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Cumulene Complexes

Stabilization of Tetrafluorobutatriene by Complex Formation**

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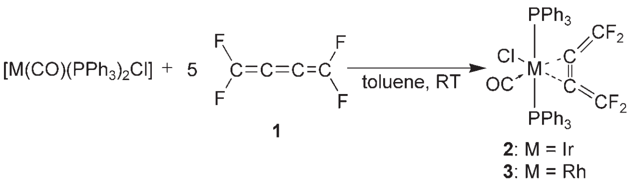
Dedicated to Professor Neil Bartlett on the occasion of his 75th birthday

1,1,4,4-Tetrafluorobutatriene (**1**) was first synthesized by Martin and Sharkey in 1959 and was characterized by IR and ^{19}F NMR spectroscopy.[1] Later, Raman and PE spectroscopic data were added.[2] The compound is very unstable: it polymerizes even at −85 °C and is reported to explode violently on warming to −5 °C or contact with air. These properties precluded further investigations, limiting the known chemistry of **1** to a few derivatives, which were also prepared by Martin and Sharkey by addition of bromine and chlorine and by oxidation.[1]

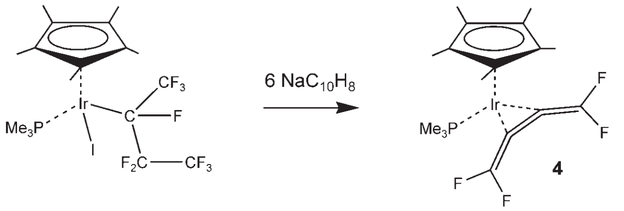
After development of a more efficient synthesis of 1,1,4,4-tetrafluorobutatriene, we were able to determine its crystal structure and charge density by high-resolution X-ray diffraction.[3] Handling the triene is quite challenging. Once prepared, it can be transferred only by condensation at reduced pressure and must be stored at −196 °C. These precautions have so far prevented explosions as well as polymerization of the substance. Since compound **1** decomposes even in absolute solvents within a few hours, further reactions or characterization involving solutions must be conducted immediately after its preparation.

The reaction of Vaska's complex ([Ir(CO)(PPh$_3$)$_2$Cl])[5] in anhydrous toluene with 3–5 equiv of **1** yielded **2**, the first transition-metal complex prepared directly from the free cumulene. The rhodium analogue also reacted with **1**, yielding the 2,3-η^2-triene complex **3** (Scheme 1).



Scheme 1. Syntheses of tetrafluorobutatriene complexes **2** and **3**.

In 1994 Hughes et al. reported the preparation of [IrCp*(PMe$_3$)(C$_4$F$_4$)] (**4**; Cp* = C$_5$Me$_5$), the first coordination compound of **1**.[4] The cumulene ligand in this complex was prepared in the coordination sphere of iridium by reduction of a *sec*-perfluorobutyl ligand using 6 equiv of sodium naphthalide (Scheme 2). Like other iridium complexes of reactive unsaturated compounds, **4** is reported to be relatively stable.



Scheme 2. Synthesis of [IrCp*(PMe$_3$)(C$_4$F$_4$)] (Hughes et al.[4]).

Single crystals suitable for X-ray analysis of **2** and **3** were prepared by crystallization from dichloromethane (Figure 1).[6] Both compounds crystallize as dichloromethane solvates containing one (**2**) or two (**3**) solvent molecules. The chloroform solvate of the iridium compound **2** contains three solvent molecules, one of which is strongly disordered. The molecular structures of the complexes are very similar. Both of them possess a distorted trigonal-bipyramidal coordination sphere, with the triphenylphosphine ligands occupying the axial positions. Coordination to the metal centers greatly elongates the central double bond of the triene ligand. The C-C-C bond angles are markedly smaller than 180° (Figure 2, Table 1). The terminal double bonds are strikingly short compared to those in **1**. The bonds between the carbon atoms (C3B) bound *trans* to the chloro ligand and the metal are

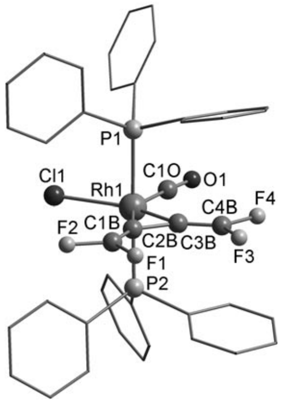


Figure 1. Molecular structure of **3**·2 CH$_2$Cl$_2$.[6] Solvent molecules and hydrogen atoms omitted for clarity, selected bond lengths [Å]: Rh1-Cl1 2.491(10), Rh1-P1/P2 2.361(5)/2.373(6), Rh1-C1O 1.911(8).

