Supporting Information

Noncovalent n → π*, C−H···π, and C−H···O Interactions Mediated Supramolecular Assembly in a $Re(CO)_3$(trifluoroacetate) Complex Bearing a Bulky Tetraazaphenanthrene Ligand: A Combined CSD Study and Theoretical Calculations

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Table S1. Bond lengths [Å] and angles [°] for the **Complex**.

Re(1)-C(1)	1.918(5)
Re(1)-C(3)	1.929(6)
Re(1)-C(2)	1.930(6)
Re(1)-O(4)	2.163(3)
Re(1)-N(1)	2.215(4)
Re(1)-N(2)	2.217(4)
O(4)-C(14)	1.259(7)
O(2)-C(2)	1.145(7)
O(3)-C(3)	1.140(7)
N(2)-C(12)	1.330(6)
N(2)-C(8)	1.361(6)
N(4)-C(13)	1.321(6)
N(4)-C(9)	1.361(6)
N(1)-C(4)	1.334(6)
N(1)-C(7)	1.368(6)
N(3)-C(5)	1.325(6)
N(3)-C(6)	1.351(6)
O(1)-C(1)	1.128(6)
C(10)-C(11)	1.361(7)
C(10)-C(9)	1.419(6)
C(10)-H(10)	0.9300
C(21)-C(20)	1.388(7)
C(21)-C(16)	1.402(7)
C(21)-H(21)	0.9300
C(29)-C(30)	1.391(7)
C(29)-C(28)	1.392(7)
C(29)-H(29)	0.9300
C(9)-C(8)	1.394(6)
O(5)-C(14)	1.214(7)
C(7)-C(6)	1.392(7)
C(7)-C(8)	1.435(6)
C(12)-C(13)	1.439(6)
C(12)-C(28)	1.485(6)
C(4)-C(5)	1.446(6)
C(4)-C(16)	1.488(6)
C(20)-C(19)	1.386(7)
C(20)-H(20)	0.9300

C(5)-C(22)	1.480(6)
C(28)-C(33)	1.389(7)
C(39)-C(38)	1.378(7)
C(39)-C(34)	1.396(7)
C(39)-H(39)	0.9300
C(34)-C(35)	1.391(7)
C(34)-C(13)	1.490(6)
C(11)-C(6)	1.434(6)
C(11)-H(11)	0.9300
C(16)-C(17)	1.384(6)
C(23)-C(22)	1.393(7)
C(23)-C(24)	1.395(7)
C(23)-H(23)	0.9300
C(27)-C(26)	1.391(7)
C(27)-C(22)	1.396(7)
C(27)-H(27)	0.9300
C(24)-C(25)	1.378(9)
C(24)-H(24)	0.9300
C(38)-C(37)	1.401(8)
C(38)-H(38)	0.9300
C(33)-C(32)	1.379(7)
C(33)-H(33)	0.9300
C(35)-C(36)	1.380(7)
C(35)-H(35)	0.9300
C(17)-C(18)	1.384(7)
C(17)-H(17)	0.9300
C(30)-C(31)	1.381(8)
C(30)-H(30)	0.9300
C(19)-C(18)	1.387(8)
C(19)-H(19)	0.9300
C(37)-C(36)	1.386(8)
C(37)-H(37)	0.9300
C(18)-H(18)	0.9300
C(25)-C(26)	1.389(9)
C(25)-H(25)	0.9300
C(36)-H(36)	0.9300
C(26)-H(26)	0.9300
C(32)-C(31)	1.389(8)

C(32)-H(32)	0.9300
C(31)-H(31)	0.9300
C(14)-C(15)	1.539(9)
C(15)-F(2A)	1.142(19)
C(15)-F(1A)	1.224(18)
C(15)-F(3)	1.31(2)
C(15)-F(1)	1.316(15)
C(15)-F(2)	1.383(16)
C(15)-F(3A)	1.26(5)

C(1)-Re(1)-C(3)	87.4(2)
C(1)-Re(1)-C(2)	88.0(2)
C(3)-Re(1)-C(2)	83.9(2)
C(1)-Re(1)-O(4)	174.71(18)
C(3)-Re(1)-O(4)	95.70(18)
C(2)-Re(1)-O(4)	96.55(17)
C(1)-Re(1)-N(1)	98.47(19)
C(3)-Re(1)-N(1)	172.70(17)
C(2)-Re(1)-N(1)	100.59(17)
O(4)-Re(1)-N(1)	78.14(13)
C(1)-Re(1)-N(2)	97.79(18)
C(3)-Re(1)-N(2)	99.08(17)
C(2)-Re(1)-N(2)	173.55(16)
O(4)-Re(1)-N(2)	77.50(13)
N(1)-Re(1)-N(2)	75.91(14)
C(14)-O(4)-Re(1)	123.8(3)
C(12)-N(2)-C(8)	117.2(4)
C(12)-N(2)-Re(1)	130.4(3)
C(8)-N(2)-Re(1)	111.5(3)
C(13)-N(4)-C(9)	117.1(4)
C(4)-N(1)-C(7)	117.2(4)
C(4)-N(1)-Re(1)	130.1(3)
C(7)-N(1)-Re(1)	111.2(3)
C(5)-N(3)-C(6)	118.0(4)
C(11)-C(10)-C(9)	121.0(4)
C(11)-C(10)-H(10)	119.5
C(9)-C(10)-H(10)	119.5
C(20)-C(21)-C(16)	118.7(5)

