Supplementary Material (ESI) for Dalton Transactions

Supporting information for:

Phosphine Induced Migratory CO Insertion into the Fe-CH_2 bond of the Organometallic Polymer, $-[(\eta^5\text{-}C_5H_4)Fe(CO)_2CH_2SiMe_2]_n-$ and Characterization of Model Iron Complexes

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Table S1. Crystal data and structure refinement parameters of 11 and 13

Identification code	**11**	**13**
Formula	$C_{44}H_{44}Fe_2O_4P_2$▪0.5(C_6H_6)	$C_{22}H_{32}Fe_2O_4P_2$
Formula weight	849.49	534.12
Crystal System	Monoclinic	Monoclinic
Space Group	C2/c	$P2_1/n$
a (Å)	18.989(7)	8.8837(7)
b (Å)	20.819(8)	11.7307(9)
c (Å)	20.946(8)	11.9300(9)
α (°)	90	90
β (°)	91.567(9)	90.048(2)
γ (°)	90	90
V **(Å^3)**	8278(5)	1243.25(17)
Z	8	2
ρ_{calc} (gcm^{-3})	1.363	1.427
μ(Mo K*α*) (mm^{-1})	0.821	1.320
F(000)	3544	556
T (K)	100(2)	298(2)
$2\theta_{max}$ (°), completeness (%)	53.30, 99.9	53.78,100.0
Index ranges: *-h +h, -k +k, -l +l*	-23 23, -26 26, -26 26	-11 11; -14 14; -15 15
Total number reflections	42561	13366
Independent reflections [R_{int}]	8706 [0.1531]	2681 [0.0270]
Refinement methods	Full-matrix least-squares on F^2	
Data/restraints/parameters	8706 / 107 / 527	2681 / 0 / 192
Goodness-of-fit on F^2	0.954	1.190
R_1 [I>2σ(I)]	0.0693	0.0465
Largest difference in Peak and hole (e.Å^{-3})	0.840 and -0.531	0.629 and -0.367

Table S2. Selected bond lengths [Å] and angles [°] for **11**.

11a		**11b**[a]	
Fe(1)-C(6)	1.741(5)	Fe(2)-C(6B)	1.730(6)
Fe(1)-C(7)	1.923(6)	Fe(2)-C(7B)	1.931(6)
Fe(1)-P(1)	2.1890(15)	Fe(2)-P(1B)	2.1901(16)
P(1)-C(9)	1.831(5)	P(1B)-C(9B)	1.826(5)
P(1)-C(15)	1.829(4)	P(1B)-C(15B)	1.820(5)
P(1)-C(21)	1.825(5)	P(1B)-C(21B)	1.833(5)
O(1)-C(6)	1.136(6)	O(1B)-C(6B)	1.160(6)
O(2)-C(7)	1.201(6)	O(2B)-C(7B)	1.214(7)
C(6)-Fe(1)-C(7)	91.9(2)	C(6B)-Fe(2)-C(7B)	95.6(3)
C(6)-Fe(1)-P(1)	93.49(17)	C(6B)-Fe(2)-P(1B)	93.44(19)
C(7)-Fe(1)-P(1)	93.19(17)	C(7B)-Fe(2)-P(1B)	91.49(18)
C(21)-P(1)-C(15)	101.9(2)	C(15B)-P(1B)-C(9B)	103.4(2)
C(21)-P(1)-C(9)	102.2(2)	C(15B)-P(1B)-C(21B)	102.5(2)
C(15)-P(1)-C(9)	102.0(2)	C(9B)-P(1B)-C(21B)	101.1(2)
C(21)-P(1)-Fe(1)	119.56(18)	C(15B)-P(1B)-Fe(2)	113.39(16)
C(15)-P(1)-Fe(1)	113.11(15)	C(9B)-P(1B)-Fe(2)	116.24(17)
C(9)-P(1)-Fe(1)	115.62(16)	C(21B)-P(1B)-Fe(2)	118.13(16)
O(1)-C(6)-Fe(1)	179.2(5)	O(1B)-C(6B)-Fe(2)	176.1(5)
O(2)-C(7)-Fe(1)	126.2(4)	O(2B)-C(7B)-Fe(2)	124.5(4)
C(8)-C(7)-Fe(1)	117.7(4)	C(8B)-C(7B)-Fe(2)	118.9(5)
C(6)-Fe(1)-P(1)-C(21)	-66.9(2)	C(6B)-Fe(2)-P(1B)-C(21B)	66.1(3)
C(7)-Fe(1)-P(1)-C(21)	25.3(3)	C(7B)-Fe(2)-P(1B)-C(21B)	-29.6(2)
C(6)-Fe(1)-C(7)-O(2)	133.1(6)	C(6B)-Fe(2)-C(7B)-O(2B)	-146.6(5)
C(6)-Fe(1)-C(7)-C(8)	-53.8(5)	C(6B)-Fe(2)-C(7B)-C(8B)	34.8(5)
Fe(1)-P(1)-C(9)-C(10)	-171.7(4)	Fe(2)-P(1B)-C(9B)-C(10B)	172.2(4)
Fe(1)-P(1)-C(9)-C(14)	10.2(5)	Fe(2)-P(1B)-C(9B)-C(14B)	-6.8(5)
Fe(1)-P(1)-C(15)-C(16)	78.4(4)	Fe(2)-P(1B)-C(15B)-C(16B)	-75.6(4)
Fe(1)-P(1)-C(15)-C(20)	-94.4(4)	Fe(2)-P(1B)-C(15B)-C(20B)	100.2(4)
Fe(1)-P(1)-C(21)-C(22)	61.0(4)	Fe(2)-P(1B)-C(21B)-C(22B)	-66.4(4)
P(1)-C(21)-C(22)-C(22)#1	165.8(2)	P(1B)-C(21B)-C(22B)-C(22B)#3	-171.8(4)

