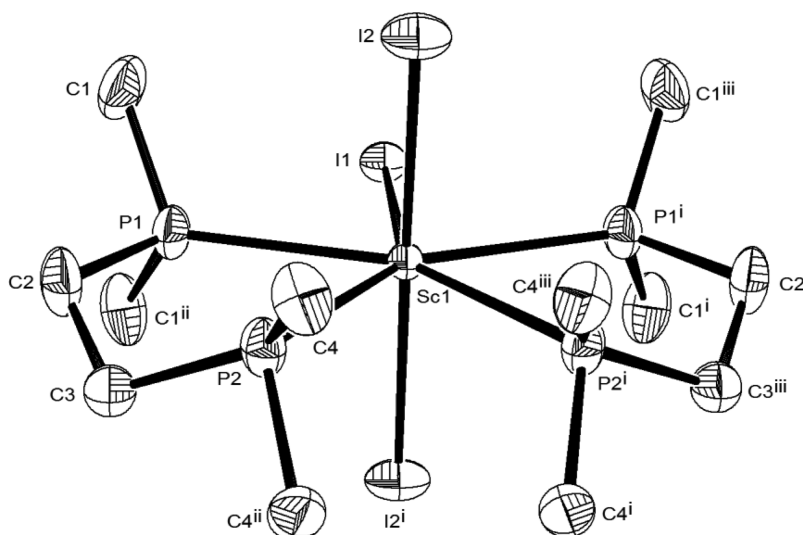


Figure 1. Structure of $[\text{ScI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ with ellipsoids drawn at the 50% level and with the disorder omitted. Selected bond lengths (Å) and angles (deg): $\text{Sc}(1)-\text{I}(1) = 3.049(2)$, $\text{Sc}(1)-\text{I}(2) = 2.7686(7)$, $\text{Sc}(1)-\text{P}(1) = 2.7881(19)$, $\text{Sc}(1)-\text{P}(2) = 2.828(2)$; $\text{I}(2)-\text{Sc}(1)-\text{I}(1) = 93.16(4)$, $\text{I}(2^i)-\text{Sc}(1)-\text{I}(2) = 173.67(7)$, $\text{I}(2)-\text{Sc}(1)-\text{P}(1) = 90.944(9)$, $\text{I}(2)-\text{Sc}(1)-\text{P}(2) = 87.49(3)$, $\text{P}(1)-\text{Sc}(1)-\text{P}(2) = 69.97(6)$, $\text{P}(1)-\text{Sc}(1)-\text{I}(1) = 72.63(5)$, $\text{P}(2)-\text{Sc}(1)-\text{P}(2^i) = 74.80(9)$. Symmetry codes: (i) $1 - x, 1.5 - y, z$; (ii) $1 - x, y, z$; (iii) $x, 1.5 - y, z$.

81 pressurized liquid nitrogen, using the spinning frequency $\nu_r = 20$ kHz.
 82 The temperature was set to 293 K and was not further calibrated to
 83 include small variations due to the sample spinning under MAS.
 84 Measurements on ^{31}P were performed with direct excitation, with a
 85 pulse delay of 3–5 min between scans, sufficient to fully relax to
 86 thermal equilibrium as verified experimentally. Measurements on ^{45}Sc
 87 were performed with direct excitation using a 1 s pulse delay, using at
 88 least two different spinning frequencies in order to identify the
 89 position of the central band. Measurements on ^{89}Y were performed
 90 using cross-polarization with 2048 scans, contact times in the range
 91 between 10 and 20 ms,¹⁰ and a 10 s pulse delay, to transfer
 92 magnetization from fast-relaxing neighboring ^1H spins in order to
 93 overcome problems with the very long relaxation time of ^{89}Y .

94 The ^{31}P , ^{45}Sc , and ^{89}Y chemical shifts were referenced to 0 ppm
 95 using 85% H_3PO_4 , $\text{Y}(\text{NO}_3)_3$, and $\text{Sc}(\text{NO}_3)_3$ (0.1 M in water adjusted
 96 to pH 1 with HNO_3), respectively.¹¹ Microanalyses were performed by
 97 London Metropolitan University.

98 **X-ray Experiments.** Data collections used a Rigaku AFC12
 99 goniometer equipped with an enhanced sensitivity (HG) Saturn724+
 100 detector mounted at the window of an FR-E+ SuperBright
 101 molybdenum ($\lambda = 0.71073$ Å) rotating anode generator with VHF
 102 Varimax optics (70 μm focus) with the crystal held at 100 K. Structure
 103 solution and refinement were performed using SHELX(S/L)97,
 104 SHELX-2013, or SHELX-2014/7 and were straightforward¹² except
 105 for some disorder in the CH_3 and CH_2 groups of the diphosphine in
 106 the structure of $[\text{ScI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$, which was satisfactorily
 107 modeled with 50:50 split occupancies. H atoms were placed in
 108 calculated positions. Details of the crystallographic parameters are
 109 given in Table S1 in the Supporting Information. CCDC reference
 110 numbers are CCDC 1479049–1479051.

