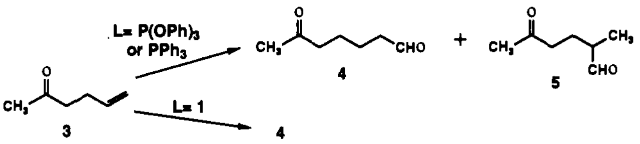
latter two ligands produced aldehydes **4** and **5** in ratios of 3:1 and 2.4:1, respectively. In contrast, when the bis-organophosphite ligand **1** was used under identical reaction conditions, **4** was the only observable product as determined by ^{1}H NMR.



In summary, we have shown that the bis-organophosphite rhodium(I) complex prepared from **1** can effect the regioselective hydroformylation of terminal olefins under mild reaction conditions to produce a variety of ω-functionalized aldehydes. That this catalyst system operates under significantly milder conditions, demonstrates notably increased regioselectivity, and is tolerant of a variety of potentially reactive functional groups bodes well for its use in organic synthesis. We are currently investigating the extension of this methodology to the syntheses of various acyclic, carbocyclic, and heterocyclic systems.

Acknowledgment. We thank Union Carbide for financial support. Preliminary work was funded, in part, by the National Institutes of Health. G.D.C. thanks the National Science Foundation for a graduate fellowship. S.L.B. acknowledges additional support as a Fellow of the Alfred P. Sloan Foundation and a Camille & Henry Dreyfus Teacher-Scholar. We thank Dr. Chang Byon for carrying out some preliminary work and Dr. James Babin of Union Carbide for technical advice and stimulating discussions.

Supplementary Material Available: Experimental section containing the preparations and spectroscopic and analytical characterization of compounds (6 pages). Ordering information is given on any current masthead page.

Syntheses, Properties, and Crystal Structures of Thiolate-Bridged Ruthenium Complexes $[Ru(\mu\text{-}SPh)(S_2CNMe_2)(CO)(PPh_3)]_2(NO_3)_n$ (*n* = 0, 4) and Their Novel Electrochemical One-Step Four-Electron Redox Reactions

Masaki Kawano, Hiroyuki Uemura, Takehide Watanabe, and Kazuko Matsumoto*

Department of Chemistry, Waseda University
Tokyo 169, Japan

Received August 27, 1992

Multielectron redox reactions in biological and catalytic chemistry have been continuously attractive topics.[1] Our ultimate goal is to design multielectron-transfer reagents for the activation of inactive molecules such as N_2 and RCN. In general, one-electron-transfer reactions are widely known in natural metalloenzymes and synthetic metal complexes, but one-step two-electron-transfer reactions have been found only in several transition-metal complexes.[2] Little is known about one-step four-electron-transfer reactions, although such process is important, e.g., in reduction of O_2 to H_2O in fuel cells.[3] We have synthesized electron-rich binuclear Ru(II,II) complexes and their oxidized forms with unusually high oxidation state Ru(IV,IV), $[Ru(\mu\text{-}SR)(S_2CNMe_2)(CO)(PPh_3)]_2(NO_3)_n$ (R = Ph, Et; *n* = 0, 4). The compound with R = Ph has been found to exhibit unprecedented reversible one-step 4e redox reaction corresponding to Ru(II,II)/Ru(IV,IV).