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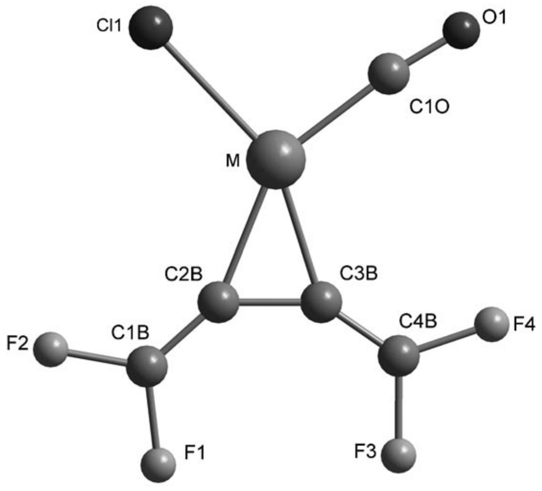

Figure 2. Structure of the butatriene ligand in **2** and **3**. Other ligands and solvent molecules omitted; bond lengths and angles in Table 1.

Table 1: Bond lengths [Å] and angles [°] in the butatriene ligands of **2**·CH_2Cl_2, **3**·2 CH_2Cl_2,[6] and **4**,[4] and in **1**.[3]

Distance	**2**[6]	**3**[6]	**4**[4]	**1**[3]
C1B-C2B	1.275(12)	1.298(9)	1.279(4)	1.3162(3)
C3B-C4B	1.297(12)	1.287(9)	1.283(4)	1.3162(3)[b]
C2B-C3B	1.412(12)	1.390(9)	1.418(5)	1.2679(5)
C1B-F1	1.352(10)	1.358(8)	1.352(4)	1.3198(3)
C4B-F3	1.336(10)	1.353(7)	1.346(3)	1.3198(3)[b]
C1B-F2	1.323(11)	1.326(9)	1.348(4)	1.3222(3)
C4B-F4	1.329(11)	1.324(8)	1.343(4)	1.3222(3)[b]
C2B-M[a]	2.112(9)	2.072(7)	2.039(3)	–
C3B-M[a]	2.072(8)	2.034(8)	2.042(3)	–
F1-F3	3.199(5)	3.246(10)	3.356(3)	–
Angle	**2**[6]	**3**[6]	**4**[4]	C_4F_4[3]
C1B,2B,3B	139.0(9)	137.5(6)	142.3(3)	122.3(1)[b]
C2B,3B,4B	142.0(9)	145.4(5)	140.4(3)	122.3(1)[b]
F1,C1B,F2	106.6(8)	107.7(6)	106.9(3)	109.7(1)
F3,C4B,F4	108.2(8)	108.3(5)	106.6(3)	109.7(1)[b]

[a] M = Ir (**2**, **4**), M = Rh (**3**); in **2** and **3** C1B and C2B are *cis* relative to the chloro ligand, C3B and C4B are *cis* relative to the carbonyl ligand, the environment of the triene ligand in **4** is symmetric. [b] Generated by symmetry operations.

about 0.04 Å shorter than those *trans* to the carbonyl ligand (C2B).

The *trans* effects of these two equatorial ligands on the triene ligand can also be seen in the ^{19}F and ^{13}C NMR spectra. The two groups of NMR signals could not be assigned to one particular half of the triene ligand as the chemical shifts could not be predicted quantitatively. The fluorine atoms could be assigned to the corresponding carbon atoms using two-dimensional NMR spectroscopy. All atoms of the triene ligands in **2** and **3** are chemically inequivalent. In **2**, the two ^{13}C NMR signals of the terminal CF_2 groups share the same chemical shift. In **3**, the corresponding signals are only $\delta = 0.21$ ppm apart. The ^{13}C NMR signals of the phenyl rings exhibit pseudo-triplet splitting due to coupling with the phosphorus atom bound to those rings. This effect can be explained by a large coupling constant between the phosphorus atoms in *trans* coordination. It has been observed in many *trans* bisphosphine complexes.[8] The ^{19}F NMR spectra show large coupling constants between F1 and F3 (32 Hz in **2**, 34 Hz in **3**), which can be explained only by through-space coupling.[9] In **4**, such a coupling is also observed.[4] The ^{19}F NMR spectrum of **2** in [D_8]toluene does not change significantly in the temperature range −60 to +120 °C. This leads to the conclusion that there is no propeller rotation of the triene ligand at these temperatures. Compounds **2** and **3** are stable against air and water in solution and in crystalline form.

