

complete listings of bond lengths and angles, the cyclic voltammogram of **1**, **2**, **3**, and **4** (15 pages); listings of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Use of the 2,4,6-Tris(trifluoromethyl)phenyl Ligand To Stabilize Indium–Indium and Gallium–Gallium Bonds

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Several solid-state structures involve short Ga–Ga and In–In contacts;¹ however, examples of organometallic molecules that feature such bonds are rare.^{1,2} Necessarily, these compounds imply formal oxidation states of +1 or +2 on the part of the group 13 element. As part of our ongoing interest in low oxidation state main group chemistry, we have recently explored the utility of the 2,4,6-(CF₃)₃C₆H₂ (R_F) ligand in the context of the heavier group 13 elements. Although this ligand was discovered over 40 years ago,³ it is only recently that its useful combination of steric bulk, electronegativity, and *o*-CF₃ interactions has become recognized.⁴ Herein we report (i) the first R_F derivatives of gallium and indium,⁵ (ii) the capability of the R_F ligand to stabilize Ga(+2) and In(+2) derivatives with M–M bonds, and (iii) unusual coordination geometries for In(+2) and In(+3).

The In(+2) dimer (R_F)₂InIn(R_F)₂ (**1**) was isolated in 25% yield from the reaction of equimolar quantities of InCl and R_FLi in Et₂O solution at –78 °C.⁶ The implied disproportionation 2In(+1) →

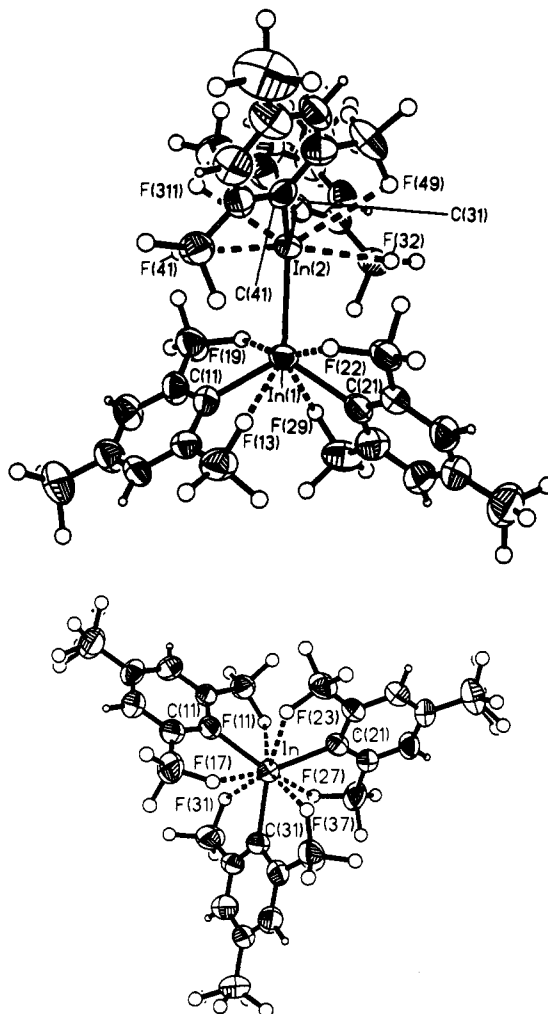


Figure 1. ORTEP views of **1** (above) and **2** (below). Important intramolecular distances (Å) and angles (deg): **1**, In(1)–In(2), 2.744(2), In(1)–C(11), 2.213(16), In(1)–C(21), 2.220(13), In(2)–C(31), 2.216(12), In(2)–C(41), 2.195(15), In(1)–F(13), 2.885(10), In(1)–F(19), 2.801(10), In(1)–F(22), 2.837(10), In(1)–F(29), 2.840(11), In(2)–F(32), 2.848(8), In(2)–F(41), 2.866(8), In(2)–F(49), 2.957(13), In(2)–F(31), 2.816(10), C(11)–In(1)–C(21), 116.1(5), In(2)–In(1)–C(11), 121.8(3), In(2)–In(1)–C(21), 122.1(4), C(31)–In(2)–C(41), 117.6(5), In(1)–In(2)–C(31), 119.2(4), In(1)–In(2)–C(41), 123.2(3); **2**, In–C(11), 2.182(8), In–C(21), 2.189(6), In–C(31), 2.197(9), In–F(11), 2.772(7), In–F(17), 2.775(6), In–F(23), 2.776(6), In–F(27), 2.798(5), In–F(31), 2.734(7), In–F(37), 2.727(7), C(11)–In–C(21), 121.3(3), C(11)–In–C(31), 118.8(3), C(21)–In–C(31), 119.9(3).

In(0) + In(+2) is unusual; however, it was also possible to isolate traces of the In(+3) species (R_F)₃In (**2**) from the reaction mixture. Compound **2** however, can be prepared more satisfactorily (41% yield) by treatment of InI₃ with 3.0 equiv of R_FLi in Et₂O at –78 °C.⁶ Initial identification of **1** and **2** was made on the basis of CI mass spectral data.⁸ Both **1** and **2** exhibit molecular ions; the CIMS of **2** also features a prominent peak corresponding to (R_F)₂In⁺. The ¹⁹F and ¹H NMR data indicate that there is only one type of R_F ligand environment in each compound. Structural details for **1** and **2** were provided by X-ray analyses.⁹

(7) In solution. **1** undergoes slow decomposition to **2** and indium metal.