C(20)-C(21)-H(21)	120.7
C(16)-C(21)-H(21)	120.7
C(30)-C(29)-C(28)	119.5(5)
C(30)-C(29)-H(29)	120.3
C(28)-C(29)-H(29)	120.3
N(4)-C(9)-C(8)	120.5(4)
N(4)-C(9)-C(10)	119.7(4)
C(8)-C(9)-C(10)	119.8(4)
N(1)-C(7)-C(6)	121.8(4)
N(1)-C(7)-C(8)	118.4(4)
C(6)-C(7)-C(8)	119.8(4)
N(2)-C(12)-C(13)	119.9(4)
N(2)-C(12)-C(28)	120.1(4)
C(13)-C(12)-C(28)	120.0(4)
N(1)-C(4)-C(5)	120.4(4)
N(1)-C(4)-C(16)	118.3(4)
C(5)-C(4)-C(16)	121.3(4)
C(19)-C(20)-C(21)	120.7(5)
C(19)-C(20)-H(20)	119.6
C(21)-C(20)-H(20)	119.6
N(2)-C(8)-C(9)	122.3(4)
N(2)-C(8)-C(7)	118.1(4)
C(9)-C(8)-C(7)	119.6(4)
N(3)-C(5)-C(4)	121.3(4)
N(3)-C(5)-C(22)	115.8(4)
C(4)-C(5)-C(22)	122.9(4)
C(33)-C(28)-C(29)	119.9(4)
C(33)-C(28)-C(12)	119.2(4)
C(29)-C(28)-C(12)	120.5(4)
C(38)-C(39)-C(34)	119.8(5)
C(38)-C(39)-H(39)	120.1
C(34)-C(39)-H(39)	120.1
C(35)-C(34)-C(39)	119.8(5)
C(35)-C(34)-C(13)	120.4(4)
C(39)-C(34)-C(13)	119.8(4)
C(10)-C(11)-C(6)	120.3(4)
C(10)-C(11)-H(11)	119.9
C(6)-C(11)-H(11)	119.9

C(17)-C(16)-C(21)	120.5(4)
C(17)-C(16)-C(4)	119.9(4)
C(21)-C(16)-C(4)	119.6(4)
C(22)-C(23)-C(24)	120.3(5)
C(22)-C(23)-H(23)	119.9
C(24)-C(23)-H(23)	119.9
N(3)-C(6)-C(7)	121.0(4)
N(3)-C(6)-C(11)	119.4(4)
C(7)-C(6)-C(11)	119.6(4)
O(2)-C(2)-Re(1)	174.6(4)
C(26)-C(27)-C(22)	121.1(5)
C(26)-C(27)-H(27)	119.5
C(22)-C(27)-H(27)	119.5
N(4)-C(13)-C(12)	122.5(4)
N(4)-C(13)-C(34)	116.7(4)
C(12)-C(13)-C(34)	120.8(4)
C(25)-C(24)-C(23)	119.8(5)
C(25)-C(24)-H(24)	120.1
C(23)-C(24)-H(24)	120.1
C(23)-C(22)-C(27)	118.9(4)
C(23)-C(22)-C(5)	123.6(4)
C(27)-C(22)-C(5)	117.4(4)
C(39)-C(38)-C(37)	120.3(5)
C(39)-C(38)-H(38)	119.8
C(37)-C(38)-H(38)	119.8
O(3)-C(3)-Re(1)	176.1(4)
C(32)-C(33)-C(28)	120.2(5)
C(32)-C(33)-H(33)	119.9
C(28)-C(33)-H(33)	119.9
O(1)-C(1)-Re(1)	178.5(5)
C(36)-C(35)-C(34)	120.2(5)
C(36)-C(35)-H(35)	119.9
C(34)-C(35)-H(35)	119.9
C(16)-C(17)-C(18)	120.3(5)
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-H(17)	119.8
C(31)-C(30)-C(29)	120.3(5)
C(31)-C(30)-H(30)	119.8

C(29)-C(30)-H(30)	119.8
C(20)-C(19)-C(18)	120.2(5)
C(20)-C(19)-H(19)	119.9
C(18)-C(19)-H(19)	119.9
C(36)-C(37)-C(38)	119.4(5)
C(36)-C(37)-H(37)	120.3
C(38)-C(37)-H(37)	120.3
C(17)-C(18)-C(19)	119.7(5)
C(17)-C(18)-H(18)	120.2
C(19)-C(18)-H(18)	120.2
C(24)-C(25)-C(26)	121.0(5)
C(24)-C(25)-H(25)	119.5
C(26)-C(25)-H(25)	119.5
C(35)-C(36)-C(37)	120.4(5)
C(35)-C(36)-H(36)	119.8
C(37)-C(36)-H(36)	119.8
C(25)-C(26)-C(27)	118.9(5)
C(25)-C(26)-H(26)	120.5
C(27)-C(26)-H(26)	120.5
C(33)-C(32)-C(31)	120.1(5)
C(33)-C(32)-H(32)	120.0
C(31)-C(32)-H(32)	120.0
C(30)-C(31)-C(32)	120.0(5)
C(30)-C(31)-H(31)	120.0
C(32)-C(31)-H(31)	120.0
O(5)-C(14)-O(4)	129.6(5)
O(5)-C(14)-C(15)	117.5(5)
O(4)-C(14)-C(15)	112.8(5)
F(2A)-C(15)-F(1A)	107.2(17)
F(3)-C(15)-F(1)	103.7(15)
F(3)-C(15)-F(2)	102.1(15)
F(1)-C(15)-F(2)	115.3(14)
F(2A)-C(15)-F(3A)	99(2)
F(1A)-C(15)-F(3A)	111(2)
F(2A)-C(15)-C(14)	117.1(10)
F(1A)-C(15)-C(14)	117.0(11)
F(3)-C(15)-C(14)	118.9(9)
F(1)-C(15)-C(14)	110.1(9)

