Undecacarbonyl(μ_2-trifluoromethyl isocyanide)triruthenium, a Derivative of $[Ru_3(CO)_{12}]$ with $[Fe_3(CO)_{12}]$ Structure

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$[Ru_3(CO)_{10}(\mu_2\text{-CO})(\mu_2\text{-CNCF}_3)]$ (**1**), $[Ru_3(CO)_{10}(CNCF_3)_2]$ (**2**), and $[Ru_2(CO)_6(\mu_2\text{-CNCF}_3)_3]$ (**3**) are obtained by the reaction of $[Ru_3(CO)_{11}(CH_3CN)]$ with $CNCF_3$. An X-ray crystal structure determination revealed, that **1** has an unusual $[Fe_3(CO)_{12}]$ structure, different from most other derivatives of $[Ru_3(CO)_{12}]$.

$[Ru_3(CO)_{12}]$[1] and most of its derivatives $[Ru_3(CO)_n(L)_{12-n}]$[2] have only terminal ligands. $[Ru_3(\mu_2\text{-CO})_2(CO)_6\{PPh(OMe)_2\}_4]$[3] is the only example with a $[Fe_3(CO)_{12}]$[4] structure. However, this compound has strongly asymmetric carbonyl bridges, and the structure of the compound is a result of the presence of four bulky strong σ donor ligands.

One of the major properties of the strong π-accepting ligand trifluoromethyl isocyanide is its tendency to occupy the bridging position[5]. $[Cp^*Mo(CO)_2(\mu_2\text{-CNCF}_3)]_2$[5a] has two bridging isocyanide ligands[5a], whereas $[Cp^*Mo(CO)_3]_2$[6], $[Cp_2Mo_2(CO)_5(CNCH_3)]$[7], and $[Cp_2Mo_2(CO)_4(CNtBu)_2]$[8] possess only terminal ligands. The compounds $[Fe_3(CO)_{10}(L)(\mu_2\text{-CNCF}_3)]$ [L = CO, PMe_3, PEt_3, $P(OMe)_3$, $P(OEt)_3$] containing a μ_2-bridging isocyanide ligand are the only derivatives of $[Fe_3(CO)_{12}]$ known so far, which are rigid on the NMR time scale below $-80\,^\circ C$[5b].

In order to check whether this tendency of the $CNCF_3$ ligand to occupy the bridging position is sufficient for the structural change from a $[Ru_3(CO)_{12}]$ structure to a $[Fe_3(CO)_{12}]$ structure we have tried to synthesize trifluoromethyl isocyanide substituted derivatives of $[Ru_3(CO)_{12}]$.

In this paper we report on the synthesis and crystal structure determination of $[Ru_3(CO)_{10}(\mu_2\text{-CNCF}_3)]$ (**1**), which possesses the unusual $[Fe_3CO_{12}]$ structure without the presence of strong σ donor or bulky ligands. **1** can be prepared in a straightforward reaction (Scheme 1) from $[Ru_3(CO)_{11}(CH_3CN)]$[9] and $CNCF_3$[10]. The byproducts $[Ru_3(CO)_{10}(CNCF_3)_2]$ (**2**) and $[Ru_2(CO)_6(\mu_2\text{-CNCF}_3)_3]$ (**3**) can be easily separated by TLC. In an attempt to obtain higher yields of the disubstituted compound **2** by the reaction of $[Ru_3(CO)_{10}(CH_3CN)_2]$ with $CNCF_3$, **3** has been isolated as the major product.