111 **Complex Synthesis.** $[\text{ScI}_3(\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)_2)_2]$. To a suspension of
 112 ScI_3 (53 mg, 0.125 mmol) in anhydrous acetonitrile (5 mL) was added
 113 $\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)_2$ (55 mg, 0.27 mmol) with stirring. After 3 days when
 114 everything had dissolved, the volatiles were removed in vacuo. The
 115 white solid residue was washed with *n*-pentane to remove the excess
 116 ligand, and the solid was dried in vacuo. Yield: 98 mg, 95%. Colorless
 117 single crystals were grown by slow evaporation from an acetonitrile
 118 solution under N_2 . Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{I}_3\text{P}_4\text{Sc}$ (822.03): C, 29.2; H,
 119 3.9. Found: C, 29.2; H, 3.9. ^1H NMR (CD_2Cl_2): 298 K, 1.99 (s,
 120 [24H], Me), 7.61 (m, [4H], aromatic CH), 7.78 (m, [4H], aromatic
 121 CH); 180 K, 1.93 (s, [24H], Me), 7.62 (m, [4H], aromatic CH), 7.84
 122 (m, [4H], aromatic CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): 293 K, -20.8 [P],
 123 -25.8 [P]; 180 K, -21.6 (s). ^{45}Sc NMR (CD_2Cl_2): 293 K, $+371$ (s);
 124 180 K, $+364$ (s).

$[\text{ScI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$. To a suspension of ScI_3 (53 mg, 0.125
 125 mmol) in dry acetonitrile (5 mL) was added $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (40
 126 mg, 0.26 mmol) with stirring. After the mixture was stirred for 3 days,
 127 a completely clear solution had formed and the volatiles were then
 128 removed in vacuo. The white solid residue was washed with *n*-pentane
 129 to remove any excess ligand, and the solid was dried in vacuo. Yield: 80
 130 mg, 88%. Colorless single crystals were grown by slow evaporation
 131 from an acetonitrile solution under N_2 . Anal. Calcd for $\text{C}_{12}\text{H}_{32}\text{I}_3\text{P}_4\text{Sc}$
 132 (725.94): C, 19.8; H, 4.4. Found: C, 19.7; H, 4.4. ^1H NMR (CD_2Cl_2 ,
 133 298 K): 1.97 (s, [24H], Me), 2.33 (m, [8H], CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR
 134 (CD_2Cl_2): 293 K, -21.0 (s) ppm; 180 K, -14.9 (s), -20.2 (s). ^{45}Sc
 135 NMR (CD_2Cl_2): 293 K, $+361$ (s); 180 K, $+362$ (s).
 136

$[\text{YI}_3(\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)_2)_2(\text{CH}_3\text{CN})]$. To a suspension of YI_3 (58 mg,
 137 0.125 mmol) in dry acetonitrile (5 mL) was added $\text{o}-\text{C}_6\text{H}_4(\text{PMe}_2)_2$
 138 (54 mg, 0.27 mmol) with stirring. After 12 h all the YI_3 had dissolved
 139 to give a clear solution, and hence the volatiles were removed in vacuo.
 140 The white solid residue was washed with *n*-pentane to remove any
 141 excess ligand, and the solid was dried in vacuo. Yield: 92 mg, 90%.
 142 Colorless single crystals were grown by slow evaporation from an
 143 acetonitrile solution under N_2 . Anal. Calcd for $\text{C}_{22}\text{H}_{35}\text{I}_3\text{N}_1\text{P}_4\text{Y}$
 144 (907.03): C, 29.1; H, 3.8; N, 1.5. Found: C, 29.2; H, 3.7; N, 1.5.
 145 ^1H NMR (CD_2Cl_2): 298 K, 1.85 (s, [24H], Me), 2.01 (s, CH_3CN),
 146 7.55 (m, [4H], aromatic CH), 7.81 (m, [4H], aromatic CH); 180 K,
 147 1.78 (s), 1.95 (s), 7.50 (m), 7.90 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): 293
 148 K, -38.3 (d, $^1J_{\text{PY}} = 37$ Hz); 180 K, -37.5 (d, $^1J_{\text{PY}} = 37$ Hz). ^{89}Y NMR
 149 (CD_2Cl_2 , 293 K): not observed. IR (Nujol/ cm^{-1}): 2313, 2276
 150 (MeCN).
 151