F(2)-C(15)-C(14)	106.9(8)
F(3A)-C(15)-C(14)	104.1(14)

C(13)-N(4)-C(9)-C(8)	2.8(6)
C(13)-N(4)-C(9)-C(10)	-176.4(4)
C(11)-C(10)-C(9)-N(4)	177.8(4)
C(11)-C(10)-C(9)-C(8)	-1.4(7)
C(4)-N(1)-C(7)-C(6)	4.7(6)
Re(1)-N(1)-C(7)-C(6)	-162.7(4)
C(4)-N(1)-C(7)-C(8)	-176.3(4)
Re(1)-N(1)-C(7)-C(8)	16.4(5)
C(8)-N(2)-C(12)-C(13)	4.4(6)
Re(1)-N(2)-C(12)-C(13)	-163.3(3)
C(8)-N(2)-C(12)-C(28)	-175.3(4)
Re(1)-N(2)-C(12)-C(28)	17.0(6)
C(7)-N(1)-C(4)-C(5)	-2.1(6)
Re(1)-N(1)-C(4)-C(5)	162.4(3)
C(7)-N(1)-C(4)-C(16)	177.3(4)
Re(1)-N(1)-C(4)-C(16)	-18.2(6)
C(16)-C(21)-C(20)-C(19)	0.0(7)
C(12)-N(2)-C(8)-C(9)	-6.5(6)
Re(1)-N(2)-C(8)-C(9)	163.4(3)
C(12)-N(2)-C(8)-C(7)	173.7(4)
Re(1)-N(2)-C(8)-C(7)	-16.4(5)
N(4)-C(9)-C(8)-N(2)	2.9(7)
C(10)-C(9)-C(8)-N(2)	-177.8(4)
N(4)-C(9)-C(8)-C(7)	-177.2(4)
C(10)-C(9)-C(8)-C(7)	2.0(6)
N(1)-C(7)-C(8)-N(2)	0.0(6)
C(6)-C(7)-C(8)-N(2)	179.1(4)
N(1)-C(7)-C(8)-C(9)	-179.8(4)
C(6)-C(7)-C(8)-C(9)	-0.8(6)
C(6)-N(3)-C(5)-C(4)	4.9(7)
C(6)-N(3)-C(5)-C(22)	-177.0(4)
N(1)-C(4)-C(5)-N(3)	-2.7(7)
C(16)-C(4)-C(5)-N(3)	177.9(4)
N(1)-C(4)-C(5)-C(22)	179.3(4)
C(16)-C(4)-C(5)-C(22)	-0.1(7)

C(30)-C(29)-C(28)-C(33)	0.8(7)
C(30)-C(29)-C(28)-C(12)	-172.7(4)
N(2)-C(12)-C(28)-C(33)	61.1(6)
C(13)-C(12)-C(28)-C(33)	-118.6(5)
N(2)-C(12)-C(28)-C(29)	-125.4(5)
C(13)-C(12)-C(28)-C(29)	55.0(6)
C(38)-C(39)-C(34)-C(35)	-1.7(7)
C(38)-C(39)-C(34)-C(13)	179.7(5)
C(9)-C(10)-C(11)-C(6)	-0.5(7)
C(20)-C(21)-C(16)-C(17)	-0.2(7)
C(20)-C(21)-C(16)-C(4)	177.2(4)
N(1)-C(4)-C(16)-C(17)	-64.3(6)
C(5)-C(4)-C(16)-C(17)	115.1(5)
N(1)-C(4)-C(16)-C(21)	118.3(5)
C(5)-C(4)-C(16)-C(21)	-62.3(6)
C(5)-N(3)-C(6)-C(7)	-2.4(7)
C(5)-N(3)-C(6)-C(11)	177.2(4)
N(1)-C(7)-C(6)-N(3)	-2.5(7)
C(8)-C(7)-C(6)-N(3)	178.4(4)
N(1)-C(7)-C(6)-C(11)	177.9(4)
C(8)-C(7)-C(6)-C(11)	-1.1(7)
C(10)-C(11)-C(6)-N(3)	-177.8(4)
C(10)-C(11)-C(6)-C(7)	1.7(7)
C(9)-N(4)-C(13)-C(12)	-4.9(6)
C(9)-N(4)-C(13)-C(34)	175.7(4)
N(2)-C(12)-C(13)-N(4)	1.3(7)
C(28)-C(12)-C(13)-N(4)	-179.0(4)
N(2)-C(12)-C(13)-C(34)	-179.4(4)
C(28)-C(12)-C(13)-C(34)	0.3(6)
C(35)-C(34)-C(13)-N(4)	-125.6(5)
C(39)-C(34)-C(13)-N(4)	52.9(6)
C(35)-C(34)-C(13)-C(12)	55.0(6)
C(39)-C(34)-C(13)-C(12)	-126.5(5)
C(22)-C(23)-C(24)-C(25)	-0.3(8)
C(24)-C(23)-C(22)-C(27)	-0.6(7)
C(24)-C(23)-C(22)-C(5)	-177.9(5)
C(26)-C(27)-C(22)-C(23)	0.6(7)
C(26)-C(27)-C(22)-C(5)	178.0(5)