All new compounds have been fully characterized by spectroscopic techniques. The X-ray structure determination of **1** (Figure 1) has revealed the presence of two independent molecules in the asymmetric unit which, apart from their orientation, show only minor differences. **1** has the same structure as the corresponding iron compound $[Fe_3(CO)_{10}(\mu_2\text{-CO})(\mu_2\text{-CNCF}_3)]$[5b] crystallizing in the same space group with only slightly different lattice constants. Ru1 and Ru2 are bridged nearly symmetrically by a carb-

Scheme 1

$$Ru_3(CO)_{11}(CH_3CN) \xrightarrow{CF_3NC} \underset{1}{Ru_3(CO)_{10}(\mu\text{-CO})(\mu\text{-CNCF}_3)} + \underset{2}{Ru_3(CO)_{10}(CNCF_3)_2} + \underset{3}{Ru_2(CO)_6(\mu\text{-CNCF}_3)_3}$$

$$Ru_3(CO)_{10}(CH_3CN)_2 \xrightarrow{CF_3NC} 1 + 2 + 3$$

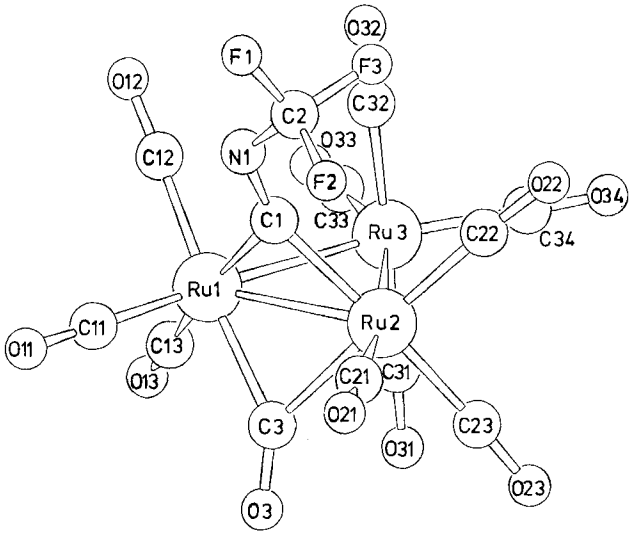

Figure 1. Molecular structure of the cluster $[Ru_3(CO)_{10}(\mu_2\text{-CO})(\mu_2\text{-CNCF}_3)]$ (**1**), molecule 1. Selected bond lengths [pm] and angles [°] molecule 1/molecule 2: Ru1–Ru2 275.0(1)/275.6(1), Ru1–Ru3 282.3(1)/281.9(1), Ru2–Ru3 282.0(1)/282.2(1), Ru1–C1 211.1(8)/211.1(8), Ru2–C1 204.7(8)/209.6(9), Ru1–C3 210.5(9)/216.6(9), Ru2–C3 220(1)/216.1(9), C1–N1 124(1)/123(1), C2–N1 140(1)/139(1), Ru–CO(term) 191(1)/198(1), Ru2–Ru1–Ru3 60.8(1)/60.8(1), Ru1–Ru2–Ru3 60.9(1)/60.7(1), Ru1–Ru3–Ru2 58.3(1)/58.5(1), Ru1–C1–Ru2 82.8(3)/81.8(3), Ru1–C3–Ru2 79.3(3)/79.1(3), Ru1–C1–N1 129.6(6)/132.0(7), Ru2–C1–N1 147.5(7)/146.2(7), Ru1–C3–O3 143.8(8)/140.7(8), Ru2–C3–O3 137.4(7)/140.2(8), C1–N1–C2 123.8(8)/124.5(8)

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onyl and a trifluoromethyl isocyanide ligand with a maximum difference in bond length of 10 pm between Ru1–C(bridge) and Ru2–C(bridge). The carbonyl bridges in $[Ru_3(\mu_2\text{-}CO)_2(CO)_6\{PPh(OMe)_2\}]$[3] are much less symmetrical [Ru1–C 205.7(8) and 239.9(8) and Ru2–C 238.9(7) and 206.8(8) pm]. In contrast, $[Ru_3(CO)_{11}(CNtBu)]$[2b] has only terminally coordinated ligands. A similar structure has been observed for $[Os_3(CO)_{10}(\mu_2\text{-}CO)(\mu_2\text{-}CH_2)]$[11]. The IR spectrum of **1** in *n*-hexane indicates that the bridged structure is the prevailing form even in solution. However, as the ^{13}C-NMR spectrum shows a single broad resonance for the eleven carbonyl carbon atoms, the molecule is non-rigid on the NMR time scale at ambient temperature.