[a]With the exception of Iron, Fe(2), all non-H atom labels for conformer 11B have added the tag **B**.

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+1/2, #2 -x+1,y,-z+1/2, #3 -x,-y+1,-z+1

Table S3. Selected bond lengths [Å] and angles [°] for **13**.

Fe(1)-C(6)	1.735(3)	C(10)-P(1)-C(9)	100.40(19)
Fe(1)-C(7)	1.949(3)	C(11)-P(1)-Fe(1)	116.21(15)
Fe(1)-P(1)	2.1744(8)	C(10)-P(1)-Fe(1)	116.73(16)
O(1)-C(6)	1.138(4)	C(9)-P(1)-Fe(1)	116.37(13)
O(2)-C(7)	1.213(4)	O(1)-C(6)-Fe(1)	176.4(3)
P(1)-C(10)	1.816(4)	O(2)-C(7)-Fe(1)	123.1(2)
P(1)-C(11)	1.803(4)	C(8)-C(7)-Fe(1)	121.4(3)
P(1)-C(9)	1.842(3)	C(9)#3-C(9)-P(1)	114.5(3)
C(6)-Fe(1)-C(7)	97.16(14)	Fe(1)-P(1)-C(9)-C(9)#3	-54.3(4)
C(6)-Fe(1)-P(1)	92.05(10)	C(6)-Fe(1)-C(7)-C(8)	-20.1(4)
C(7)-Fe(1)-P(1)	88.15(9)	C(6)-Fe(1)-C(7)-O(2)	163.7(3)
C(11)-P(1)-C(10)	101.8(2)	C(6)-Fe(1)-P(1)-C(9)	78.11(16)
C(11)-P(1)-C(9)	102.8(2)	C(7)-Fe(1)-P(1)-C(9)	175.21(16)

Symmetry transformations used to generate equivalent atoms: #3 -x,-y+1,-z+1

Table S4 Geometrical parameters for intermolecular HB's in the crystal structure of compound **13**.

D-H···A	r(D-H)	R(D-H···A)	R(D···A)	∠(D-H···A	∠(X-A···H)
C5-H5···O2#4	0.84(5)	2.43(5)	3.254(5)	167(4)	118
C11-H11B···O2#5	0.92(3)	2.57(4)	3.475(5)	166(3)	148
C2-H2···O1#6	1.01(7)	2.83(6)	3.728(5)	148(5)	146

Symmetry transformations used to generate equivalent atoms:
#4 -1/2+x,1/2-y,-1/2+z, #5 1/2-x,1/2+y,3/2-z, #6 -1/2+x,1/2-y,1/2+z

Table S5: Geometrical parameters for HB's in the crystal structure of compound **11**.

D-H···A	Type	r(D-H)	R(D-H···A)	R(D···A)	∠(D-H···A	∠(X-A···H)
C16-H16···O2	Intra	0.95	2.71	3.425(7)	132.2	123.4
C16B-H16B···O2B	Intra	0.95	2.48	3.232(6)	135.9	124.7
C18-H18···O1#7	Inter	0.95	2.67	3.291(6)	123.4	134.7
C3B-H3B···O2	Inter	0.95	2.43	3.325(7)	156.9	176.9
[a]C25_a-H25_a···O2B#8	Inter	0.95	2.32	3.168(13)	149.0	149.3
C21B-H21D···Cp	Inter	0.99	2.88	3.817	157.9	

[a] Belongs to the benzene molecule. #7 x, -y, z+1/2, #8 -x+1/2, -y+1/2, -z+1

Table S6: Geometrical parameters for intermolecular parallel (P) and T-stacking interactions for **11**.