$[\text{YI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$. $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (40 mg, 0.26 mmol)
 152 was added to a suspension of YI_3 (58 mg, 0.125 mmol) in anhydrous
 153 acetonitrile (5 mL) with stirring. After 12 h a completely clear solution
 154 was obtained and the volatiles were then removed in vacuo. The white
 155 solid residue was washed with *n*-pentane to remove any excess ligand,
 156 and the solid was dried in vacuo. Yield: 85 mg, 88%. Anal. Calcd for
 157 $\text{C}_{12}\text{H}_{32}\text{I}_3\text{P}_4\text{Y}$ (769.89): C, 18.7; H, 4.1. Found: C, 18.8; H, 4.6. ^1H
 158 NMR (CD_2Cl_2): 298 K, 1.53 (s, [24H], Me), 1.85 (m, [8H], CH_2);
 159 190 K, 1.47 (d, $^2J_{\text{PH}} = 19$ Hz), 1.81 (br). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2):
 160 293 K, -28.7 (s); 190 K, -23.3 (s), -30.8 (s). ^{89}Y NMR (CD_2Cl_2 ,
 161 293 K): not observed.
 162

RESULTS AND DISCUSSION

Complexes of ScI_3 and YI_3 . Our initial studies used
 164 anhydrous scandium(III) and yttrium(III) iodides as the metal
 165 source, since previous work with lanthanide complexes of O/S-
 166

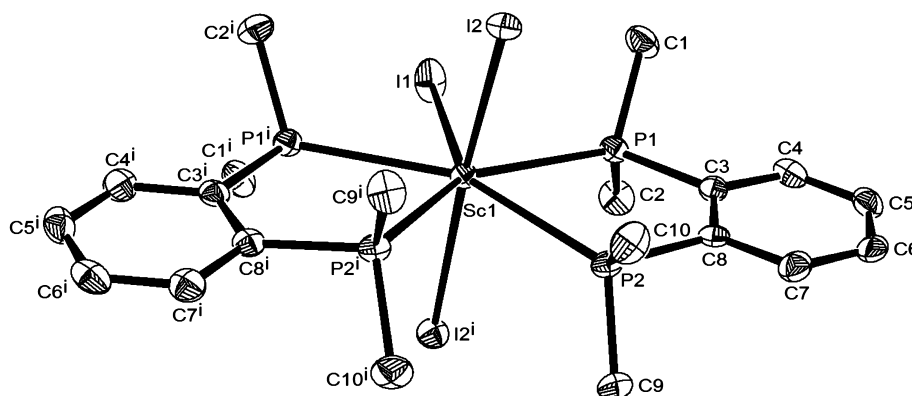


Figure 2. Structure of $[\text{ScI}_3\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]$ with ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): $\text{Sc}(1)\text{--I}(1) = 2.9226(13)$, $\text{Sc}(1)\text{--I}(2) = 2.8046(4)$, $\text{Sc}(1)\text{--P}(1) = 2.7767(11)$, $\text{Sc}(1)\text{--P}(2) = 2.8627(14)$; $\text{P}(1)\text{--Sc}(1)\text{--I}(2) = 95.03(3)$, $\text{P}(1)\text{--Sc}(1)\text{--I}(2^i) = 88.55(3)$, $\text{I}(2)\text{--Sc}(1)\text{--I}(2^i) = 168.59(5)$, $\text{P}(1)\text{--Sc}(1)\text{--P}(2) = 69.72(3)$, $\text{I}(2)\text{--Sc}(1)\text{--P}(2) = 85.25(3)$, $\text{I}(2)\text{--Sc}(1)\text{--P}(2^i) = 85.85(3)$, $\text{P}(1)\text{--Sc}(1)\text{--I}(1) = 71.71(3)$, $\text{I}(2)\text{--Sc}(1)\text{--I}(1) = 95.70(2)$, $\text{P}(2)\text{--Sc}(1)\text{--P}(2^i) = 77.31(5)$. Symmetry codes: (i) $x, y, -z$.

