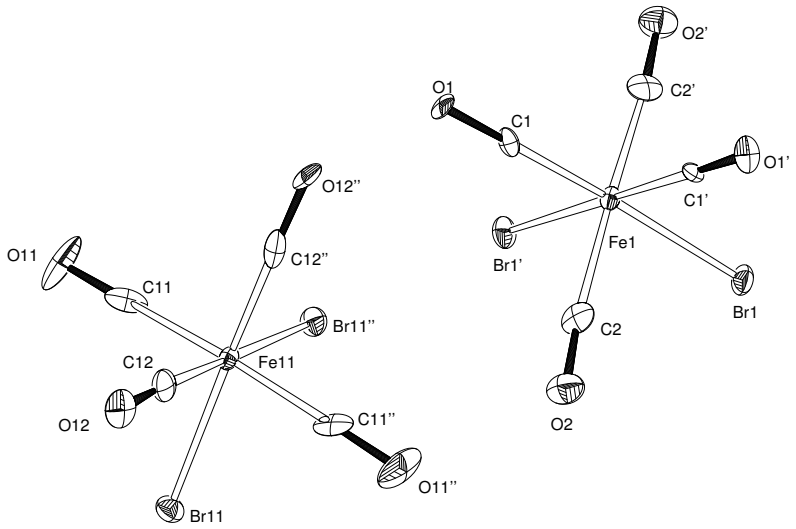

Figure S1: ORTEP representation of one of the two independent molecules of $Fe(CO)_4Br_2$ in the unit cell showing 50 % probability ellipsoids.

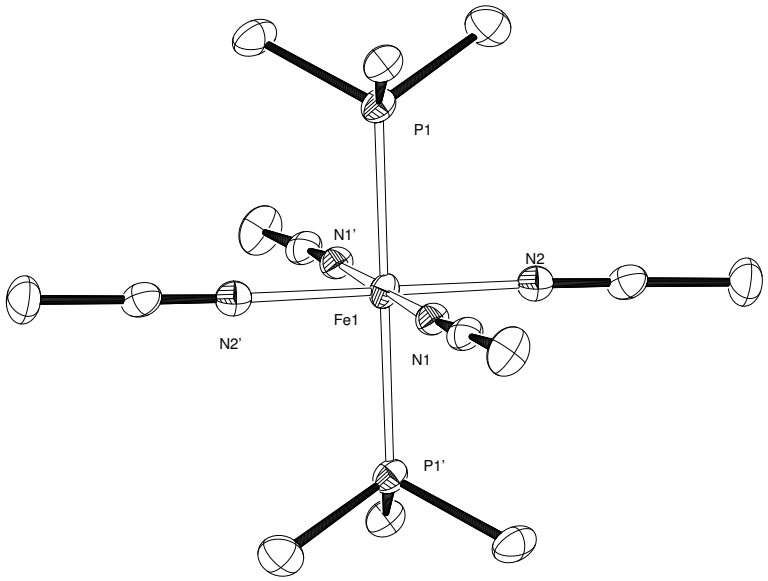

Figure S2: ORTEP representation of cation of $[Fe(MeCN)_4(PMe_3)_2][(Br_3Fe)_2O]$ showing 50 % probability ellipsoids; hydrogen atoms have been omitted for clarity.

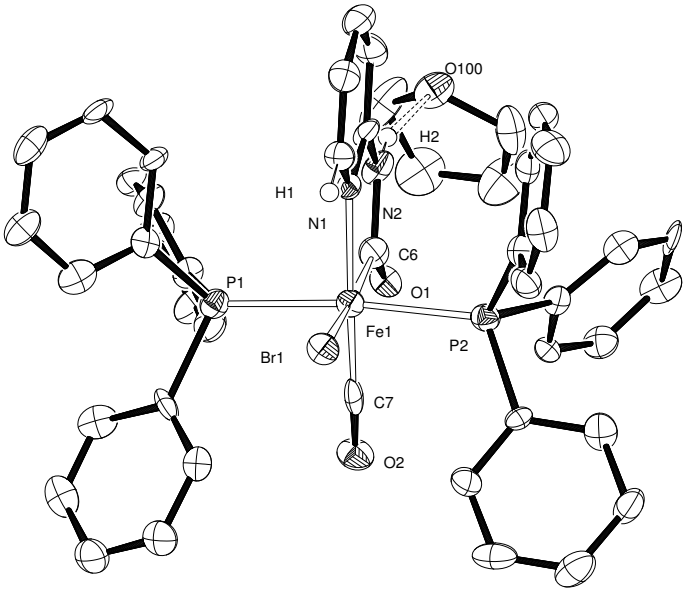

Figure S3: ORTEP representation of structure of $Fe(CO)(PPh_3)_2(Br)(C_6H_5N_2CO)\cdot THF$ showing 50 % probability ellipsoids; hydrogen atoms except for H(2) have been omitted for clarity.