R1	H	R2	r(cent···cent)/ r(H···cent)	R(D···A)	Slip-angle/ Dihedral angle[c]
[a]C15	--	C15#9	4.506	4.073	25
Cp	H2	C15B#8	2.653		44
Bz	H33	C9B#10	3.009		72

#8 -x+1/2, -y+1/2, -z+1; #9 -x, -y, -z+1; #10 x+1/2, y-1/2, z.

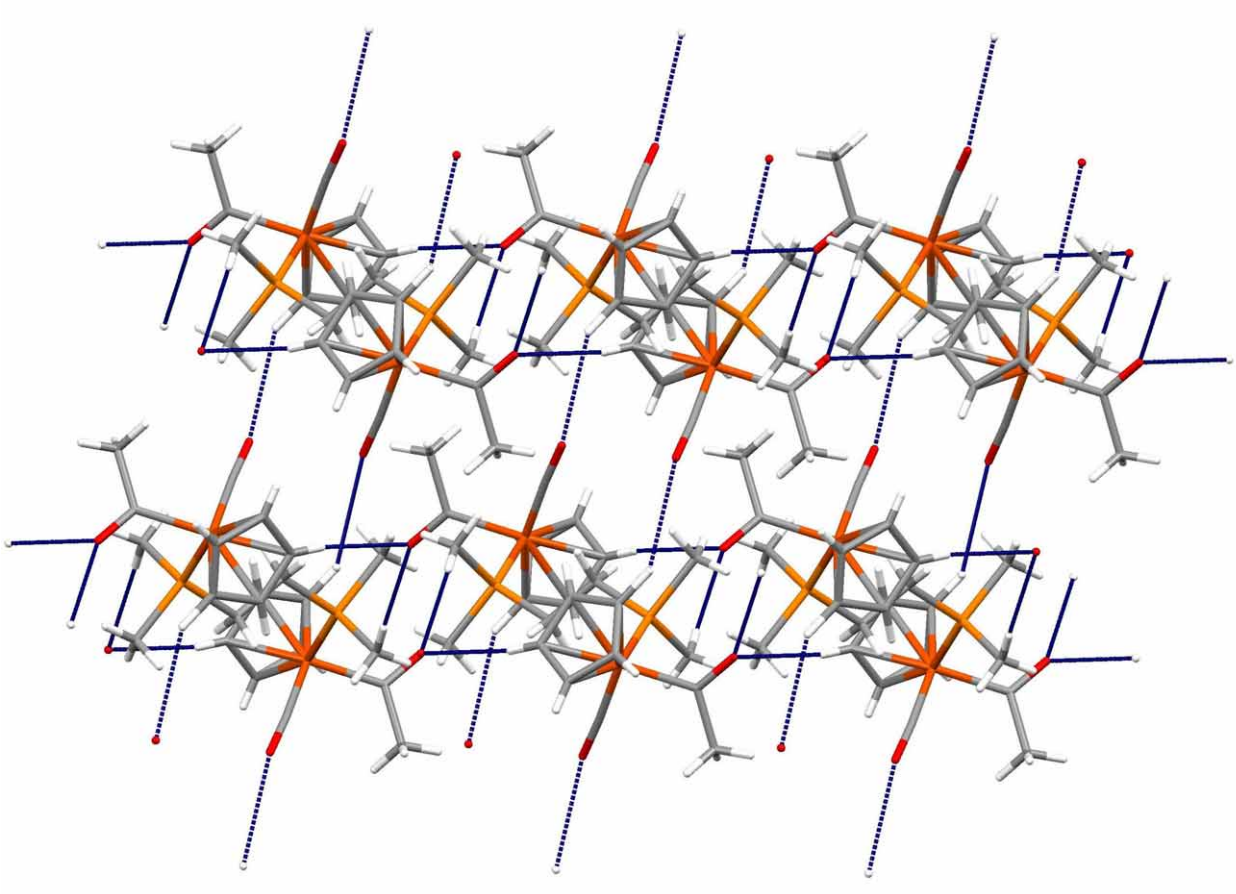


Figure S1 Lateral view of two layers in the crystal packing of **13** with the HB that interlink them.