N(3)-C(5)-C(22)-C(23)	140.7(5)
C(4)-C(5)-C(22)-C(23)	-41.1(7)
N(3)-C(5)-C(22)-C(27)	-36.6(6)
C(4)-C(5)-C(22)-C(27)	141.5(5)
C(34)-C(39)-C(38)-C(37)	2.7(8)
C(29)-C(28)-C(33)-C(32)	-0.8(7)
C(12)-C(28)-C(33)-C(32)	172.8(4)
C(39)-C(34)-C(35)-C(36)	-0.2(7)
C(13)-C(34)-C(35)-C(36)	178.4(5)
C(21)-C(16)-C(17)-C(18)	0.6(7)
C(4)-C(16)-C(17)-C(18)	-176.8(5)
C(28)-C(29)-C(30)-C(31)	0.2(8)
C(21)-C(20)-C(19)-C(18)	-0.1(8)
C(39)-C(38)-C(37)-C(36)	-1.7(8)
C(16)-C(17)-C(18)-C(19)	-0.7(8)
C(20)-C(19)-C(18)-C(17)	0.5(8)
C(23)-C(24)-C(25)-C(26)	1.4(8)
C(34)-C(35)-C(36)-C(37)	1.1(8)
C(38)-C(37)-C(36)-C(35)	-0.2(8)
C(24)-C(25)-C(26)-C(27)	-1.4(8)
C(22)-C(27)-C(26)-C(25)	0.4(8)
C(28)-C(33)-C(32)-C(31)	-0.2(7)
C(29)-C(30)-C(31)-C(32)	-1.3(8)
C(33)-C(32)-C(31)-C(30)	1.3(8)
Re(1)-O(4)-C(14)-O(5)	6.3(10)
Re(1)-O(4)-C(14)-C(15)	-170.1(5)
O(5)-C(14)-C(15)-F(2A)	-134(2)
O(4)-C(14)-C(15)-F(2A)	43(2)
O(5)-C(14)-C(15)-F(1A)	-5(2)
O(4)-C(14)-C(15)-F(1A)	172(2)
O(5)-C(14)-C(15)-F(3)	155.5(16)
O(4)-C(14)-C(15)-F(3)	-27.7(18)
O(5)-C(14)-C(15)-F(1)	36.2(16)
O(4)-C(14)-C(15)-F(1)	-147.0(14)
O(5)-C(14)-C(15)-F(2)	-89.8(15)
O(4)-C(14)-C(15)-F(2)	87.1(15)
O(5)-C(14)-C(15)-F(3A)	118.4(19)
O(4)-C(14)-C(15)-F(3A)	-65(2)

Table S2. Cartesian coordinates of the optimized structure of the title **complex**.

Re	**0.11263212**	**-1.31428131**	**0.32669291**
O	**0.10457229**	**0.26054029**	**1.84265544**
O	**-2.00087404**	**-3.05045733**	**1.74767281**
O	**2.17968459**	**-2.97809174**	**1.88579192**
N	**1.50280977**	**0.28974678**	**-0.52443916**
N	**2.84136354**	**2.73425281**	**-0.82403793**
N	**-1.25448792**	**0.23781987**	**-0.63471652**
N	**-2.66080450**	**2.63436031**	**-0.98585661**
O	**0.22336425**	**-3.31794123**	**-2.00569676**
C	**0.74978897**	**3.89956506**	**-0.90894250**
H	**1.31258382**	**4.82762120**	**-0.96856468**
C	**-4.29671440**	**-1.22483018**	**0.33229760**
H	**-4.52518419**	**-0.41243044**	**1.01842661**
C	**4.55503242**	**-1.05429866**	**0.60848687**
H	**4.75611678**	**-0.21631813**	**1.27428832**
C	**1.49725999**	**2.68633171**	**-0.80363757**
O	**-2.14259341**	**0.26669186**	**2.17710909**
C	**-0.60303008**	**1.42683205**	**-0.75235270**
C	**2.84237465**	**0.33447543**	**-0.56629204**
C	**-2.58813194**	**0.23276013**	**-0.75028268**
C	**-4.95930776**	**-2.44143183**	**0.42708655**
H	**-5.72591670**	**-2.57778699**	**1.18676742**
C	**0.81839108**	**1.45239112**	**-0.69981075**
C	**-3.29336585**	**1.46530877**	**-0.96587761**
C	**3.58204032**	**-0.92717958**	**-0.38929706**
C	**5.60909135**	**2.82476768**	**-0.31475429**
H	**5.00012934**	**3.53943913**	**0.23445279**
C	**4.98149885**	**1.71187534**	**-0.89162968**

C	**-0.61080676**	**3.87455538**	**-0.95007573**
H	**-1.20264612**	**4.78177295**	**-1.04173028**
C	**-3.28938234**	**-1.05410632**	**-0.62426197**
C	**-5.46324412**	**0.61191821**	**-1.94524005**
H	**-4.94086275**	**-0.21989210**	**-2.41299049**
C	**-1.31907813**	**2.63471394**	**-0.89115763**
C	**-1.22943197**	**-2.37788649**	**1.19874627**
C	**-5.45022562**	**2.61600853**	**-0.59920069**
H	**-4.89436710**	**3.34042330**	**-0.00826244**
C	**3.51350142**	**1.58855491**	**-0.76130674**
C	**-6.83025861**	**0.76107055**	**-2.14535511**
H	**-7.36299680**	**0.04183277**	**-2.76418594**
C	**-4.75622695**	**1.53645991**	**-1.16320238**
C	**6.98003233**	**3.00841398**	**-0.44023957**
H	**7.45454017**	**3.86855886**	**0.02801896**
C	**1.41100613**	**-2.34407433**	**1.28327481**
C	**3.32772054**	**-2.00586104**	**-1.24487307**
H	**2.58282804**	**-1.90062927**	**-2.03134166**
C	**0.18527265**	**-2.55911950**	**-1.11419513**
C	**5.75741603**	**0.80404032**	**-1.62647953**
H	**5.28784708**	**-0.05279166**	**-2.10505748**
C	**-2.96274022**	**-2.10894289**	**-1.48462550**
H	**-2.18708638**	**-1.96723954**	**-2.23546337**
C	**5.24804927**	**-2.24906700**	**0.75669246**
H	**5.98869432**	**-2.34711988**	**1.54735554**
C	**-4.63435175**	**-3.48853457**	**-0.43408848**
H	**-5.15719026**	**-4.43975774**	**-0.35454052**
F	**-1.87541008**	**2.38198892**	**3.78484029**
C	**7.74335358**	**2.09611998**	**-1.16594776**

