

Supplementary information

Table S1

Most significant bonding interactions (Å) for [Cs][Fe₄(CO)₁₂(μ₄-η²-CO)(μ-H)].

Fe(1)-Fe(2) 2.644(4)	Fe(1)-Fe(3) 2.598(4)	Fe(2)-Fe(3) 2.602(4)
Fe(2)-Fe(4) 2.658(4)	Fe(3)-Fe(4) 2.628(4)	
Fe(1)-C(1) 1.876(18)	Fe(1)-C(2) 1.77(2)	Fe(1)-C(3) 1.81(2)
Fe(1)-C(4) 1.78(2)	Fe(1)-C(8) 2.50(2)	Fe(2)-C(1) 2.132(18)
Fe(2)-C(5) 1.80(2)	Fe(2)-C(6) 1.79(2)	Fe(2)-C(7) 1.82(2)
Fe(3)-C(1) 2.095(18)	Fe(3)-C(8) 1.75(2)	Fe(3)-C(9) 1.80(2)
Fe(3)-C(10) 1.79(2)	Fe(4)-C(1) 2.132(18)	Fe(4)-C(11) 1.77(2)
Fe(4)-C(12) 1.81(2)	Fe(4)-C(13) 1.84(2)	
Fe(2)-H(1) 1.43(6)	Fe(3)-H(1) 1.43(6)	Fe(4)-O(1) 1.990(13)
C(1)-O(1) 1.22(2)	C(2)-O(2) 1.14(3)	C(3)-O(3) 1.12(2)
C(4)-O(4) 1.11(2)	C(5)-O(5) 1.15(2)	C(6)-O(6) 1.14(2)
C(7)-O(7) 1.11(2)	C(8)-O(8) 1.17(2)	C(9)-O(9) 1.11(2)
C(10)-O(10) 1.13(2)	C(11)-O(11) 1.15(2)	C(12)-O(12) 1.12(3)
C(13)-O(13) 1.11(3)		
O(1)···Cs(1) 3.121(13)	O(3)···Cs(1) 3.179(18)	O(6)···Cs(1) 3.136(16)
O(8)···Cs(1) 3.026(16)	O(10)···Cs(1) 3.179(16)	O(11)···Cs(1) 3.133(14)

Table S2

Most significant bonding interactions (Å) for [K][Fe₄(CO)₁₂(μ₄-η²-CO)(μ-H)].

Fe(1)-Fe(2) 2.6173(17)	Fe(1)-Fe(3) 2.5910(13)	Fe(1)-Fe(4) 2.6322(13)
Fe(2)-Fe(3) 2.6507(15)	Fe(2)-Fe(4) 2.6666(12)	
Fe(1)-C(1) 2.055(3)	Fe(1)-C(8) 1.781(3)	Fe(1)-C(9) 1.803(3)
Fe(1)-C(10) 1.785(3)	Fe(2)-C(1) 2.115(3)	Fe(2)-C(5) 1.791(3)
Fe(2)-C(6) 1.783(3)	Fe(2)-C(7) 1.786(3)	Fe(3)-C(1) 1.855(3)
Fe(3)-C(2) 1.753(3)	Fe(3)-C(3) 1.792(3)	Fe(3)-C(4) 1.820(3)
Fe(4)-C(1) 2.148(3)	Fe(4)-C(11) 1.767(3)	Fe(4)-C(12) 1.814(4)
Fe(4)-C(13) 1.815(4)		
Fe(1)-H(1) 1.69(4)	Fe(2)-H(1) 1.57(4)	Fe(4)-O(1) 2.011(2)
C(1)-O(1) 1.272(3)	C(2)-O(2) 1.151(4)	C(3)-O(3) 1.141(4)

C(4)-O(4) 1.148(4)	C(5)-O(5) 1.148(4)	C(6)-O(6) 1.150(4)
C(7)-O(7) 1.139(4)	C(8)-O(8) 1.153(4)	C(9)-O(9) 1.143(4)
C(10)-O(10) 1.164(4)	C(11)-O(11) 1.155(4)	C(12)-O(12) 1.137(4)
C(13)-O(13) 1.139(4)		
K(1)···O(10) 2.748(3)	K(1)···O(4) 2.873(3)	K(1)···O(6) 2.926(3)
O(1)···K(1) 2.942(3)		

Table S3

Most significant bonding interactions (Å) in the $[\text{Fe}(\text{dmf})_4]\{[\text{Fe}_4(\text{CO})_{12}(\mu_4\text{-}\eta^2\text{-CO})(\mu\text{-H})]\}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ salt.