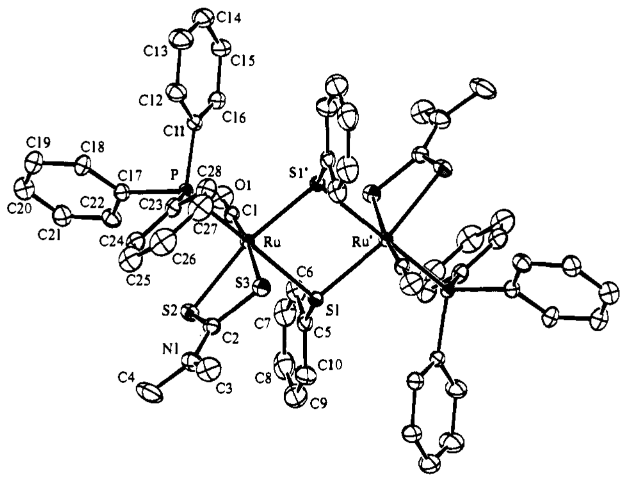


Figure 1. Molecular structure of $[Ru(\mu\text{-}SPh)(S_2CNMe_2)(CO)(PPh_3)]_2\cdot CH_2Cl_2$ (H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ru–Ru′, 3.683(1); Ru–S1, 2.458(1); Ru-S1′, 2.413(1); Ru–S2, 2.409(1); Ru–S3, 2.469(1); Ru–C1, 1.844(5); Ru–P, 2.326(1); C1–O1, 1.148(6); C2–N1, 1.319(6); S1–Ru–S1′, 81.80(4); Ru–S1–Ru′, 98.21(4); S2–Ru–S3, 71.61(5).

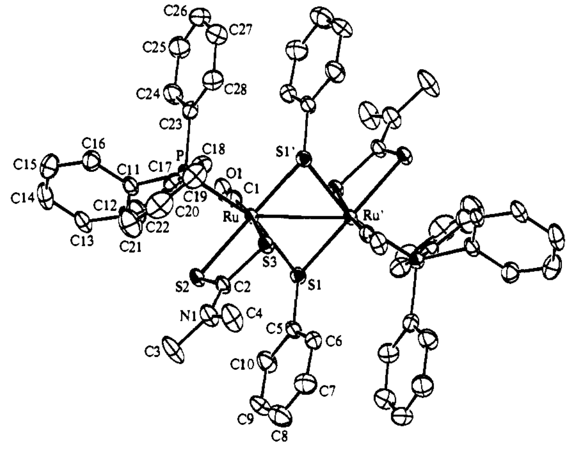


Figure 2. Molecular structure of $[Ru(\mu\text{-}SPh)(S_2CNMe_2)(CO)(PPh_3)]_2^{4+}$ (H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Ru–Ru′, 2.876(2); Ru–S1, 2.405(3); Ru–S1′, 2.310(3); Ru–S2, 2.404(3); Ru–S3, 2.425(3); Ru–C1, 1.891(10); Ru–P, 2.409(3); C1–O1, 1.145(10); C2–N1, 1.297(11); S1–Ru–S1′, 104.83(9); Ru–S1–Ru′, 75.17(8); S2–Ru–S3, 72.0(1).

$RuH(S_2CNMe_2)(CO)(PPh_3)_2$[4] (1.0 g) was reacted with excess RSH (R = Ph (1.5 mL), Et (5 mL)) in 50 mL of benzene (65 °C) for 2 h (R = Ph) or 24 h (R = Et) under nitrogen with H_2 evolution to produce suspensions of yellow powders. The suspensions were filtered, and $[Ru(\mu\text{-}SR)(S_2CNMe_2)(CO)(PPh_3)]_2$ (R = Ph (**1**)[5], Et (**2**)[6]) were obtained as yellow powders which

---

[1] (a) Nakamura, A.; Ueyama, N. *Adv. Inorg. Chem.* **1989**, *44*, 39. (b) Chang, I. J.; Nocera, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 4901. (c) Eisenberg, R.; Hendrickson, D. E. *Adv. Catal.* **1979**, *28*, 79. (d) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69*, 1990.

[2] (a) $[Rh_2(dimen)_4]^{2+}$ (dimen = 1,8-diisocyanomethane): Hill, M. G.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 1429. (b) $[Pt_2^{III}(NH_3)_4(C_5H_4NO)_2(NO_3)_2]^{2+}$: Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2605. (c) $[Mo_2^{II}(CO)_8(SR)_2]^{2-}$ (R = Ph, *t*-Bu): Zhuang, B.; McDonald, J. W.; Schultz, F. A.; Newton, W. E. *Organometallics* **1984**, *3*, 943. (d) $[Fe_2^{I}(PPh_2)_2(CO)_6]^{2}$: Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146. (e) *trans*-$(O)_2Re^V(py\text{-}X)_4^+$ (py-X = substituted pyridine), *cis*-$(O)_2Re^V(bpy\text{-}Y_2)(py\text{-}X)_2^+$ (bpy-Y = doubly substituted 2,2′-bipyridine ligand): Ram, M. S.; Jones, L. M.; Ward, H. J.; Wong, Y.-H.; Johnson, C. S.; Subramanian, P.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 2928.