Experimental Section

2: Vaska's complex ([Ir(CO)(PPh_3)$_2$Cl]; 83 mg, 0.107 mmol) was put into a dried Schlenk flask equipped with a magnetic stirrer bar. Anhydrous toluene (8 mL) and triene **1** (0.5 mmol) were condensed into the evacuated flask cooled with liquid nitrogen. On warming to room temperature, the yellow starting material dissolved completely, and within 10 min the color of the solution had changed from yellow to almost colorless. Stirring was continued at room temperature for an additional 4 h. The solution darkened slightly during this time, and a colorless precipitate formed. The solvent was removed in high vacuum, and the residue was dissolved in dichloromethane together with the precipitate. The resulting solution was filtered using a 5-μm syringe filter, and the threefold volume of hexane was added. Slow cooling to −35 °C yielded colorless needles and plates of [Ir(CO)(C_4F_4)(PPh_3)$_2$Cl]·CH_2Cl_2 after seven days; solvent evaporated from the crystals under high vacuum and 70 mg of the dried substance was obtained (0.077 mmol, 72 %).

Elemental analysis: ($IrP_2F_4OC_{41}H_{30}$) C 54.95 (calcd 54.46), H 3.01 (calcd 3.34); m.p. 239–241 °C (decomp.); ^{1}H NMR (399.65 MHz, 21 °C, [D_2]dichloromethane, TMS): $\delta = 7.67$–7.62 (m, 12 H; *meta*-PPh_3), 7.49–7.39 ppm (m, 18 H; *ortho*/*para*-PPh_3); $^{13}C\{^1H,^{19}F\}$ NMR (100.40 MHz, 20 °C, [D_2]dichloromethane, TMS): $\delta = 176.30$ (t, ^2J(C,P) = 9.1 Hz; CO), 148.50 (s; 2 =CF_2), 134.69 (*ortho*-PPh_3), 131.83 (*para*-PPh_3), 129.09 (*ipso*-PPh_3), 128.43 (*meta*-PPh_3), 66.66 (=C=C=), 59.06 ppm (=C=C=); ^{19}F NMR (376.00 MHz, 20 °C, [D_2]dichloromethane, $CFCl_3$): $\delta = -68.03$ (d[a], ^2J(*gem*-F,F) = 65.2 Hz, 1 F; =CF_2), −81.48 (d[a], ^2J(*gem*-F,F) = 74.1 Hz, 1 F; =CF_2), −91.21 (ddtd, ^2J(*gem*-F,F) = 65.2 Hz, ^5J(F,F[b]) = 32.1 Hz, ^4J(F,P) = 4.0 Hz, ^5J(F,F) = 3.5 Hz, 1 F; =CF_2), −96.90 ppm (dddt, ^2J(*gem*-F-F) = 74.1 Hz, ^5J(F,F[b]) = 32.1 Hz, ^5J(F,F) = 7.0 Hz, ^4J(F,P) = 2.1 Hz, 1 F; =CF_2); $^{31}P\{^1H\}$ NMR (161.70 MHz, 21 °C, [D_2]dichloromethane, 70 % H_3PO_4): $\delta = 0.49$ (m; PPh_3); IR ($CHCl_3$): $\tilde{\nu}$ = (C≡O) 2018 cm^{-1} (s); IR (CH_2Cl_2): $\tilde{\nu}$(C≡O) 2015 cm^{-1} (s); IR (KBr): $\tilde{\nu}$ = 3057 (w), 2012 (vs), 1960 (w), 1870 (vw), 1820 (s), 1700 (vs), 1588 (vw), 1573 (w), 1482 (m), 1435 (s), 1383 (w), 1332 (vw), 1315 (w), 1289 (vw), 1265 (vw), 1237 (m), 1204 (m), 1189 (m), 1159 (w), 1096 (s), 1074 (w), 1028 (w), 999 (w), 974 (m), 849 (vw), 815 (m), 743 (m), 723 (w), 710 (m), 694 (s), 618 (vw), 605 (vw), 581 (w), 559 (vw), 536 (w), 520 (vs), 506 (m), 456 (vw), 424 cm^{-1} (vw); Raman (crystals): 3172 (w), 3146 (w), 3060 (vs), 3006 (w), 2957 (w), 2006 (s), 1821 (m), 1586 (m), 1573 (w), 1482 (vw), 1436 (w), 1188 (w), 1159 (w), 1097 (m), 1074 (w), 1028 (m), 1000 (vs), 722 (vw), 710 (w), 688 (w), 616 (m), 604 (w), 558 (w), 537 (m), 517 (w), 472 (w), 455 (vw), 435 (vw), 424 (vw), 382 (vw), 304 (w), 276 (s), 258 (m), 230 (m), 203 (m), 161 cm^{-1} (s); MS (70 eV): *m*/*z* (%) = 904 (0.1) [M^+], 876 (10) [M^+−CO], 780 (2) [$M^+-C_4F_4$], 752 (4) [*M*−CO, $-C_4F_4$], 716 (2) [Ir(PPh_3)$_2^+$], 637 (3), 387 (6), 365 (4), 336 (2), 262 (100), [PPh_3^+], 183 (33) [PPh_2^+], 108 (13) [PPh^+].