According to its spectroscopic data, **3** has the same structure as $[Ru_2(CNiPr)_9]$[12] and $[Fe_2(CO)_9]$[13], but a structure different from the unstable $[Ru_2(CO)_9]$ and $[Os_2(CO)_9]$[14]. Again, the IR absorptions at $\tilde{\nu}$ = 1698 and 1676 cm^{-1} prove that the strong π-accepting ligands, trifluoromethyl isocyanide, occupy the bridging positions.

The structure of **2** needs further study. The presence of three bands in the IR spectrum in the bridging CN stretching region indicates that **2** may exist as a mixture of isomers, although the ^{19}F-NMR spectrum exhibits a single resonance at δ = −59.0.

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Experimental

IR: Perkin-Elmer 883. – ^{1}H, ^{19}F, ^{13}C NMR: Jeol FX90Q. – MS: Varian MAT 711. – All reactions were caried out under dry argon by using standard Schlenk tube and vacuum-line techniques. $Ru_3(CO_{11}(CH_3CN)$[9], $Ru_3(CO)_{10}(CH_3CN)_2$[9], and CF_3NC[10] were prepared by using literature methods.

$Ru_3(CO)_{10}(\mu_2\text{-}CO)(\mu_2\text{-}CF_3NC)$ (**1**): An excess of trifluoromethyl isocyanide was condensed onto a solution of $Ru_3(CO_{11}(CH_3CN)$ [prepared from 0.2 g (0.31 mmol) of $Ru_3(CO)_{12}$] in 30 ml of CH_2Cl_2. The mixture was stirred for 18 h at −78°C during which time the color changed from orange to dark red. The solution was subjected to TLC (silica, Merck, 1 mm) by using light petroleum ether (40–60°C) as eluant. Four bands migrated significantly, the first being $Ru_3(CO)_{12}$ (traces), the second **3** (traces) and the third **2**, followed by the major product **1**. The remainder was composed of decomposition products. **1**, isolated as a red solid, was crystallized from *n*-pentane to yield 88 mg (40%). Crystalline **1** does not show any changes up to 300°C. – MS: *m/z* = 709 [M$^+$] and smaller fragment ions from successive loss of 11 CO, the molecular ion exhibited the correct isotopic pattern. – IR (*n*-pentane): $\tilde{\nu}$ = 2073 cm^{-1} (vs), 2069 (vs), 2046 (s), 2039 (s), 2027 (m), 2011 (w), 1897 (w) (CO), 1661 (w) (CN). – ^{19}F NMR (CD_2Cl_2): δ = −59.0. – ^{13}C NMR (CD_2Cl_2): δ = 117.0 (CF_3, $^1J_{CF}$ = 261 Hz), 195.0 (CO).

$C_{13}F_3NO_{11}Ru_3$ (706.3) Calcd. C 22.11 N 1.98
Found C 22.60 N 1.98

$Ru_2(\mu\text{-}CNCF_3)_3(CO)_6$ (**3**): The reaction procedure was similar to that described above, except that $Ru_3(CO)_{10}(CH_3CN)_2$ was used as starting material. TLC (silica, Merck, 1 mm, light petroleum ether) gave the same four bands, except that compound **3** was the major product. Sublimation in vacuo (50°C/10^{-2} mbar) yielded 58 mg (28%) of **3** as orange crystals, m.p. 63°C. – MS (80 eV): *m/z* = 657 [M$^+$] and smaller fragment ions from successive loss of 6 CO. The molecular ion exhibited the correct isotopic pattern. – IR (*n*-pentane): $\tilde{\nu}$ = 2102 cm^{-1} (s), 2076 (s), 2028 (w) (CO), 1698 (m), 1676 (m) (CN). – ^{19}F NMR ($CDCl_3$): δ = −59.0.