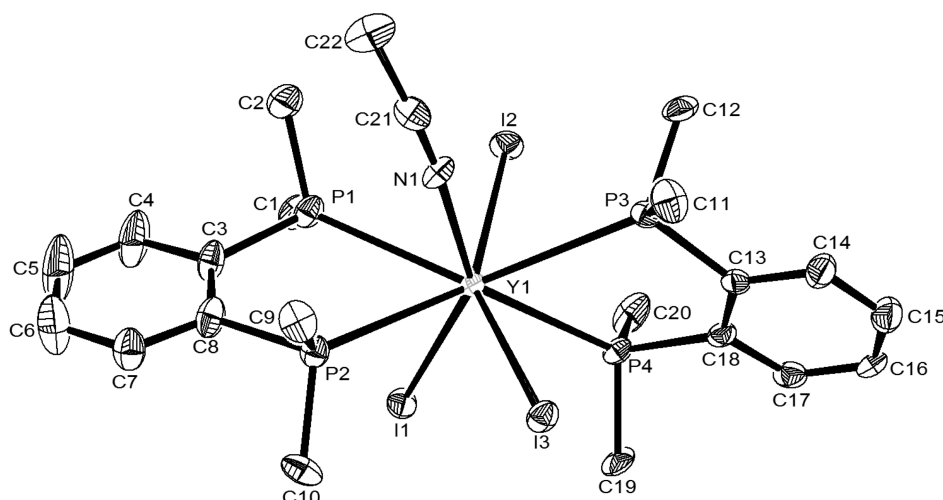


Figure 3. Structure of $[\text{YI}_3\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2(\text{CH}_3\text{CN})]$ with ellipsoids at the 50% level. Selected bond lengths (Å) and angles (deg): $\text{Y}(1)\text{--I}(1) = 3.0197(12)$, $\text{Y}(1)\text{--I}(2) = 3.0257(13)$, $\text{Y}(1)\text{--I}(3) = 3.0610(15)$, $\text{Y}(1)\text{--N}(1) = 2.428(9)$, $\text{Y}(1)\text{--P}(4) = 2.975(3)$, $\text{Y}(1)\text{--P}(2) = 3.019(3)$, $\text{Y}(1)\text{--P}(1) = 3.023(3)$, $\text{Y}(1)\text{--P}(3) = 3.045(2)$; $\text{N}(1)\text{--Y}(1)\text{--P}(2) = 74.0(2)$, $\text{N}(1)\text{--Y}(1)\text{--P}(1) = 75.0(2)$, $\text{N}(1)\text{--Y}(1)\text{--I}(2) = 85.5(2)$, $\text{N}(1)\text{--Y}(1)\text{--P}(3) = 73.5(2)$, $\text{P}(2)\text{--Y}(1)\text{--P}(1) = 65.87(8)$, $\text{I}(1)\text{--Y}(1)\text{--P}(1) = 74.04(6)$, $\text{P}(4)\text{--Y}(1)\text{--I}(2) = 80.19(6)$, $\text{I}(1)\text{--Y}(1)\text{--I}(2) = 99.52(3)$, $\text{P}(1)\text{--Y}(1)\text{--I}(2) = 71.27(6)$, $\text{P}(4)\text{--Y}(1)\text{--P}(3) = 65.92(7)$, $\text{I}(2)\text{--Y}(1)\text{--P}(3) = 76.39(5)$, $\text{N}(1)\text{--Y}(1)\text{--I}(3) = 93.9(2)$, $\text{P}(4)\text{--Y}(1)\text{--I}(3) = 79.72(6)$, $\text{P}(2)\text{--Y}(1)\text{--I}(3) = 73.17(6)$, $\text{I}(1)\text{--Y}(1)\text{--I}(3) = 98.86(4)$, $\text{P}(3)\text{--Y}(1)\text{--I}(3) = 73.18(6)$.

167 and O/Se-donor macrocycles,¹³ the trithia macrocycle [9]-
168 aneS₃,¹⁴ and zirconium(IV) and hafnium(IV) diphosphine
169 complexes¹⁵ found that the iodides were better suited for
170 forming complexes of soft donor groups on the hard oxophilic
171 metal centers in comparison to the lighter halides. In addition,
172 the resulting complexes were often more soluble in weakly
173 coordinating solvents such as chlorocarbons, facilitating
174 spectroscopic studies of their properties. This probably largely
175 reflects the lower lattice energies of the metal iodides. The
176 reactions of anhydrous ScI_3 with $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ or o-
177 $\text{C}_6\text{H}_4(\text{PMe}_2)_2$ (L–L) in a 1:2 molar ratio in anhydrous MeCN
178 produced clear solutions, from which the colorless $[\text{ScI}_3(\text{L-}$
179 $\text{L})_2]$ complexes were obtained after removing the solvent and
180 washing the residue with *n*-pentane. The same products were
181 isolated using a 1:3 M:L–L ratio. There is no evidence for
182 incorporation of MeCN in the IR spectra of the scandium
183 complexes. The synthesis and manipulation of these complexes
184 must be conducted with rigorous exclusion of air and moisture,
185 since water immediately displaces the diphosphine, while trace
186 dioxygen produces phosphine oxides. Formation of the latter is