3: In a similar procedure as for **2**, [Rh(PPh_3)$_2$(CO)Cl] (60 mg, 0.085 mmol) was reacted with **1** (0.26 mmol, volumetric). Crystals of **3** (25 mg, 0.032 mmol; 38 % yield) were obtained by recrystallization from dichloromethane/hexane 1:2 (yellow needles of **3**$\cdot$2 CH_2Cl_2) and evaporation of the solvent in high vacuum.

Elemental analysis: ($RhP_2F_4OC_{41}H_{30}$) C 59.41 (calcd 60.42), H 3.48 (calcd 3.71); m.p. 218–220 °C (decomp.); ^{1}H NMR (399.65 MHz, 21 °C, [D_2]dichloromethane, TMS): $\delta = 7.67$–7.62 (m, 12 H; *meta*-PPh_3), 7.49–7.39 ppm (m, 18 H; *ortho*/*para*-PPh_3); $^{13}C\{^1H, ^{19}F\}$ NMR (100.40 MHz, 24 °C, [D_2]dichlormethane, TMS): $\delta = 190.87$ (m; CO), 150.13 (s; $=CF_2$), 149.98 (s, $=CF_2$) 134.68 (*ortho*-PPh_3), 131.27 (*para*-PPh_3), 130.46 (*ipso*-PPh_3), 128.44 (*meta*-PPh_3) 86.26 (m; $=C=C=$), 72.45 ppm (m; $=C=C=$); ^{19}F NMR (376.00 MHz, 20 °C, [D_2]dichloromethane, $CFCl_3$): $\delta = -66.14$ (d[a], $^2J(gem\text{-F,F}) = 65.5$ Hz, 1 F; $=CF_2$), -79.87 (dd[a], $^2J(gem\text{-F,F}) = 76.2$ Hz, $^3J(\text{F,Rh}) = 8.5$ Hz, 1 F; $=CF_2$), -90.61 (dd[a], $^2J(gem\text{-F,F}) = 65.5$ Hz, $^5J(\text{F,F}^{[b]}) = 34.3$ Hz, 1 F; $=CF_2$), -95.93 ppm (dd[a], $^2J(gem\text{-F-F}) = 76.2$ Hz, $^5J(\text{F,F}^{[b]}) = 34.3$ Hz, 1 F; $=CF_2$); $^{31}P\{^1H\}$ NMR (161.70 MHz, 26 °C, [D_2]dichloromethane, 70 % H_3PO_4):$\delta = -30.91$ (d[a], $^1J(\text{P-Rh}) = 86.5$ Hz; PPh_3); IR (CH_2Cl_2): $\tilde{\nu} = (C\equiv O)$ 2044 cm^{-1} (s); IR (KBr): $\tilde{\nu} = 3143$ (vw), 3089 (vw), 3058 (w), 3024 (vw), 3005 (vw), 2989 (vw), 2960 (vw), 2045 (vs), 2006 (m), 2000 (m), 1984 (m), 1909 (vw), 1887 (vw), 1778 (vw), 1854 (m), 1843 (s), 1745 (vw), 1703 (vs), 1587 (w), 1574 (w), 1541 (vw), 1483 (m), 1436 (s), 1398 (vw), 1385 (vw), 1332 (w), 1314 (w), 1289 (vw), 1261 (m), 1248 (s), 1208 (s), 1191 (m), 1178 (m), 1157 (m), 1093 (s), 1090 (s), 1071 (m), 1028 (m), 999 (w), 960 (s), 168 (vw), 852 (vw), 790 (m), 755 (m), 746 (m), 739 (m), 619 (w), 604 (w), 569 (m), 519 (vs), 506 (s), 475 (m), 451 (w), 439 (w), 429 (w), 419 cm^{-1} (w); Raman (crystals): 3173 (vw), 3143 (vw), 3089 (w), 3061 (m), 3005 (vw), 2990 (vw), 2959 (vw), 2906 (vw), 2047 (w), 2005 (vw), 1842 (vw), 1586 (m), 1573 (w), 1437 (w), 1190 (m), 1072 (vw), 1029 (m), 1001 (vs), 751 (vw), 707 (w), 686 (w), 617 (w), 604 (w), 533 (m), 527 (m), 518 (w), 510 (w), 473 (vw), 449 (m), 441 (m), 428 (w), 416 (w), 406 (w), 384 (vw), 324 (w), 283 (w), 263 (s), 224 (m), 194 (m), 173 (m), 153 cm^{-1} (vs); MS (70 eV): m/z (%) = 786 (0.2) [$M^+ - CO$], 663 (1) [$M^+ - CO - C_4F_4$], 626 (0.1) [$Rh(PPh_3)_2{}^+ - H$], 400 (0.1) [$Rh(PPh_3)Cl^+$], 364 (0.1) [$Rh(PPh_3)^+$], 262 (100) [$PPh_3{}^+$], 183 (37) [$PPh_2{}^+ - 2H$] 108 (7) [PPh^+].