[3] (a) Yeager, B. *Electrochim. Acta* **1984**, *29*, 1527. (b) Collman, J. P.; Kim, K. *J. Am. Chem. Soc.* **1986**, *108*, 7847.

[4] Critchlow, P. B.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1367–1372.

[5] Anal. Calcd for $C_{57}Cl_2H_{54}N_2O_2P_2Ru_2S_6$ (MW = 1326.42): C, 51.62; H, 4.10; N, 2.11. Found: C, 51.22; H, 4.49; N, 2.14. IR ν(CO) = 1940, 1916; ν(CN) = 1516 cm^{-1} (KBr). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 85% H_3PO_4 as the external standard) 47.6 ppm. The ^{31}P NMR spectrum for the component soluble in benzene is observed at 45.7 ppm. UV–Vis (CH_2Cl_2) 445(1080), 328 (sh) (22 800), 274 (sh) nm (51 800 M^{-1} cm^{-1}).

0002-7863/93/1515-2068$04.00/0

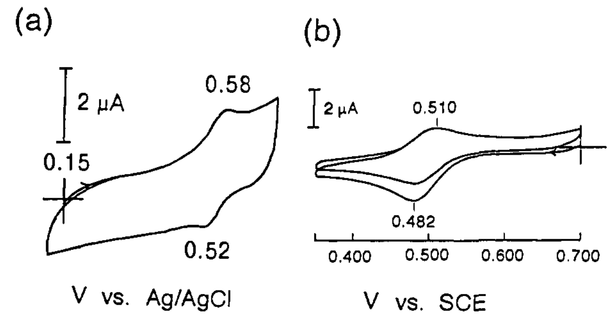
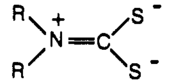


Figure 3. Cyclic voltammograms of $[Ru(\mu\text{-SPh})(S_2CNMe_2)(CO)(PPh_3)]_2$ [**1**] (a) in $CH_3CN + CH_2Cl_2$ (8:2)–0.1 M $n\text{-}Bu_4NClO_4$; scan rate = 20 mV s^{-1}; $F_c^{0/+}(\Delta E)$ = 0.47 V (80 mV) and of $[Ru(\mu\text{-SPh})(S_2CNMe_2)(CO)(PPh_3)]_2(NO_3)_4$ [**3**] (b) in CH_3CN –0.37 M $n\text{-}Bu_4NClO_4$; scan rate = 20 mV s^{-1}; $F_c^{0/+}(\Delta E)$ = 0.430 V (59 mV); Pt working and counter electrodes.

could be recrystallized from CH_2Cl_2/ether in 22% and 28% yields, respectively. The reactions of **1** (0.5 g) or **2** (0.5 g) with 2 mL of nitric acid (13 M) in 20 mL of acetonitrile at room temperature for 3 min gave reddish-brown solutions. Ether (30 mL) was added to the solutions, and $[Ru(\mu\text{-SR})(S_2CNMe_2)(CO)(PPh_3)]_2(NO_3)_4$ (R = Ph (**3**)[7], Et (**4**)[8]) were obtained as reddish-brown microcrystals in 80% and 70% yields, respectively. The acetonitrile solutions of **3** and **4** are not stable, and the reddish-brown solutions gradually become pale yellow after dissolution under N_2. Ruthenium(IV) thiolate complexes which have been characterized by X-ray crystallography are rare, e.g., $Ru(S_2CNEt_2)_3Cl$[9], $Ru(S_2CNMe_2)_3I_3$,[10] $Ru(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4L$ (L = CO, acetonitrile),[11] and $Ru(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4$.[12]