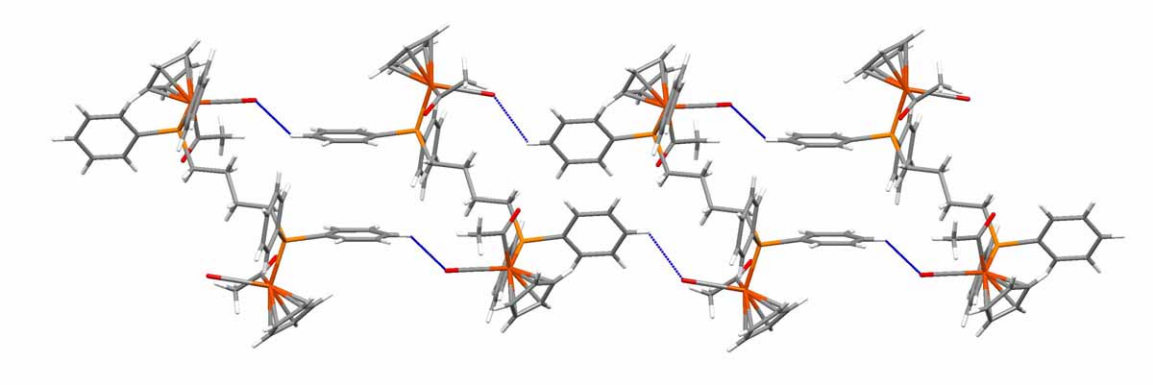


Figure S2: The ribbons generated by **11A** via CO···H interactions

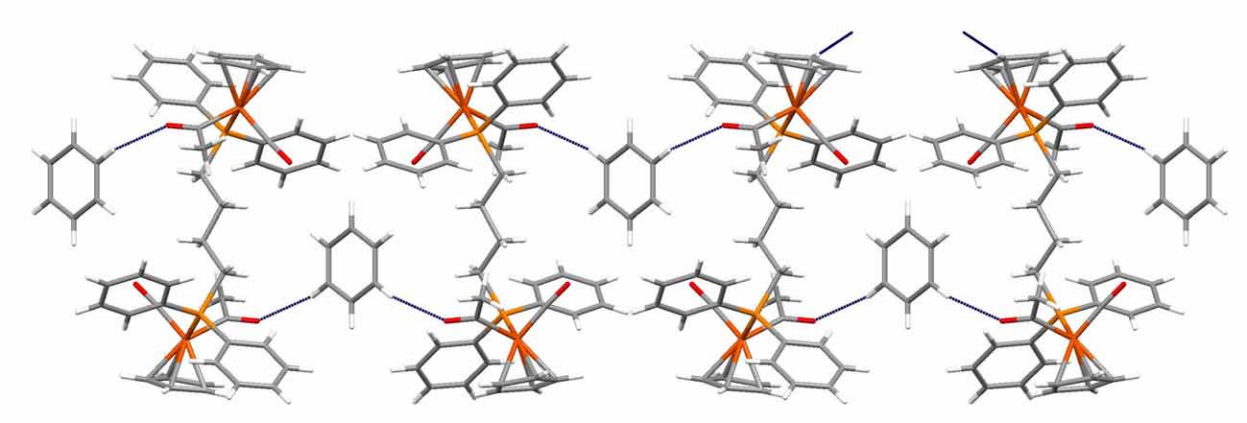
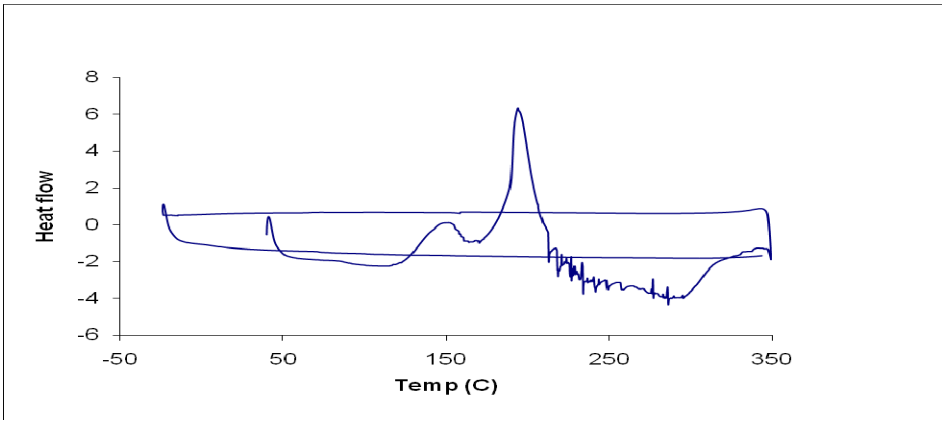


Figure S3 Ribbon formed by **11B** through interaction with the benzene. Only one position of the benzene is drawn for clarity. The second position is in the same place, but with a rotation of 30° in the axis orthogonal to its molecular plane.