(8) HRMS (CI): **1** for C₃₆H₈F₁₆In₂ (M⁺) calcd 1353.8129, found 1353.8136; **2** for C₃₇H₈F₁₇In (M⁺) calcd 957.9077, found 957.9070; **3** for C₃₆H₈F₁₆Ga (M⁺) calcd 1261.8563, found 1261.8561; **4** for C₃₇H₈F₁₇Ga (M⁺) calcd 911.9294, found 911.9283. ¹H NMR (300.15 MHz, THF/C₆D₆, 295 K, TMS ext): **1**, δ 8.63 (s, 8 H, *m*-H); **2**, δ 8.28 (s, 6 H, *m*-H); **3**, δ 7.89 (s, 8 H, *m*-H); **4**, δ 8.84 (s, 6 H, *m*-H). ¹⁹F NMR (282.41 MHz, THF/C₆D₆, 295 K, CFCl₃ ext): **1**, δ –59.09 (s, 12 F, *p*-CF₃), –55.47 (s, 24 F, *o*-CF₃); **2**, δ –63.68 (s, 9 F, *p*-CF₃), –60.65 (s, 18 F, *o*-CF₃); **3**, δ –58.90 (s, 12 F, *p*-CF₃), –53.15 (s, 24 F, *o*-CF₃); **4**, δ –63.97 (s, 9 F, *p*-CF₃), –58.42 (s, 18 F, *o*-CF₃).

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(5) The compound R_FGaCl₂ has been mentioned in a review article;⁴ however, no further details are available. We have prepared both R_FGaCl and (R_F)₂GaCl and found the former to be a chloride-bridged dimer in the solid state by X-ray crystallography (orthorhombic, *P*_{bcn}, *a* = 9.569(2) Å, *b* = 16.608(3) Å, *c* = 16.787(1) Å, and *Z* = 4).

(6) Syntheses of **1–4**: Under dry nitrogen, a solution of 12.4 mmol of R_FLi[†] in 30 mL of Et₂O was added via cannula to a slurry of 1.86 g (12.4 mmol) of InCl in 30 mL of Et₂O at –78 °C. Upon warming to –10 °C, the reaction mixture changed color from light green to red-brown. Further warming to 25 °C resulted in the precipitation of some indium metal (0.18 g). Concentration and cooling (–20 °C) of the filtrate afforded 1.05 g (25% yield) of pale orange crystalline **1** (mp 164 °C dec). The reaction of 7.0 mmol of R_FLi[†] in 30 mL of Et₂O with 1.11 g (2.3 mmol) of InI₃ in 20 mL of Et₂O at –78 °C resulted in 0.9 g (41% yield) of pale orange crystalline **2** (mp 184 °C dec). Compound **3** was prepared by two routes. Using the method described above for **1** (route 1), a solution of 0.3 g (0.7 mmol) of Ga₂Cl₂·2dioxane¹⁶ in 10 mL of Et₂O was treated with a solution of 3.2 mmol of R_FLi[†] in 20 mL of Et₂O at –78 °C. The yield of pale yellow microcrystalline **3** (mp 136–138 °C) was 45%. Anal. Calcd for C₃₆H₈F₁₆Ga₂: C, 34.21; H, 0.64. Found: C, 33.91; H, 0.59. Alternatively, **3** was prepared (route 2) by stirring a hexane solution of (R_F)₂GaCl¹⁶ with 1 equiv of Na/K alloy at 25 °C. The spectroscopic properties of **3** prepared by routes 1 and 2 were identical. Pale yellow microcrystalline **4** (mp 179–181 °C) was prepared in 35% yield via the reaction of a solution of 1.3 g (7.4 mmol) of GaCl₃ in 30 mL of Et₂O with 22.4 mmol of R_FLi[†] in 30 mL of Et₂O. Anal. Calcd for C₃₇H₈F₁₇Ga: C, 35.52; H, 0.66. Found: C, 35.15; H, 0.81.

The solid states of **1** and **2** comprise individual molecules (Figure 1), and there are no short intermolecular contacts. The In(+2) dimer, **1**, features an In–In bond of length 2.744(2) Å. This distance is comparable to those reported for systems with short indium–indium contacts¹ and consistent with a bond order of unity. Within experimental error, both indium centers adopt trigonal planar geometries with the C–In–C angles $\sim 3^\circ$ smaller than the others. The dihedral angle between the C–In–C planes is 94.1(5)°, presumably as a consequence of minimizing steric repulsions between *o*-CF₃ groups and maximizing intramolecular In...F interactions (vide infra). As in the case of B₂R₄ derivatives,¹⁰ there is no evidence for π -type interaction between the group 13 elements. Eight intramolecular In...F contacts (one for each *o*-CF₃ group) fall in the range 2.801(10)–2.957(13) Å and are thus shorter than the sum of van der Waals radii (3.40 Å).¹¹ However, the average In...F contact of 2.856(13) Å is considerably longer than the sum of covalent radii (2.16 Å)¹¹ or the In–F bond distances in [InF₆]²⁻ and InF₃ which range from 2.03 to 2.06 Å.¹² Nevertheless, as in the cases of (R_F)₂Sn¹³ and (R_F)₂Pb,¹⁴ these interactions may contribute to the stability of **1**. The geometry of each InF₄ secondary coordination sphere of **1** is distorted tetrahedral.