Although **1**[13] and **3**[14] have the same planar Ru_2S_2 core structure (Figures 1 and 2), a remarkable structural difference is observed between their Ru–Ru bond distances (**1**, 3.683(1) and **3**, 2.876(2) Å). Apparently a metal–metal bond (32e dimer with formal bond order of 2) is formed in **3**. The Ru–Ru bond distance is somewhat longer than that found in $[Cp^*Ru^{III}H(\mu\text{-S-}i\text{-Pr})_2Ru^{III}Cp^*H]$ (2.784(5) Å),[15] in which the Ru_2S_2 core is not planar but has a butterfly structure. In fact, the Ru–Ru bond length of **3** may correspond to a bond order of about 1, if compared to the Ru–Ru distances with a half bond ($[Cp^*Ru^{II}(\mu\text{-S-}i\text{-Pr})_3Ru^{III}Cp^*]$, 2.968(2) Å),[15] with a single bond ($[Cp^*Ru^{III}(\mu\text{-SPh})_3Ru^{III}Cp^*]Cl$, 2.630(1) Å),[16] and without a Ru–Ru bond ($[(Me_2PhP)_3Ru^{II}(\mu\text{-SH})_3Ru^{II}(SH)(PMe_2Ph)_2]$, 3.371(3) Å;[17]). The distances of Ru–P and Ru–CO in **3** are longer than those in **1**, which indicates decreased π-back-donation from $Ru(t_{2g})$ to $P(\pi)$ and $CO(\pi^*)$ in **3**. This fact is supported by the increased CO band in the IR spectra of **3**.[5,7] The unusually high oxidation state of Ru(IV) in **3** is stabilized by the following factors: (1) the significant contribution of the ligand resonance form (shown below) which can strongly donate electrons to metals,[18] (2) the donation of lone-pair



electrons from S(3p) to Ru(d), and (3) the formation of a metal–metal bond. The distance of Ru–S1′ in **3** is 0.1 Å shorter than that in **1** due to pπ–dπ bonding and also to the increased Ru oxidation number. Similarly short Ru–S distances and CO high frequencies are observed in $Ru^{IV}(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4L$ (L = CO and CH_3CN).[11]

Redox reactions of many dithiocarbamate complexes have been studied in considerable detail.[19] The dithiocarbamate-bridged dimer $[Ru_2(S_2CNEt_2)_5]^+$ shows four consecutive one-electron-transfer steps in acetonitrile as follows: Ru(II,II)/Ru(II,III), –1.11 V; Ru(II,III)/Ru(III,III), –0.58 V; and Ru(III,III)/Ru(III,IV), 0.98 V vs SCE.[20] The triply bridged ruthenium dimer $[Cp^*Ru(\mu\text{-SPh})_3RuCp^*]$ shows three redox waves in THF at Ru(II,II)/Ru(II,III), –1.50 V; Ru(II,III)/Ru(III,III), –0.65 V; and Ru(III,III)/Ru(III,IV) (probably), 0.71 V vs $F_c^{0/+}$.[15] In contrast to these complexes, compound **1** shows a reversible one-step 4e redox reaction. The cyclic voltammetry of compounds **1** and **3** shows a single reversible redox wave at 0.55 V vs Ag/AgCl (ΔE = 60 mV)[21a] and at 0.496 V vs SCE (ΔE = 28 mV),[21b] respectively, both of which correspond to an identical redox couple Ru(II,II)/Ru(IV,IV) (Figure 3). The coulometry of **1** at 0.8 V indicated that 3.76 electrons are consumed in the oxidation of **1**. Compounds **2** and **4**, on the other hand, show two consecutive reversible two-electron redox waves at 0.37 V (ΔE = 90 mV) and 0.52 V (ΔE = 90 mV) vs SCE assignable to $[\mathbf{2}]^{0/2+}$ and $[\mathbf{2}]^{2+/4+}$, respectively.[22]

The 4-electron oxidations of **1** and **2** associated with a metal–metal bond formation are reminiscent of the one-step two-electron reactions of $[Mo_2(CO)_8(SR)_2]^{2-}$ and $[Fe_2(PPh_2)_2(CO)_6]^{2-}$, which also form metal–metal bondings on oxidation to satisfy the 18-electron rule.[2c,d] Compound **1** is the first example in any metal complex that exhibits one-step four-electron oxidation followed by a metal–metal bond formation. Compounds **1** and **2** also offer a notable class of compounds in which the electron number of the simultaneous electron transfer can be varied by slight difference of the bridging ligand.