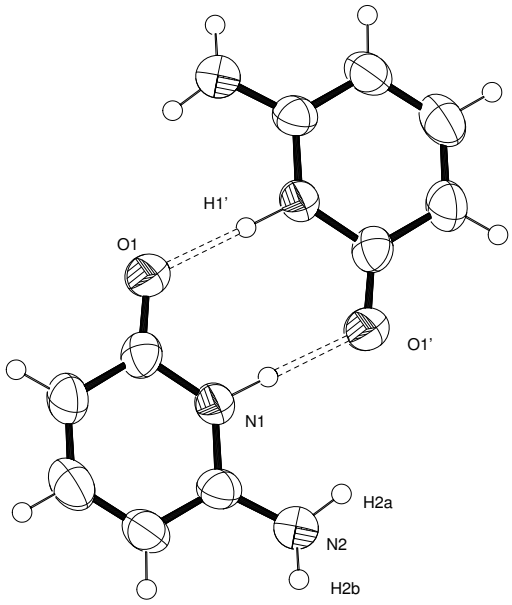

Figure S4: ORTEP representation of the a dimer of one of the two independent molecules of **4a′** · H_2O showing 50 % probability ellipsoids; the hydrogen-bonded water molecule has been omitted for clarity.

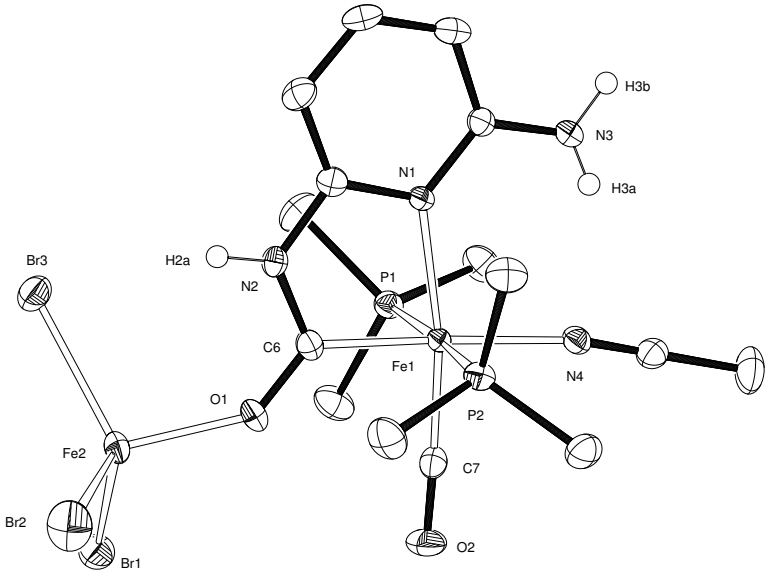

Figure S5: ORTEP representation of structure of $Fe(CO)(PMe_3)_2C_6H_6N_3CO(FeBr_3)(MeCN)$ showing 50 % probability ellipsoids; hydrogen atoms except for those on nitrogen have been omitted for clarity.

Table S1: Summary of crystallographic data for supporting structures

	$[Fe(MeCN)_4(PMe_3)_2][(Br_3Fe)_2O]$	$Fe(CO)(PPh_3)_2(Br)(C_6H_5N_2CO)\cdot THF$	**4a**	$Fe(CO)(PMe_3)_2\{C_6H_6N_3CO(FeBr_3)\}(MeCN)$
Formula	$C_{14}H_{30}FeN_4P_2,Br_6Fe_2O$	$C_{43}H_{35}BrFeN_2O_2P_2,C_4H_8O$	$C_5H_6N_2O,_{0\cdot5}(H_2O)$	$C_{15}H_{27}Br_3Fe_2N_4O_2P_2$
M	979.37	881.53	119.13	708.78
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	10.1505(3)	11.061(5)	4.8603(6)	10.0743(3)
b/Å	12.4119(4)	12.238(5)	9.3209(11)	13.2511(3)
c/Å	13.1800(4)	15.979(5)	13.5944(19)	18.8476(5)
α/°	90	69.894(5)	97.673(10)	90
β/°	110.162(2)	86.657(5)	92.141(10)	92.460(2)
γ/°	90	77.321(5)	609.59(13)	90
V/Å^3	1558.76(8)	1981.3(14)	609.59(13)	2513.75(12)
T/K	120(2)	120(2)	298(2)	140(2)
Z	2	2	4	4
R_{int}	0.045	0.138	0.055	0.035
$R_1[I > 2\sigma_I]$	0.038	0.089	0.054	0.026
wR_2[all data]	0.079	0.173	0.117	0.056