H	**8.81730224**	**2.24068733**	**-1.26785732**
C	**-3.63528419**	**-3.32223303**	**-1.39063075**
H	**-3.37316621**	**-4.13701344**	**-2.06271198**
C	**-7.51461846**	**1.82304287**	**-1.55830937**
H	**-8.58768054**	**1.92928443**	**-1.70669494**
C	**7.12590814**	**1.00117163**	**-1.76641960**
H	**7.71238925**	**0.29421303**	**-2.34972695**
C	**-6.81988631**	**2.75077086**	**-0.78476594**
H	**-7.34757244**	**3.58390568**	**-0.32463835**
C	**4.03128381**	**-3.19592589**	**-1.10084228**
H	**3.82375620**	**-4.02778018**	**-1.77096079**
C	**4.99020190**	**-3.31946084**	**-0.09774318**
H	**5.53582994**	**-4.25337884**	**0.02132813**
C	**-1.00312118**	**0.69346192**	**2.32812968**
F	**0.21797265**	**1.86766699**	**4.02718491**
C	**-0.77741468**	**1.98626225**	**3.13334788**
F	**-0.43209196**	**2.98020877**	**2.27440412**

Table S3. Found structures based on the model scheme in CSD

CSD Code	Interactions	**References**
FIDBEA	Intramolecular n → π* interaction	R.Kia, V.Mirkhani, A.Deak, A.Kalman (2005), **Acta Crystallogr**.,Sect.E:Struct.Rep.Online ,61,m566.
HATNAS	Intramolecular n → π* interaction	J.Bravo, J.A.Castro, E.Freijanes, S.Garcia-Fontan, E.M.Lamas,P.Rodriguez-Seoane (2005) **Z.Anorg.Allg.Chem**. ,631, 2067.
HATPAU	Intramolecular n → π* interaction	J.Bravo, J.A.Castro, E.Freijanes, S.Garcia-Fontan, E.M.Lamas, P.Rodriguez-Seoane (2005) **Z.Anorg.Allg.Chem**. ,631, 2067.
IVAKIB	Intramolecular n → π* interaction	D.Sieh, C.P.Kubiak (2016) **Chem.-Eur.J**. ,22, 10638.
ODIQIC	Intramolecular n → π* interaction	R.Kia, V.Mirkhani, A.Kalman, A.Deak (2007) **Polyhedron**, 26,2906.
RODWIR	**Intra- and intermolecular n → π* interactions**	**R.Kia, H.-K.Fun (2008) Acta Crystallogr.,Sect.E:Struct.Rep.Online ,64,m1314.**
RURZEK	Intramolecular n → π* interaction	S.Bolano, J.Bravo, J.Castro, S.Garcia-Fontan, M.C.Rodriguez (2009) **Polyhedron** ,28,2431.
YIBRIL	**Intra- and intermolecular n → π* interactions**	**R.Kia, V.Mirkhani, A.Kalman, A.Deak (2007) Polyhedron, 26,1711.**

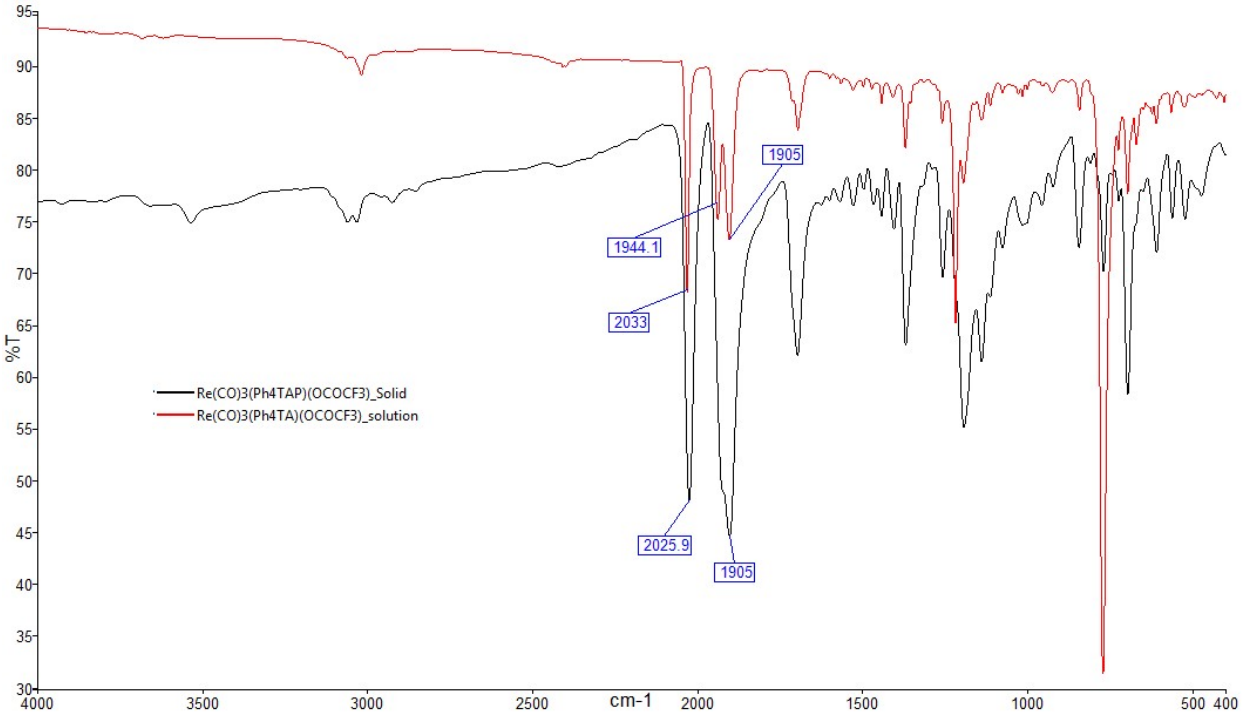


Fig. S1. FT-IR spectra of $[Re(CO)_3(CH_3CN)_2(OCOCF_3)]$ complex in solid (black) and solution (red) phases.