possibly promoted by the Lewis acidic center.¹⁶ Similar
reactions using YI_3 produced $[\text{YI}_3\{\text{o-}$
 $\text{C}_6\text{H}_4(\text{PMe}_2)_2\}_2(\text{CH}_3\text{CN})]$ and $[\text{YI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$
(with no evidence for associated MeCN in the latter). Attempts
to isolate diphosphine complexes with the related o-
 $\text{C}_6\text{H}_4(\text{PPh}_2)_2$ and $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2$ or with the diarsine o-
 $\text{C}_6\text{H}_4(\text{AsMe}_2)_2$ using similar conditions were unsuccessful, and
we comment on the case of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ below.

Given the paucity of Sc(III) and Y(III) complexes with
phosphine ligands in the literature, it was imperative to obtain
crystallographic authentication for the new complexes. Crystals
suitable for X-ray analysis were obtained for $[\text{ScI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$,
 $[\text{ScI}_3\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]$, and $[\text{YI}_3\{\text{o-C}_6\text{H}_4(\text{PMe}_2)_2\}_2(\text{CH}_3\text{CN})]$,
by slow evaporation of acetonitrile solutions under nitrogen in a glovebox.
The structure of $[\text{ScI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ (Figure 1) shows a
seven-coordinate scandium center with a distorted-pentagonal-
bipyramidal coordination geometry, composed of a strictly
planar P_4I pentagon and two axial iodide ligands. The latter
have short Sc–I distances of 2.7686(7) Å, while the in-plane

$d(\text{Sc}-\text{I})$ is markedly longer, at 3.049(2) Å. These distances may be compared with the $d(\text{Sc}-\text{I})$ of 2.915(2) Å in the eight-coordinate $[\text{ScI}_2(18\text{aneO}_4\text{S}_2)]\text{I}$ ($[18]\text{aneO}_4\text{S}_2 = 1,4,10,13$ -tetraoxa-7,16-dithiacyclooctadecane), which has a *cis*- ScI_2 unit.¹³ The $d(\text{Sc}-\text{P})$ values are 2.7881(19) and 2.828(2) Å, and the chelate angle, $\angle\text{P}-\text{Sc}-\text{P}$, is acute at 69.97(6)°. The $d(\text{Sc}-\text{P})$ values are similar to those observed^{7a} in the complexes containing the PNP donor ligand $[\text{Sc}(\eta^5\text{-Cp})\text{X}\{\text{N}(\text{SiMe}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2\}]$ ($\text{X} = \text{Ph}, \text{Cl}$; 2.804(2)–2.836(2) Å) and organometallic scandium complexes with PMe_3 .^{6b,c}

The structure of $[\text{ScI}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]$ (Figure 2) is also pentagonal bipyramidal, but with a slightly more distorted geometry, probably reflecting the more rigid backbone in the diphosphine, although the $d(\text{Sc}-\text{I})$ and $d(\text{Sc}-\text{P})$ values are very similar to those in $[\text{ScI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ above.

Repeated attempts to obtain crystals of $[\text{YI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ were unsuccessful, but crystals of the acetonitrile adduct $[\text{YI}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2(\text{CH}_3\text{CN})]$ were obtained (Figure 3). The structure shows an eight-coordinate Y center with a $\text{P}_4\text{I}_3\text{N}$ donor set. The geometry was shown to be regular dodecahedral by identifying the plane of best fit which encompassed the metal center and four of the eight coordinating atoms and then calculating the dihedral angle between this plane and the plane defined by the metal center and the remaining four coordinating atoms (P1, P2, I2, and I3 form one plane and P3, P4, I1, and N1 form the second plane). The value obtained was 89.8°, very close to the 90° expected for an ideal dodecahedron, whereas for an ideal square antiprism this angle would be 77.4°.¹⁷

The $d(\text{Y}-\text{P})$ values of 2.975(3)–3.045(2) Å are similar to those found in yttrium complexes with the anionic PNP-donor ligands,^{7c,e} while the $d(\text{Y}-\text{I})$ values of 3.0197(12)–3.0610(15) Å are similar to those in $[\text{YI}_2(\text{thf})_5][\text{YI}_4(\text{thf})_2]$ (2.9685(6)–3.0181(6) Å).¹⁸

The IR spectrum of $[\text{YI}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2(\text{CH}_3\text{CN})]$ shows two bands at 2313 and 2276 cm^{-1} , assigned as $\nu(\text{CN})$ and $\nu(\text{C}-\text{C}) + \delta(\text{CH}_3)$ of the coordinated nitrile, of similar intensity due to Fermi resonance.¹⁹ CH_3CN itself (liquid film) exhibits bands at 2293 and 2252 cm^{-1} . It is notable that for the other three complexes the IR spectra show no CH_3CN present and there is no evidence for phosphine oxides in any of the complexes.