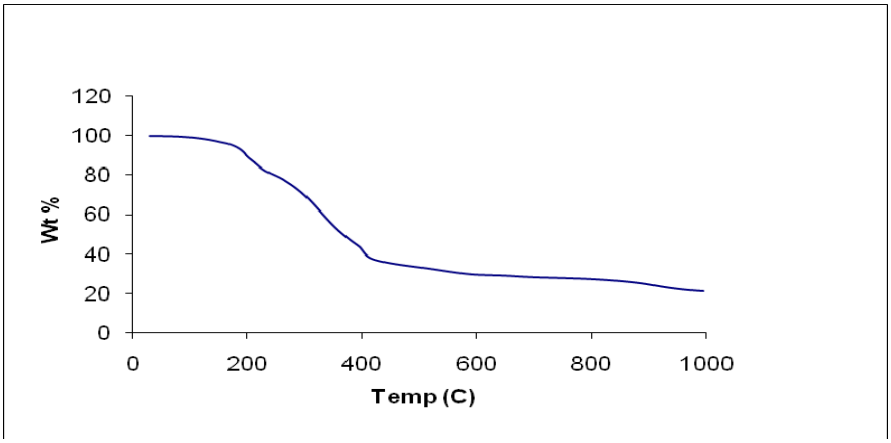
DSC Graph of -{[(η^5-C_5H_4)Fe(CO)C(O)CH_2SiMe_2]$_2$$PPh_2$$(CH_2)_3$$PPh_2$}$_n$- (6).

Peaks: (1) 144°C, (2) 193°C



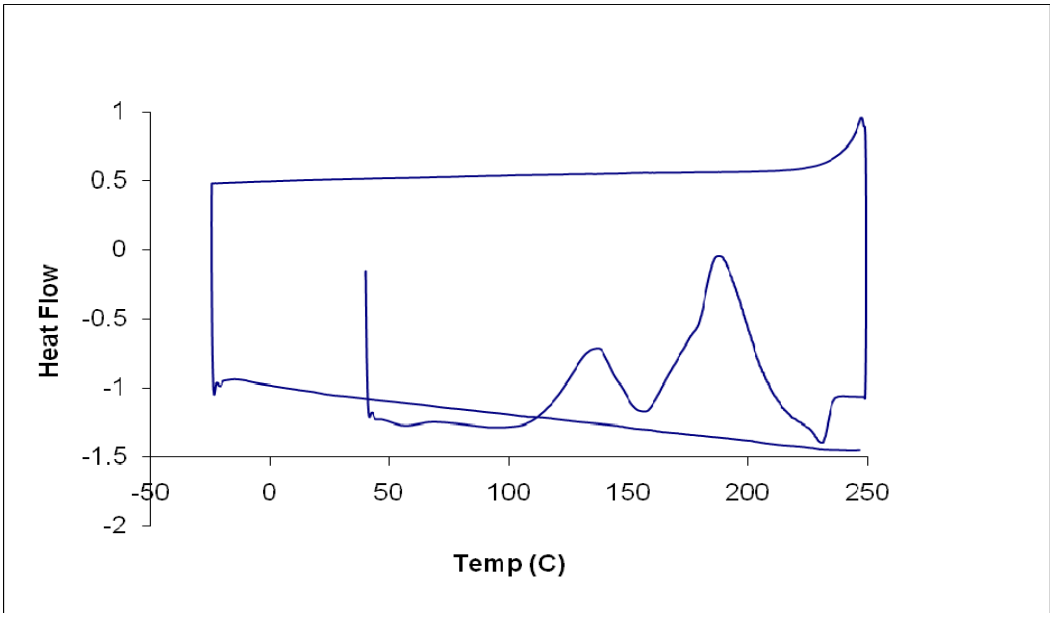
TGA graph of -{[(η^5-C_5H_4)Fe(CO)C(O)CH_2SiMe_2]$_2$$PPh_2$$(CH_2)_3$$PPh_2$}$_n$- (6).

Degradation points: (1) 160°C; (2) 230°C



DSC graph of -[(η^5-C_5H_4)Fe(CO)(PPh_3)C(O)CH_2SiMe_2]$_n$- (4)

Exothermic peaks: (1) 130°C, (2) 184°C; Endothermic peak, 225°C



TGA graph of -[(η^5-C_5H_4)Fe(CO)(PPh_3)C(O)CH_2SiMe_2]$_n$- (4)

Degradation points: (1) 140^{o}C; (2) 230^{o}C