The InC₃ geometry of monomeric **2** is trigonal planar. The observation that the average In–C bond distance in **2** (2.189(9) Å) is somewhat longer than that in the unfluorinated analogue Mes₃In (2.168(5) Å)¹⁵ is presumably due to the larger steric demands of the R_F substituent. Compound **2** adopts a propeller-type conformation in which the twist angles of the aryl rings with respect to the InC₃ plane are very similar (49.4, 49.5, and 54.8° for rings 1, 2, and 3, respectively). In contrast, (Mes)₃In features a conformation in which one ring is essentially perpendicular to the InC₃ plane. Such differences may result from packing forces. However, the six (trigonal prismatic) intramolecular In...F contacts from the *o*-CF₃ groups (average distance 2.762(7) Å) may also play a role in the conformational preference of **2**. Although C–H...In interactions could not be confirmed crystallographically in (Mes)₃In, low-temperature ¹³C NMR data are consistent with agostic behavior. In the case of **2**, no changes were observed in the ¹⁹F spectra in the temperature range –80 to 30 °C.

The analogous R_F derivatives of gallium have also been prepared. The Ga(+2) dimer (R_F)₂GaGa(R_F)₂ (**3**) was synthesized in 45% yield via the reaction of Ga₂Cl₄·2 dioxane¹⁶ with 4 equiv of R_FLi in Et₂O solution at –78 °C. Likewise, the reaction of GaCl₃ with 3 equiv of R_FLi in Et₂O solution at –78 °C afforded a 35% yield of (R_F)₃Ga (**4**). Compound **3** can also be prepared by reductive coupling of (R_F)₂GaCl¹⁵ with Na/K alloy in hexane solution. The CIMS and NMR spectral data⁷ for **3** and **4** are very similar to those of **1** and **2**, respectively, and a preliminary X-ray crystallographic study indicates that **2** and **4** are isomorphous.

In summary, the R_F ligand is capable of supporting Ga–Ga and In–In bonds as well as permitting the isolation of monomeric triaryl derivatives. As noted by Barron et al.,¹⁷ the high nucleophilicity and low basicity of the R_F anion minimize reduction at the metal center. Moreover, electrostatic repulsions for the CF₃ groups inhibit oligomerization.¹⁸

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Note Added in Proof. For an interesting indium(I) complex of the R_FO ligand, see: Scholz, M.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1383.

Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters for **1** and **2** (19 pages); listings of observed and calculated structure factors for **1** and **2** (43 pages). Ordering information is given on any current masthead page.

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Elemental White Phosphorus as a Radical Trap: A New and General Route to Phosphonic Acids

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We report that white phosphorus is a remarkably efficient trap for carbon radicals. This provides a new and convenient route for the conversion of carboxylic acids into the corresponding phosphonic acids. The latter often show interesting biological activity.¹

The bond angles in white phosphorus (P₄) are unusually small (60°), and the phosphorus–phosphorus bonds are bent as in cyclopropane.² On this basis, one could argue that this highly strained molecule might be chemically very reactive, as stated in most chemistry textbooks.³ Surprisingly, we have found that many organic compounds in CH₂Cl₂–CS₂ under dry argon at room temperature are not reduced by white phosphorus with or without

(9) Crystal data for **1** (C₁₆H₉F₁₆In₂): triclinic, space group *P* $\bar{1}$ with *a* = 11.647(2) Å, *b* = 12.166(2) Å, *c* = 16.861(3) Å, α = 73.12(3)°, β = 77.83(3)°, γ = 74.40(3)°, *V* = 2179.1(6) Å³, *Z* = 2, *d*_{calc} = 2.064 g cm⁻³, μ (Mo K α) = 1.242 mm⁻¹. Crystal data for **2** (C₂₇H₉F₂₇In): *a* = 9.010(2) Å, *b* = 12.920(3) Å, *c* = 15.391(3) Å, α = 103.72(3)°, β = 102.66(3)°, γ = 105.00(3)°, *V* = 1604.3(6) Å³, *Z* = 2, *d*_{calc} = 1.983 g cm⁻³, μ (Mo K α) = 0.914 mm⁻¹. Totals of 7607 and 4184 independent reflections were collected for **1** and **2**, respectively, on a Siemens R3m/V diffractometer at 298 K using graphite-monochromated Mo K α radiation (λ = 0.71069 Å). Both structures were solved by direct methods and refined by full-matrix least squares (SHELXTL PLUS). The final *R* values were 0.0796 and 0.0556 for **1** and **2**, respectively.

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