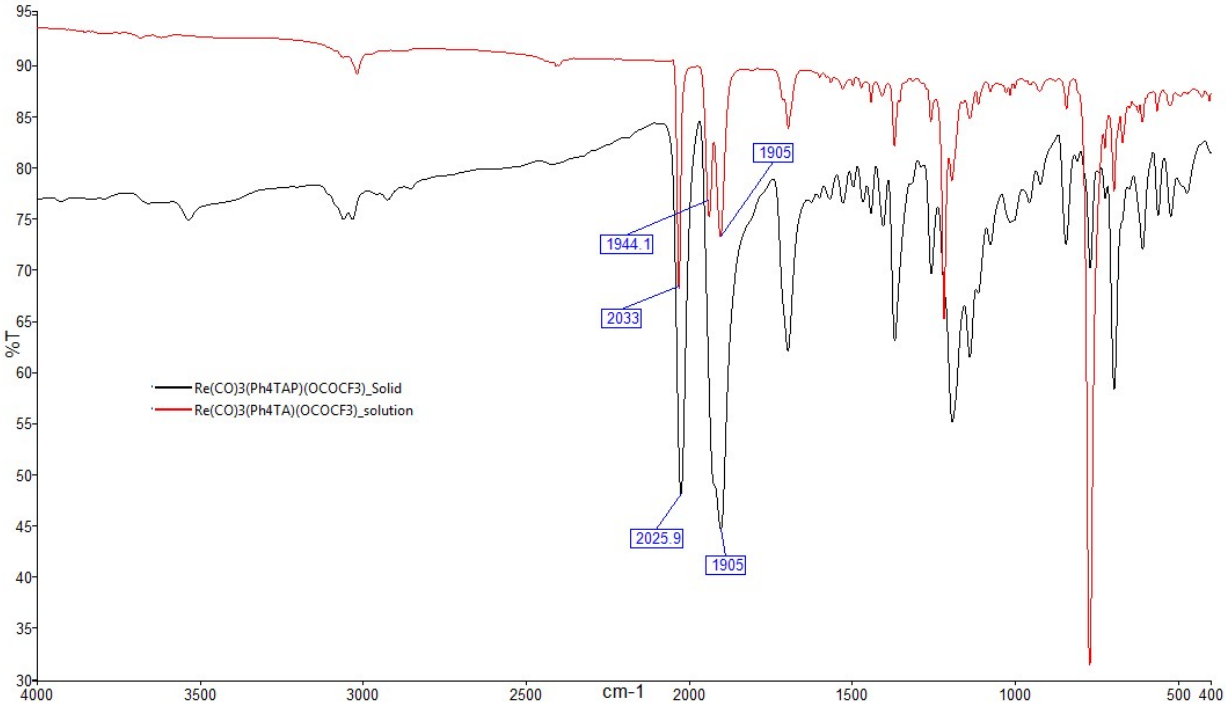


Fig. S2. FT-IR spectra of $[Re(CO)_3(Ph_4TAP)_2(OCOCF_3)]$ complex in solid (black) and solution (red) phases.

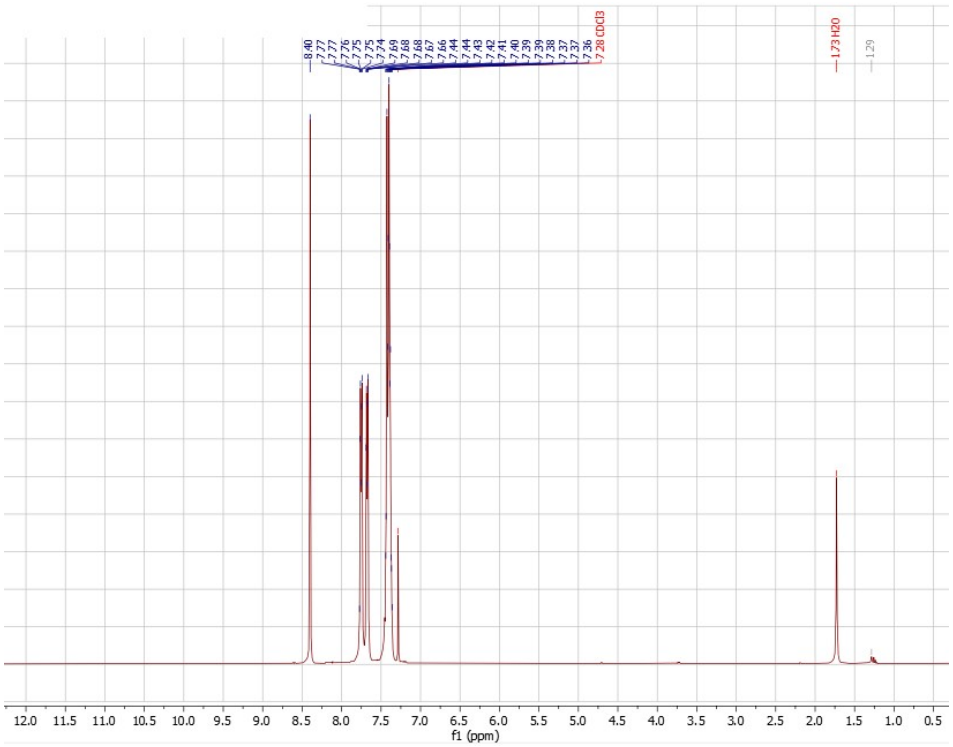


Figure S3. ^{1}H NMR (500 MHz) spectrum of Ph_4TAP in $CDCl_3$.