Solid-State and Solution NMR Spectra. Solid-state NMR experiments were performed on these complexes under a dinitrogen atmosphere, to probe both the phosphorus and the metal site, and the results are shown in Figure 4 and Table 1.

The solid-state ^{45}Sc NMR spectra of both complexes were broad singlets with very similar chemical shifts (see Figure 4b and Table 1, as well as Figure S1 in the Supporting Information for the assignment of the center band of the ^{45}Sc spinning sideband envelope). The complexes are extremely readily hydrolyzed in solution, but ^{45}Sc NMR spectra were obtained from freshly prepared and rigorously anhydrous solutions in CH_2Cl_2 . The chemical shifts are slightly different from those obtained for the solids. This provides very good evidence that the same structures are retained in solution. We were unable to observe ^{89}Y NMR resonances from CH_2Cl_2 solutions of either yttrium complex at 295 or 180 K. Despite its 100% abundance and $I = 1/2$, ^{89}Y is a difficult nucleus to observe in solution, with a low resonance frequency, poor receptivity, and very long T_1 values, and often exhibits some lability of the neutral ligands. The modest solubility of the present complexes is also unhelpful in the present cases. However, informative ^{89}Y

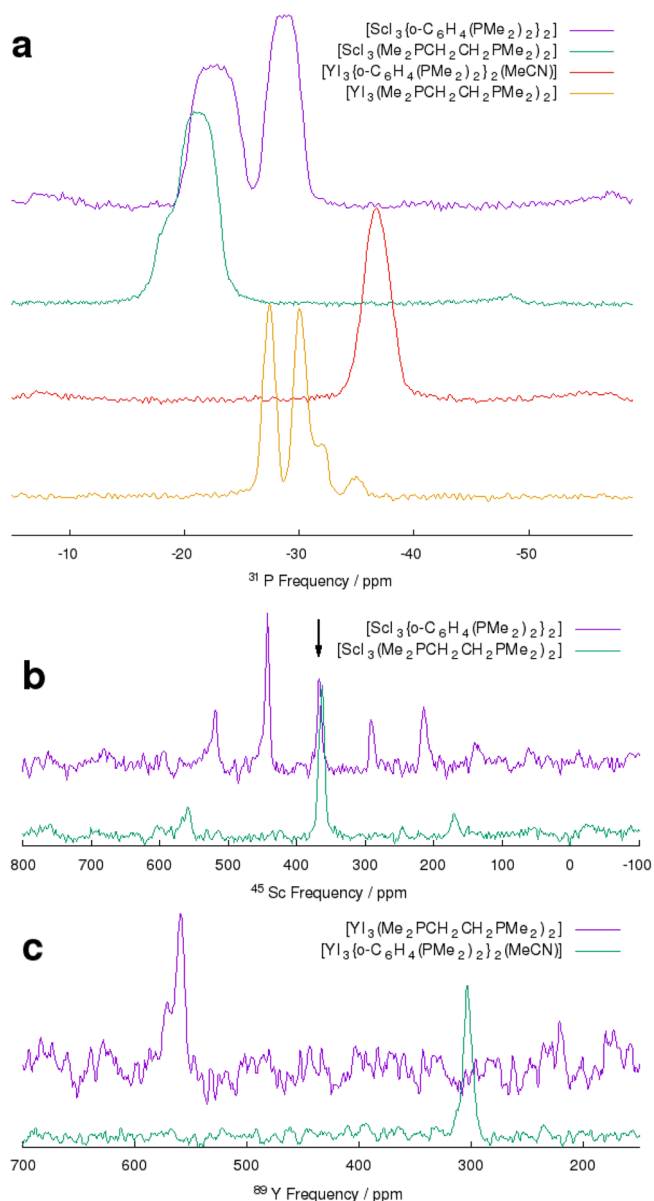


Figure 4. Experimental solid-state NMR spectra at 14.1 T under inert conditions for all samples and with MAS at 20 kHz unless otherwise specified. Peak positions are summarized in Table 1. (a) ^{31}P spectra acquired with direct excitation. (b) ^{45}Sc spectra, acquired with the following spin rates: $[\text{ScI}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]$ has $\nu_r = 11.1$ kHz, and $[\text{ScI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ has $\nu_r = 28$ kHz, with the center-band position near 360 ppm for both samples indicated by an arrow. (c) ^{89}Y spectra recorded with cross-polarization. One main site is clearly visible for both compounds.