$C_{12}F_9N_3O_6Ru_2$ (655.3) Calcd. C 22.00 N 6.62
Found C 22.96 N 6.41

$Ru_3(CO)_{10}(CNCF_3)_2$ (**2**): The red-violet fraction 3 of several runs described above was collected. After removal of the solvent in vacuo, the residue was sublimed at 25°C/10^{-2} mbar onto a cold finger cooled to −30°C to yield **2** as dark red violet crystals, m.p. 146°C. – MS (80 eV): *m/z* = 776 [M$^+$] and smaller fragment ions from successive loss of 10 CO. The molecular ion showed the correct isotopic pattern. – IR (*n*-pentane): $\tilde{\nu}$ = 2117 cm^{-1} (w), 2076 (vs), 2050 (s), 2037 (m), 2015 (w), CO), 1731 (w), 1694 (w), 1673 (m (CN). – ^{19}F NMR ($CDCl_3$): δ = −59.3.

Table 1. Atomic coordinates in undecacarbonyl(μ$_2$-trifluoromethyl isocyanide)triruthenium (**1**)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Ru1	0.0873(1)	0.3897(0)	0.3447(0)	2.64
Ru2	0.1239(1)	0.2468(0)	0.2278(0)	2.65
Ru3	-0.1530(1)	0.3247(0)	0.2337(0)	2.79
C1	0.1973(8)	0.3811(6)	0.2232(5)	2.55
C2	0.3408(11)	0.4255(7)	0.1036(7)	3.81
C3	0.1277(9)	0.2518(6)	0.3763(7)	3.46
C11	0.2677(10)	0.4260(6)	0.4122(6)	3.25
C12	0.0404(11)	0.5128(6)	0.3066(6)	3.55
C13	-0.0458(11)	0.3871(6)	0.4439(7)	4.15
C21	0.3240(11)	0.2082(6)	0.2328(7)	3.98
C22	0.0912(11)	0.2413(7)	0.0996(8)	4.27
C23	0.0335(10)	0.1236(7)	0.2449(8)	4.36
C31	-0.1912(9)	0.2322(6)	0.3245(6)	3.42
C32	-0.0913(10)	0.4163(7)	0.1451(6)	3.60
C33	-0.3058(11)	0.3986(7)	0.2765(7)	4.35
C34	-0.2672(10)	0.2566(7)	0.1411(6)	3.97
F1	0.4261(13)	0.4925(6)	0.0843(7)	13.37
F2	0.4197(10)	0.3548(6)	0.1032(6)	10.80
F3	0.2535(10)	0.4140(8)	0.0345(5)	11.24
N1	0.2707(8)	0.4410(5)	0.1838(5)	3.37
O3	0.1431(8)	0.2017(5)	0.4347(4)	4.90
O11	0.3694(8)	0.4474(5)	0.4522(5)	5.18
O12	0.0210(9)	0.5862(5)	0.2851(5)	5.75
O13	-0.1215(9)	0.3873(6)	0.5004(5)	6.17
O21	0.4414(8)	0.1866(5)	0.2364(6)	6.35
O22	0.0685(9)	0.2335(6)	0.0242(5)	6.32
O23	-0.0103(9)	0.0517(5)	0.2563(7)	7.27
O31	-0.2177(8)	0.1783(5)	0.3772(5)	5.28
O32	-0.0612(8)	0.4689(5)	0.0920(5)	5.45
O33	-0.3945(10)	0.4412(6)	0.3051(6)	7.30
O34	-0.3332(8)	0.2187(6)	0.0873(5)	5.77
Ru1I	-0.5914(1)	-0.1692(0)	0.3551(0)	2.81
Ru2I	-0.5261(1)	-0.2438(0)	0.1917(0)	2.61
Ru3I	-0.3036(1)	-0.1490(0)	0.2960(0)	2.80
C1I	-0.6442(9)	-0.1278(6)	0.2215(6)	2.93
C2I	-0.7425(12)	-0.0472(7)	0.0993(7)	4.29
C3I	-0.5936(10)	-0.3118(6)	0.3133(6)	3.55
C11I	-0.7953(10)	-0.1804(7)	0.3793(6)	4.17
C12I	-0.5690(13)	-0.0401(8)	0.3843(7)	4.93
C13I	-0.5214(10)	-0.2142(6)	0.4742(6)	3.30
C21I	-0.6948(11)	-0.2993(6)	0.1266(6)	3.75
C22I	-0.4388(10)	-0.1859(6)	0.0866(6)	3.28
C23I	-0.3920(11)	-0.3462(7)	0.1809(6)	3.72
C31I	-0.2725(10)	-0.2645(6)	0.3590(6)	3.53
C32I	-0.3539(10)	-0.0373(7)	0.2279(7)	3.77
C33I	-0.1369(11)	-0.1666(7)	0.2244(7)	4.39
C34I	-0.2115(11)	-0.0748(6)	0.3925(7)	4.01
F1I	-0.8227(10)	0.0219(6)	0.0864(5)	9.38
F2I	-0.8055(9)	-0.1187(5)	0.0559(4)	7.54
F3I	-0.6234(8)	-0.0321(6)	0.0528(5)	7.91
N1I	-0.7152(8)	-0.0636(5)	0.1909(5)	3.31
O3I	-0.6179(9)	-0.3827(5)	0.3397(5)	5.52
O11I	-0.9149(8)	-0.1866(7)	0.3962(6)	7.10
O12I	-0.5626(11)	0.0363(5)	0.3999(6)	7.01
O13I	-0.4890(8)	-0.2431(5)	0.5415(5)	5.23
O21I	-0.7935(9)	-0.3340(5)	0.0889(6)	6.30
O22I	-0.3857(8)	-0.1608(5)	0.0257(5)	5.48
O23I	-0.3115(9)	-0.4017(5)	0.1733(5)	6.16
O31I	-0.2463(8)	-0.3299(5)	0.3941(5)	4.75
O32I	-0.3733(9)	0.0276(5)	0.1907(6)	5.99
O33I	-0.0388(9)	-0.1824(7)	0.1858(6)	7.18
O34I	-0.1593(9)	-0.0295(5)	0.4472(5)	6.12