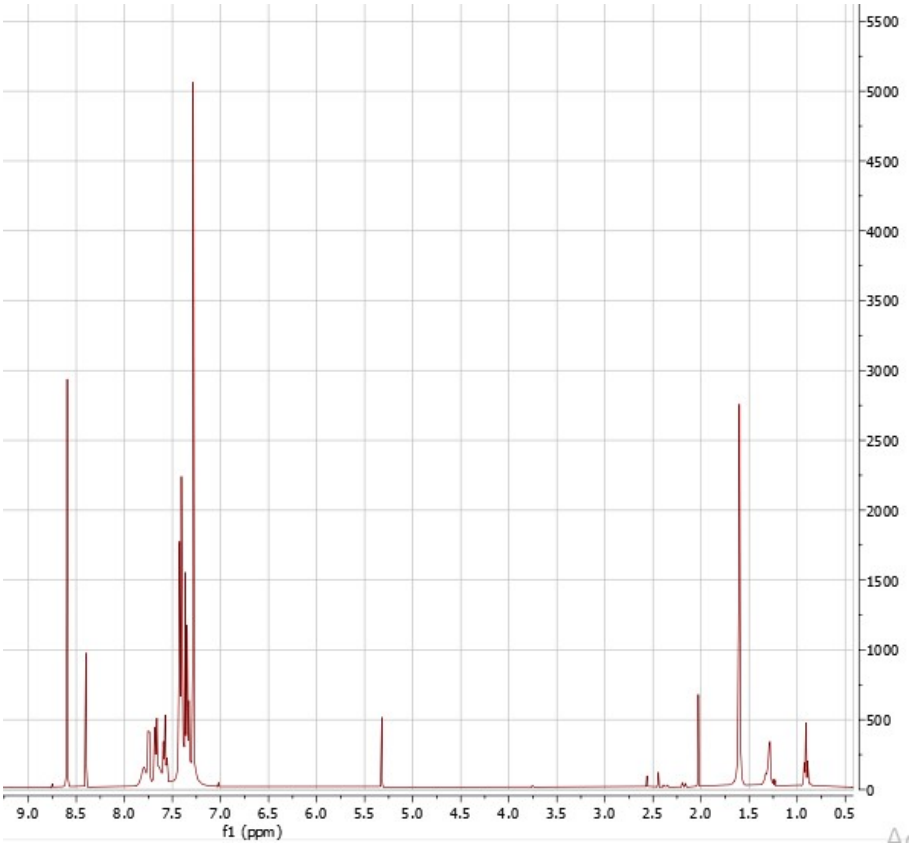


Figure S4. ^{1}H NMR spectrum of the complex.

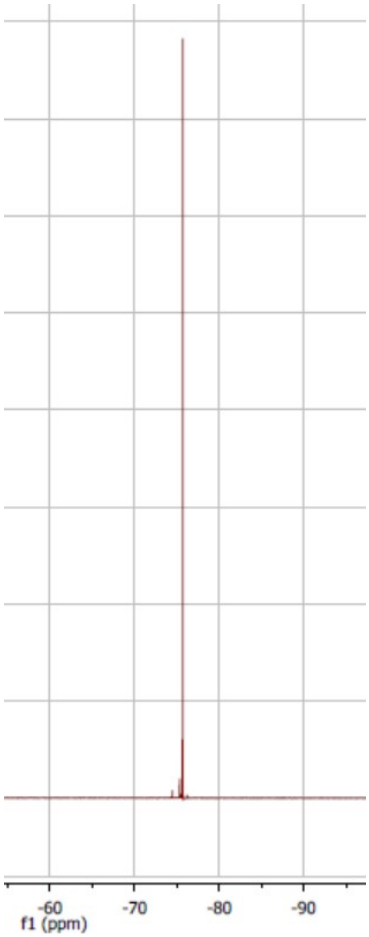
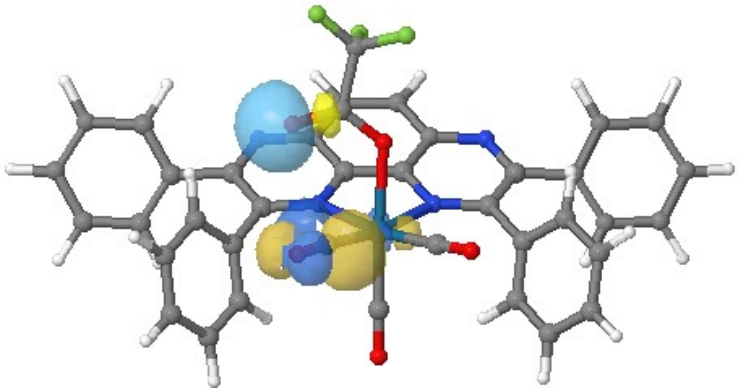
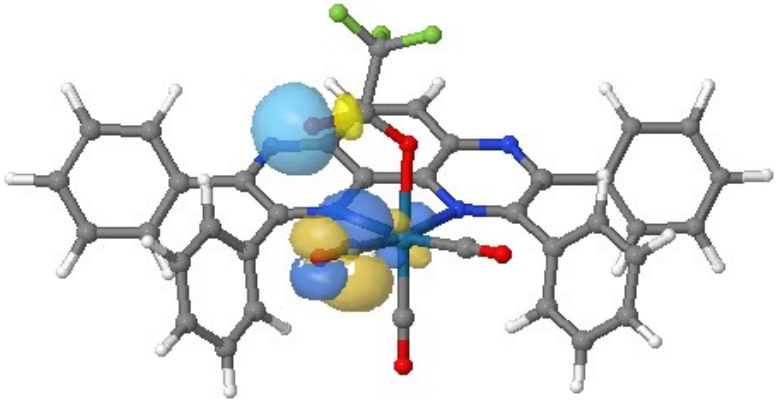