First cluster

Fe(2)-Fe(4) 2.6015(18)	Fe(5)-O(13) 1.998(5)	Fe(8)-Fe(9) 2.599(2)
Fe(2)-Fe(3) 2.6219(17)	Fe(3)-H(1) 1.53(4)	Fe(6)-C(21) 1.801(13)
Fe(3)-Fe(4) 2.6045(19)	Fe(4)-H(1) 1.53(4)	Fe(6)-C(22) 1.772(11)
Fe(3)-Fe(5) 2.6428(18)	C(1)-O(1) 1.153(11)	Fe(6)-C(23) 1.677(17)
Fe(4)-Fe(5) 2.6099(18)	C(2)-O(2) 1.146(11)	Fe(6)-C(33) 2.097(13)
Fe(4)-C(7) 1.776(10)	C(3)-O(3) 1.161(11)	Fe(7)-C(26) 1.776(11)
Fe(4)-C(8) 1.766(11)	C(4)-O(4) 1.138(10)	Fe(7)-C(25) 1.772(11)
Fe(4)-C(9) 1.770(9)	C(5)-O(5) 1.154(11)	Fe(7)-C(24) 1.778(10)
Fe(4)-C(13) 2.096(8)	C(6)-O(6) 1.157(11)	Fe(7)-C(33) 2.065(10)
Fe(2)-C(1) 1.768(10)	C(7)-O(7) 1.140(10)	Fe(8)-C(29) 1.773(10)
Fe(2)-C(2) 1.753(10)	C(8)-O(8) 1.166(11)	Fe(8)-C(28) 1.774(10)
Fe(2)-C(3) 1.821(10)	C(9)-O(9) 1.147(11)	Fe(8)-C(27) 1.794(10)
Fe(2)-C(13) 1.833(8)	C(10)-O(10) 1.164(11)	Fe(8)-C(33) 2.052(10)
Fe(3)-C(4) 1.797(10)	C(11)-O(11) 1.153(11)	Fe(9)-C(32) 1.772(12)
Fe(3)-C(5) 1.777(10)	C(12)-O(12) 1.152(11)	Fe(9)-C(31) 1.793(12)
Fe(3)-C(6) 1.779(10)	C(13)-O(13) 1.269(9)	Fe(9)-C(33) 1.857(14)
Fe(3)-C(13) 2.105(9)		Fe(9)-C(30) 1.872(14)
Fe(5)-C(10) 1.739(9)	Second cluster	Fe(6)-O(33) 2.201(7)
Fe(5)-C(12) 1.796(10)	Fe(6)-Fe(7) 2.631(2)	Fe(7)-H(2) 1.65(5)
Fe(5)-C(11) 1.802(10)	Fe(6)-Fe(8) 2.632(2)	Fe(8)-H(2) 1.65(5)
Fe(5)-C(13) 2.171(8)	Fe(7)-Fe(8) 2.5900(18)	C(21)-O(21) 1.127(12)
	Fe(7)-Fe(9) 2.5965(19)	C(22)-O(22) 1.149(11)

C(23)-O(23)	1.191(16)	N(4)-C(72)	1.424(12)	N(4)-
C(24)-O(24)	1.143(11)	C(73)	1.463(12)	
C(25)-O(25)	1.144(11)			
C(26)-O(26)	1.160(11)			
C(27)-O(27)	1.129(11)			
C(28)-O(28)	1.160(11)			
C(29)-O(29)	1.146(11)			
C(30)-O(30)	1.104(13)			
C(31)-O(31)	1.144(11)			
C(32)-O(32)	1.156(12)			
C(33)-O(33)	1.189(11)			

The [Fe(dmf)₄]²⁺ cation

Fe(1)-O(13)	2.271(5)
Fe(1)-O(33)	2.283(6)
Fe(1)-O(71)	2.083(6)
Fe(1)-O(51)	2.054(6)
Fe(1)-O(41)	2.084(6)
Fe(1)-O(61)	2.099(6)
C(41)-N(1)	1.320(12)
O(41)-C(41)	1.222(11)
N(1)-C(42)	1.446(12)
N(1)-C(43)	1.463(12)
O(51)-C(51)	1.215(11)
C(51)-N(2)	1.323(12)
N(2)-C(53)	1.426(13)
N(2)-C(52)	1.465(13)
O(61)-C(61)	1.228(11)
C(61)-N(3)	1.306(12)
N(3)-C(62)	1.444(12)
N(3)-C(63)	1.456(12)
O(71)-C(71)	1.229(10)
C(71)-N(4)	1.307(11)