Acknowledgment. Financial support by Grant-in-Aids for Scientific Research on Priority Area of "Activation of Small Molecules" (04241225) from the Ministry of Education, Science, and Culture, Japan is gratefully acknowledged.

Supplementary Material Available: Details of the X-ray crystal structure analyses of **1** and **3** including atomic coordinates and

---

(6) Anal. Calcd for $C_{48}H_{52}N_2O_2P_2Ru_2S_6$ (MW = 1145.40): C, 50.33; H, 4.58; N, 2.45. Found: C, 50.04; H, 4.64; N, 2.35. IR ν(CO) = 1928; ν(CN) = 1512 cm^{-1} (KBr). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 85% H_3PO_4 as the external standard) 45.3 ppm. The ^{31}P NMR spectrum for the component soluble in benzene is observed at 40.9 ppm. UV–Vis (CH_2Cl_2) 429 (854), 329 (21 500), 266 nm (39 600 M^{-1} cm^{-1}).

(7) Anal. Calcd for $C_{56}H_{52}N_6O_{14}P_2Ru_2S_6$ (MW = 1489.51): C, 45.16; H, 3.52; N, 5.64. Found: C, 45.56; H, 3.68; N, 5.70. IR ν(CO) = 2020 (acetonitrile), ν(CN) = 1554 cm^{-1} (KBr). UV–Vis (acetonitrile) 608 (sh) (2800), 382 (13 800), 334 (23 700), 279 nm (49 100 M^{-1} cm^{-1}).

(8) Anal. Calcd for $C_{48}H_{52}N_6O_{14}P_2Ru_2S_6$ (MW = 1393.42): C, 41.38; H, 3.76; N, 6.03. Found: C, 41.17; H, 3.85; N, 5.98. IR ν(CO) = 2024 (acetonitrile); ν(CN) = 1558 cm^{-1} (KBr). UV–Vis (acetonitrile) 545 (1890), 394 (sh) (9700), 326 (33 000), 273 nm (61 600 M^{-1} cm^{-1}).

(9) Given, K. W.; Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1977**, *15*, 3152–3156.

(10) Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1977**, *16*, 488–491.

(11) (a) Millar, M. M.; O'Sullivan, T.; de Vries, N.; Koch, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 3714–3715. (b) Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* **1983**, *105*, 3362–3363.

(12) Soong, S.-L.; Hain. J. H., Jr.; Millar, M.; Koch, S. A. *Organometallics* **1988**, *7*, 556–557.

(13) Crystal data for $\mathbf{1}\cdot CH_2Cl_2$ at 23 °C: monoclinic, space group $P2_1/c$, a = 13.884(2) Å, b = 15.845(2) Å, c = 14.207(2) Å, β = 113.00(1)°, Z = 2, ρ_{calc} = 1.53 g cm^{-1}, μ = 9.14 cm^{-1}. A total of 7328 reflections were collected in the range of 2° < 2θ < 55° (±h,k,l). Of these, 6076 were unique, and 4609 with $F_o > 5.00\sigma(F_o)$ were used in the structure solution. $R(F)$ = 0.044, $R(F_w)$ = 0.048 ($w = 1/(\sigma(F)^2 + 0.001\,222F^2)$).

(14) Crystal data for **3** at 23 °C: monoclinic, space group $C2/c$, a = 24.973(5) Å, b = 12.412(1) Å, c = 19.902(3) Å, β = 90.54(1)°, Z = 4, ρ_{calc} = 1.60 g cm^{-1}, μ = 7.97 cm^{-1}. A total of 6008 reflections were collected in the range of 4° < 2θ < 50° (±h,k,l). Of these, 4514 were unique, and 3141 with $F_o > 3.00\sigma(F_o)$ were used in the structure solution. $R(F)$ = 0.070, $R(F_w)$ = 0.055 ($w = 1/(\sigma(F)^2 + 0.000\,150F^2)$).

(15) Dev, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1990**, *29*, 4797–4801.

(16) Dev, S.; Imagawa, K.; Mizobe, Y.; Cheng, G.; Wakatsuki, Y.; Yamazaki, H.; Hidai, M. *Organometallics* **1989**, *8*, 1232–1237.