Figure S5. ^{19}F NMR spectrum of the complex.



(a)



(b)

Figure S6. The intramolecular n → π* interactions (donor-acceptor orbitals) involved in $n_s(O5) \rightarrow \pi^*_{\perp,\parallel}$ (C2≡O2), and $n_p(O5)\cdots\sigma^*(C2{\equiv}O2)$.

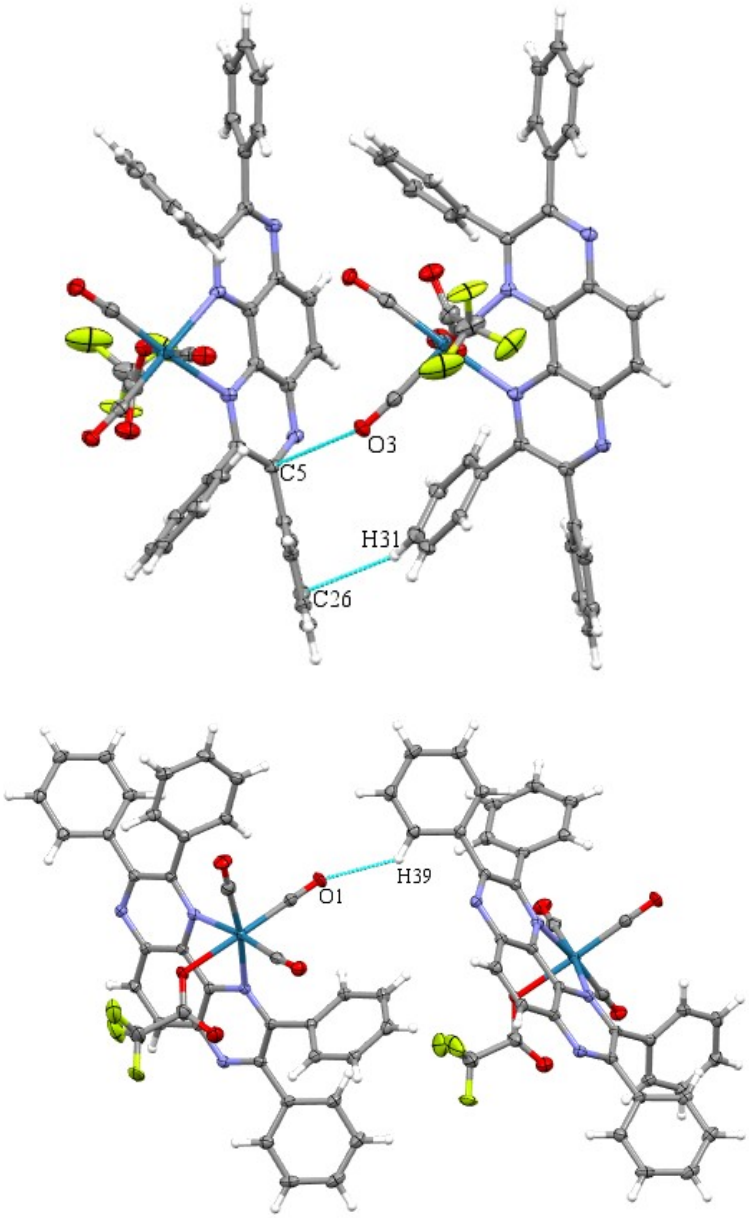


Figure S7. The crystallographic dimer associates of the complex for energy decomposition analysis (EDA).

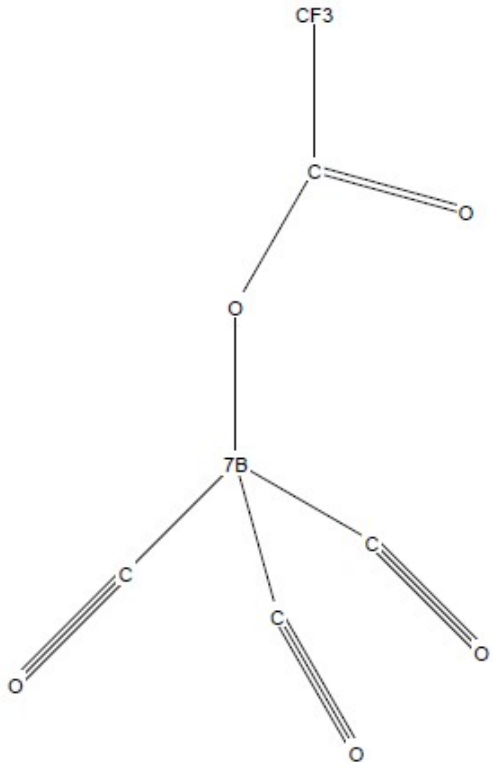


Fig. S8. Searched model scheme by CSD version 5.42 updates (Feb 2021) for group M^{7B}(tricarbonyl)(trifluoroacetate) complexes.