MAS NMR spectra were obtained (Figure 4c) using cross-polarization for the powdered solids, which partially overcomes the limitations due to poor receptivity and slow relaxation. The $[\text{YI}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2(\text{CH}_3\text{CN})]$ clearly shows a single peak at 304 ppm, while for $[\text{YI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ the main resonance is at 559 ppm, possibly with a small shoulder to high frequency.

The ^{31}P MAS NMR spectrum of $[\text{ScI}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]$ (Figure 4a) shows two well-resolved broad signals at −22.6 and −28.6 ppm of similar intensity, which are likely to originate from the inequivalent P environments seen in the crystal structure. The ^{31}P MAS NMR spectrum of $[\text{ScI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$

Table 1. Chemical Shifts (in ppm) As Obtained from Solution and Solid-State NMR Measurements at Ambient Temperature

	[ScI ₃ { <i>o</i> -C ₆ H ₄ (PMe ₂) ₂ }] ₂	[ScI ₃ (Me ₂ PCH ₂ CH ₂ PMe ₂) ₂]	[YI ₃ {(<i>o</i> -C ₆ H ₄ (PMe ₂) ₂) ₂ (CH ₃ CN)}]	[YI ₃ (Me ₂ PCH ₂ CH ₂ PMe ₂) ₂]
³¹ P, solid	−22.6, −28.6	−21.15 (main) −19.0 (shoulder)	−36.7	−27.4, −30.0 ^a
³¹ P, soln	−20.8, −25.8	−21	−38.3	−28.7
⁴⁵ Sc, solid	+366	+362		
⁴⁵ Sc, soln	+371	+361		
⁸⁹ Y, solid			304	559 (main) 570 (shoulder)

^aMinor peaks at −31.9 and −35 ppm are attributed to a small amount of impurity, most likely resulting from decomposition during data acquisition.

[ScI₃(Me₂PCH₂CH₂PMe₂)₂] shows a broad peak at −21.1 ppm, with a shoulder at ∼−19 ppm.

For comparison, the solution ³¹P{¹H} NMR spectrum of [ScI₃{*o*-C₆H₄(PMe₂)₂}]₂ shows two broad and overlapping resonances of similar intensity at −20.8 and −25.8 ppm, suggesting that the inequivalence of the P centers is retained in solution. When the solution is cooled to 180 K, this changes to a single broad and asymmetric resonance at −21.6 ppm. The original spectrum is restored on warming the sample back to ambient temperature. In contrast, the ³¹P{¹H} NMR solution spectrum of [ScI₃(Me₂PCH₂CH₂PMe₂)₂] at 295 K is a very broad (*w*_{1/2} = 885 Hz) singlet, but at 180 K two resonances of 1:1 intensity at −14.9 and −20.1 ppm are present, indicative of inequivalent phosphorus centers. The single resonance at room temperature in the latter probably indicates some fluxionality (solution lability)—this is consistent with the complex bearing the more flexible Me₂PCH₂CH₂PMe₂ (cf. that containing *o*-C₆H₄(PMe₂)₂).

Moving to the yttrium complexes, ³¹P MAS NMR spectroscopy of [YI₃(Me₂PCH₂CH₂PMe₂)₂] exhibits two resonances of equal intensity (Table 1) at −27.4 and −30.0 ppm, consistent with the structure being analogous to the scandium complex. The ³¹P{¹H} NMR solution spectrum of this complex displays a singlet at 295 K (−28.7 ppm), but, like the scandium analogue, at 180 K two singlets of equal intensity were present (−23.3, −30.8 ppm), attributed to inequivalent phosphorus centers.

The ³¹P MAS NMR spectrum of [YI₃{*o*-C₆H₄(PMe₂)₂}]₂·(MeCN) shows a broad resonance at −36.7 ppm, with no observable coupling to ⁸⁹Y (the coupling constant determined from the solution spectrum discussed below is smaller than the line width in the solid sample). In contrast, the solution ³¹P{¹H} NMR spectra of this complex show a doublet (*J*_{YP} = 35 Hz) at both 295 and 190 K, which we attribute to coupling to the *I* = 1/2 ⁸⁹Y nucleus.