(17) Osakada, K.; Yamamoto, T.; Yamamoto, A.; Takenaka, A.; Sasada, Y. *Inorg. Chim. Acta* **1985**, *105*, L9–L10.

(18) (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233; **1979**, *26*, 301. (b) Burns, R. P.; McCullough, F. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1980**, *23*, 211–280.

(19) (a) Bond, A. M. *Coord. Chem. Rev.* **1984**, *54*, 23–98. (b) Van Gaal, H. L. M.; Van Der Linder, J. G. M. *Coord. Chem. Rev.* **1982**, *47*, 41–54.

(20) Mattson, B. M.; Heiman, J. R.; Pignolet, L. H. *Inorg. Chem.* **1976**, *15*, 564–571.

(21) (a) $\Delta E = E_{pa} - E_{pc}$; Pt plate (working electrode); Pt wire (counter electrode); scan rate = 100 mV s^{-1}; $F_c^{0/+}$ = 0.47 V (ΔE = 80 mV) in acetonitrile + CH_2Cl_2 (2:8)–0.1 M $n\text{-}Bu_4NClO_4$. (b) Scan rate = 20 mV s^{-1}; $F_c^{0/+}$ = 0.430 V (ΔE = 59 mV) in acetonitrile–0.37 M $n\text{-}Bu_4NClO_4$.

(22) Scan rate = 100 mV s^{-1}; $F_c^{0/+}$ = 0.51 V (ΔE = 120 mV) in CH_2Cl_2–0.1 M $n\text{-}Bu_4NClO_4$.

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

Rodney D. Schluter,[†] Alan H. Cowley,*[,†] David A. Atwood,[†] Richard A. Jones,*[,†] Marcus R. Bond,[‡] and Carl J. Carrano[‡]

Department of Chemistry and Biochemistry
The University of Texas at Austin
Austin, Texas 78712
Department of Chemistry
Southwest Texas State University
San Marcos, Texas 78666

Received September 4, 1992

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-$(CF_3)_3C_6H_2$ (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-CF_3 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).

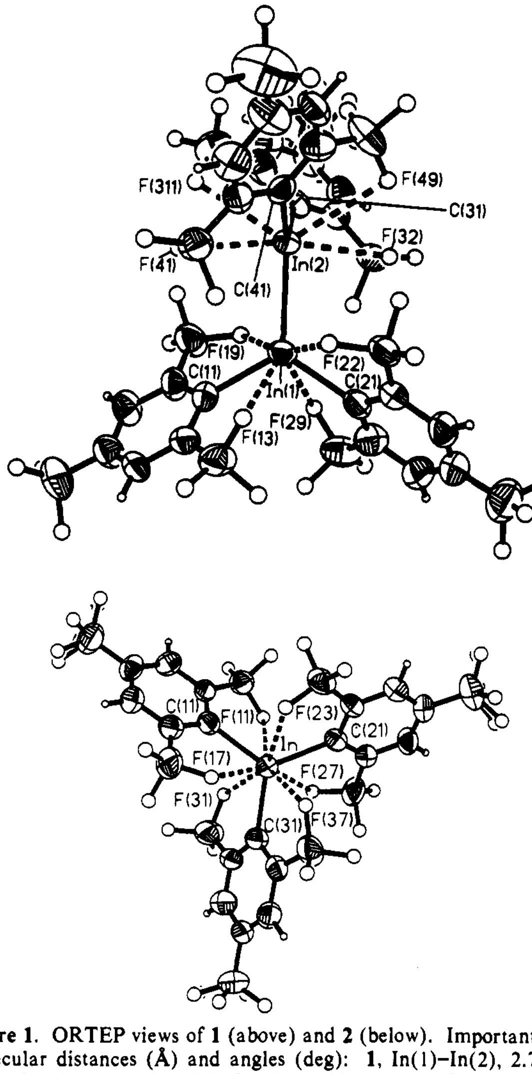


Figure 1. ORTEP views of **1** (above) and **2** (below). Important intramolecular distances (Å) and angles (deg): **1**, In(1)–In(2), 2.744(2), In(1)–C(11) 2.213(16), In(1)–C(21) 2.220(13), In(2)–C(31) 2.216(12), In(2)–C(41) 2.195(15), In(1)···F(13) 2.885(10), In(1)···F(19) 2.801(10), In(1)···F(22) 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(311) 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).