[a]: More couplings were evident but could not be assigned unambiguously. [b]: Through-space coupling.

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[6] Crystal structure determination: (SMART-CCD, Bruker): **2**$\cdot CH_2Cl_2$: structure solution: SHELXS-97,[7] direct methods, and least-squares refinement (SHELXL-97[7]), monoclinic, $P2_1/n$, $a = 12.092(3)$, $b = 23.019(5)$, $c = 13.640(3)$ Å, $\beta = 90.031(6)°$, $V = 3796.5(16)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.731\ g\,cm^{-1}$, $T = 173$ K, 30098 observed, 6885 independent ($R_{int} = 0.0956$) and 4706 reflections with $I > 2\sigma(I)$, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $2\theta_{max} = 50.10°$, $R_1 = 0.0454$, $wR_2 = 0.1161$, 478 parameters, anisotropic thermal parameters, H atoms isotropic. **2**$\cdot$3 $CHCl_3$: structure solution: SHELXS-97,[7] direct methods, and least-squares refinement (SHELXL-97[7]), monoclinic, $P2_1/c$, $a = 14.577(5)$, $b = 12.233(5)$, $c = 27.982(5)$ Å, $\beta = 101.746(5)°$, $V = 4885(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.712\ g\,cm^{-1}$, $T = 173$ K, 39494 observed, 8632 independent ($R_{int} = 0.1012$) and 5333 reflections with $I > 2\sigma(I)$, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $2\theta_{max} = 50.08°$, $R_1 = 0.0519$, $wR_2 = 0.1526$, 556 parameters, anisotropic thermal parameters, H atoms isotropic. **3**$\cdot$2 CH_2Cl_2: structure solution: SHELXS-97,[7] direct methods, and least-squares refinement (SHELXL-97[7]), triclinic, $P\bar{1}$, $a = 10.47(4)$, $b = 13.78(3)$, $c = 16.20(4)$ Å, $\alpha = 72.91(9)°$, $\beta = 73.41(14)$, $\gamma = 74.1(2)°$, $V = 2095(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.561\ g\,cm^{-1}$, $T = 173$ K, 18835 observed, 8431 independent ($R_{int} = 0.0747$) and 5242 reflections with $I > 2\sigma(I)$, $Mo_{K\alpha}$, $\lambda = 0.71073$ Å, $2\theta_{max} = 52.86$ °, $R_1 = 0.0609$, $wR_2 = 0.1586$, 505 parameters, anisotropic thermal parameters, H-atoms isotropic. CCDC-637685 (**2**$\cdot CH_2Cl_2$), CCDC-637686 (**2**$\cdot$3 $CHCl_3$), and CCDC-637687 (**3**$\cdot$2 CH_2Cl_2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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