Other Scandium Phosphine Complexes. The reaction of [ScCl₃(MeCN)₃] with *o*-C₆H₄(PMe₂)₂ in anhydrous MeCN gave a white solid that was insoluble in, or decomposed by, most donor solvents. In CH₂Cl₂ solution (in which it is only sparingly soluble) it exhibited NMR spectra with δ(⁴⁵Sc) +277 and δ(³¹P) as a very broad resonance with ill-defined couplings at δ −22.6, along with some uncoordinated diphosphine (δ −52). Addition of [Me₄N]Cl to a CH₂Cl₂ solution of [ScI₃{*o*-C₆H₄(PMe₂)₂}]₂ gave a white precipitate, but the supernatant solution showed ⁴⁵Sc and ³¹P{¹H} NMR resonances similar to those observed in the sample made from [ScCl₃(MeCN)₃] with *o*-C₆H₄(PMe₂)₂. The common product is probably [ScCl₃{*o*-C₆H₄(PMe₂)₂}]₂, but due to its limited stability and very poor solubility in chlorocarbons, we were unable to isolate a pure sample. Similar treatment of a CH₂Cl₂ solution of [ScI₃{*o*-C₆H₄(PMe₂)₂}]₂ with [Me₄N]Br gave a solution which

exhibited multiple ³¹P NMR resonances in the range δ −19 to −27 and ⁴⁵Sc resonances at δ −359, −335, −313 and −293; we attribute the resonance at δ −359 to unchanged [ScI₃{*o*-C₆H₄(PMe₂)₂}]₂ and the other three resonances to [ScI_{3−*n*}, Br_{*n*}{*o*-C₆H₄(PMe₂)₂}]₂ (*n* = 1–3). This is consistent with the hard Lewis acidic Sc(III) center showing a clear preference for chloride over iodide ligands, while the discrimination is less between Br and I. In contrast, addition of [Me₄N]F to a CH₂Cl₂ solution of [ScI₃{*o*-C₆H₄(PMe₂)₂}]₂ instantly precipitates ScF₃ and liberates the diphosphine.²⁰}

We also reacted ScCl₃ and ScI₃ with Ph₂PCH₂CH₂PPh₂ under conditions similar to those described by Greenwood and Tranter:⁵ i.e., reaction over several days in a large volume of anhydrous CHCl₃ containing ∼1% thf, followed by filtration to remove the residual insoluble material. The filtrate was taken to dryness and washed with large amounts of hot *n*-pentane. The products were white solids with highly variable analytical composition. They were partially soluble in CH₂Cl₂, the solutions revealing ³¹P{¹H} NMR resonances due to Ph₂PCH₂CH₂PPh₂ and [Ph₂PCH₂CH₂PPh₂H]⁺ with wide variation between the relative amounts in different batches. Notably, neither the NMR spectra nor the IR spectra showed evidence for phosphine oxides. Although the evidence is indicative rather than proof, it seems that the reported ScX₃–Ph₂PCH₂CH₂PPh₂ “complexes”⁵ were most likely mixtures of ScX₃, diphosphine, and phosphonium haloscanate salts. We note that phosphonium or sulfonium halometalates are commonly formed under anhydrous conditions, as well as, or instead of, metal complexes of the neutral ligand by reactions of phosphines or thioethers with very hard Lewis acids.²¹

CONCLUSIONS

The preparations of the first authenticated diphosphine complexes of scandium and yttrium trihalides have been achieved and the products characterized both in the solid state via both X-ray crystallographic studies and solid-state ³¹P, ⁴⁵Sc and ⁸⁹Y NMR measurements and in solution by variable-temperature multinuclear NMR spectroscopy. The chemical shift variations on the scandium site as a function of the diphosphine ligand are negligible, consistent with the two phosphines having similar σ-donor properties. When we look at the Y complexes, there is a significant variation in the ⁸⁹Y NMR shifts, probably originating from the extra MeCN ligand present and the resulting differences in the donor environment at yttrium and coordination geometries present. Ab initio and experimental data on ⁸⁹Y clearly highlight the problem of relating observed shifts with particular patterns in ligands or specific donor–acceptor interactions present.²²

Evidence is also presented for the existence of complexes of *o*-C₆H₄(PMe₂)₂ with ScCl₃ and ScBr₃, although these were not

isolated in a pure form. Other diphosphines with sterically small alkyl substituents will likely also form analogous complexes. The early report of scandium complexes of the much more weakly donating $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ligand has been shown to almost certainly be erroneous. Complexes with the softer and less strongly σ donating aryl diphosphine $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ or the diarsine $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$ do not appear to form.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02268.

Crystallographic data for $[\text{ScI}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2]$ (CCDC 1479049) (CIF)
 Crystallographic data for $[\text{YI}_3\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2(\text{MeCN})]$ (CCDC 1479050) (CIF)
 Crystallographic data for $[\text{ScI}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ (CCDC 1479051) (CIF)
 Spectra supporting the assignment of the scandium resonances in the MAS NMR data and data for the X-ray data collection (PDF)

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Notes

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