Crystal Data for $[Ru_3(CO)_{10}(\mu_2\text{-}CO)(\mu_2\text{-}CNCF_3)]$ (**1**): Orange-red crystal 0.35 × 0.25 × 0.1 mm, $C_{13}F_3NO_{11}Ru_3$, M = 706.34 g mol^{-1}, triclinic, $P\bar{1}$ (No. 2), a = 9.154(2), b = 14.557(3), c = 14.840(4) Å, α = 89.99(2), β = 92.58(2), γ = 92.10(2)°, V = 1974.1(7) Å^3, Z = 4, $\varrho_{calcd.}$ = 2.38 g cm^{-3}. The lattice constant and space group have been carefully checked, Mo-K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 23.8 cm^{-1}, no absorption correction, $F(000)$ = 1328. Synthex $P2_1$ diffractometer, 6975 measured reflexions [$2° \leq 2\Theta \leq 50°$], 6943 unique reflexions, final R and R_w [$w = (\sigma(F_o)^2 + 0.0006 \cdot F_o^2)^{-1}$] values 0.048 and 0.044 for 5308 data with $F_o \geq 3\sigma(F_o)$, max. shift/error 0.001, residual electron density 1.12 e Å^{-3}. Patterson methods (SHELXS-86[15]), block-matrix least-squares refinement (SHELX-76[16]) with anisotropic temperature factors for all atoms. Atomic coordinates are listed in Table 1. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-55121, the names of the authors, and the journal citation.