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 Et_2O solution at −78 °C.[6] The implied disproportionation 2In(+1) → 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 InI_3 with 3.0 equiv of R_FLi in Et_2O 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 ^{19}F 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]

[†] The University of Texas at Austin.

[‡] Southwest Texas State University.

(1) (a) Janiak, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 5924. (b) Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289. (c) Uhl, W.; Layh, M.; Hiller, W. *Ibid.* **1989**, *368*, 139.

(2) (a) Beachley, O. T., Jr.; Pazik, J. C.; Glassman, T. E.; Churchill, M. R.; Fettinger, J. C.; Blom, R. *Organometallics* **1988**, *7*, 1051. (b) Beachley, O. T., Jr.; Blom, R.; Churchill, M. R.; Faegri, K., Jr.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346. (c) Beachley, O. T., Jr.; Churchill, M. R.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *J. Am. Chem. Soc.* **1986**, *108*, 4666. (d) Schumann, H.; Janiak, C.; Gorlitz, F.; Loebel, J.; Dietrich, A. *J. Organomet. Chem.* **1989**, *363*, 243.

(3) McBee, E. T.; Sanford, R. A. *J. Am. Chem. Soc.* **1950**, *72*, 5574.

(4) Edelmann, F. T. *Comments Inorg. Chem.* **1992**, *12*, 259.

(5) The compound R_FGaCl_2 has been mentioned in a review article;[4] however, no further details are available. We have prepared both R_FGaCl_2 and $(R_F)_2GaCl$ and found the former to be a chloride-bridged dimer in the solid state by X-ray crystallography (orthorhombic, P_{bnm}, 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[4] in 30 mL of Et_2O was added via cannula to a slurry of 1.86 g (12.4 mmol) of InCl in 30 mL of Et_2O 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[4] in 30 mL of Et_2O with 1.11 g (2.3 mmol) of InI_3 in 20 mL of Et_2O 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 $Ga_2Cl_4{\cdot}2dioxane$[16] in 10 mL of Et_2O was treated with a solution of 3.2 mmol of R_FLi[4] in 20 mL of Et_2O at −78 °C. The yield of pale yellow microcrystalline **3** (mp 136–138 °C) was 45%. Anal. Calcd for $C_{36}H_8F_{36}Ga_2$: 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 $(R_F)_2GaCl$[5] 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 $GaCl_3$ in 30 mL of Et_2O with 22.4 mmol of R_FLi[4] in 30 mL of Et_2O. Anal. Calcd for $C_{27}H_6F_{27}Ga$: C, 35.52; H, 0.66. Found: C, 35.15; H, 0.81.

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

(8) HRMS (CI): **1** for $C_{36}H_8F_{36}In_2$ (M^-) calcd 1353.8129, found 1353.8136; **2** for $C_{27}H_6F_{27}In$ (M^-) calcd 957.9077, found 957.9070; **3** for $C_{36}H_8F_{36}Ga_2$ (M^-) calcd 1261.8563, found 1261.8561; **4** for $C_{27}H_6F_{27}Ga$ (M^-) calcd 911.9294, found 911.9283. ^1H NMR (300.15 MHz, THF/C_6D_6, 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). ^{19}F NMR (282.41 MHz, THF/C_6D_6, 295 K, $CFCl_3$ ext): **1**, δ −59.09 (s, 12 F, *p*-CF_3), −55.47 (s, 24 F, *o*-CF_3); **2**, δ −63.68 (s, 9 F, *p*-CF_3), −60.65 (s, 18 F, *o*-CF_3); **3**, δ −58.90 (s, 12 F, *p*-CF_3), −53.15 (s, 24 F, *o*-CF_3); **4**, δ −63.97 (s, 9 F, *p*-CF_3), −58.42 (s, 18 F, *o*-CF_3).

0002-7863/93/1515-2070$04.00/0