[1] R. Mason, A. I. M. Rae, *J. Chem. Soc. A* **1968**, 778; M. R. Churchill, F. J. Hollander, J. P. Hutchinson, *Inorg. Chem.* **16** (1977) 2655.

[2] [2a] E. J. Forbes, N. Goodhand, D. L. Jones, T. A. Hamor, *J. Organomet. Chem.* **182** (1979) 143. – [2b] M. I. Bruce, J. G. Matisons, R. C. Wallis, J. M. Patrick, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1983**, 2365. – [2c] M. I. Bruce, J. G. Matisons, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1983**, 2375. – [2d] M. I. Bruce, M. J. Liddell, C. A. Hughes, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **347** (1988) 157. – [2e] M. I. Bruce, M. J. Liddell, C. A. Hughes, J. M. Patrick, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **347** (1988) 181. – [2f] M. I. Bruce, M. J. Liddell, O. bin Shawkataly, C. A. Hughes, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **347** (1988) 207. – [2g] M. I. Bruce, M. J. Liddell, O. bin Shawkataly, C. A. Hughes, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **347** (1988) 207. – [2h] G. Lavigne, J. J. Bonnet, *Acta Crystallogr., Sect. B*, **38** (1982) 1911; M. I. Bruce, T. W. Hambley, B. K. Nicholson, and M. R. Snow, *J. Organomet. Chem.* **235** (1982) 83.

[3] M. I. Bruce, J. G. Matisons, J. M. Patrick, A. H. White, A. C. Willis, *J. Chem. Soc., Dalton Trans.* **1985**, 1223.

[4] C. H. Wei, and L. F. Dahl, *J. Am. Chem. Soc.* **91** (1969) 1351; F. A. Cotton, J. M. Troup, *ibid.* **96** (1974) 4155.

[5] [5a] D. Lentz, I. Brüdgan, H. Hartl, *J. Organomet. Chem.* **299** (1986) C38. – [5b] I. Brüdgam, H. Hartl, D. Lentz, *Z. Naturforsch., Teil B*, **39** (1984) 721; D. Lentz, *ibid.* **42** (1987) 839; D. Lentz, R. Marschall, *Organometallics*, in press.

[6] R. D. Adams, R. M. Collins, F. A. Cotton, *Inorg. Chem.* **13** (1974) 1086.

[7] R. D. Adams, M. Brice, F. A. Cotton, *J. Am. Chem. Soc.* **95** (1973) 6594.

[8] N. J. Coville, *J. Organomet. Chem.* **218** (1981) 337.

[9] G. A. Foulds, B. F. G. Johnson, J. Lewis, *J. Organomet. Chem.* **296** (1985) 147.

[10] D. Lentz, *J. Fluorine Chem.* **24** (1984) 523.

[11] M. R. Churchill, H. R. Wasserman, *Inorg. Chem.* **21** (1982) 825.

[12] J.-M. Basset, G. K. Barker, M. Green, J. A. K. Howard, F. G. A. Stone, W. C. Wolsey, *J. Chem. Soc., Dalton Trans.* **1981**, 219.

[13] F. A. Cotton, J. M. Troup, *J. Chem. Soc., Dalton Trans.* **1974**, 800; H. M. Powell, H. O. Jones, *J. Chem. Soc.* **1939**, 286; J. Dewar, H. O. Jones, *Proc. R. Soc. London, Ser. A*, **76** (1905) 558.

[14] J. R. Moss, W. A. G. Graham, *J. Chem. Soc., Dalton Trans.* **1977**, 95.

[15] G. M. Sheldrick, *SHELXS-86, A Program for Crystal Structure Solution*, Göttingen 1986.

[16] G. M. Sheldrick, SHELX-76, *A Program for Crystal Structure Determination*, Cambridge 1976.

[410/90]