Supplementary Material (ESI) for Chemical Communications

Supplementary Information

"Divergent Lewis- and Bronsted-Basicities of Diiron Dithiolates:
Remarkable Effects of Ethane- vs. Propanedithiolate"

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I. Preparative Work

General: Unless otherwise indicated, reactions were conducted using Schlenk techniques at room temperature. Chemicals were purchased from Aldrich, and solvents were either HPLC-grade from an alumina filtration system or distilled under nitrogen over an appropriate drying agent. NMR spectra were recorded at room temperature on a Varian Mercury 500 MHz spectrometer. NMR chemical shifts are quoted in ppm (δ scale); spectra are referenced to TMS for ^{1}H, $^{13}C\{^{1}H\}$ and 85% H_3PO_4 for $^{31}P\{^{1}H\}$. FT-IR spectra were recorded on a Mattson Infinity Gold FTIR spectrometer. $AlBr_3$ (Aldrich) and $B(C_6F_5)_3$ (Strem) were used as received but handled in a glovebox. CD_2Cl_2 was dried over P_2O_5, distilled onto CaH_2, and then redistilled.

$Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$, 1. A solution of 0.50 g (0.702 mmol) of **1**$(CO)_4$ in 50 mL toluene was treated with 0.28 g (0.702 mmol) of dppv in 10 mL toluene. The mixture was photolyzed with a 100 W UV immersion lamp, λmax = 356 nm (Spectroline), until the conversion was complete (~12 h) as indicated by IR spectroscopy. The solvent was

removed in vacuum, and product was extracted into 10 mL of CH_2Cl_2. The product precipitated as an olive-green powder upon the addition of 50 mL of hexanes. Crystals were grown by slow diffusion of hexanes into a CH_2Cl_2 solution. Yield: 0.56 g (76%). ^{1}H NMR (CD_2Cl_2): δ 8.1 – 7.2 (m, 40H, P(C_6H_5)$_2$), 4.3 (s, 2H, P(C*H*)$_2$P), 1.2 (s, 4H, S(C*H*$_2$)$_2$S). ^{31}P NMR (CD_2Cl_2): δ 93.2 at 20 °C; 95.8 (J_{P-P} = 21 Hz), 92.2 (J_{P-P} = 22 Hz) at -60 °C. IR (CH_2Cl_2): ν_{CO} = 1888, 1868 cm^{-1}. FD-MS: m/z = 1052.2 ([$Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$]). Anal. Calcd for $C_{56}H_{48}Fe_2O_2P_4S_2$ (found): C, 63.87 (63.48); H, 4.60 (4.54).

$Fe_2(S_2C_3H_6)(CO)_2(dppv)_2$, **2** was prepared similarly. Yield: 0.52 g (72%). ^{1}H NMR (CD_2Cl_2): δ 8.0 – 7.3 (m, 40H, P(C_6H_5)2), 4.3 (s, 2H, P(C*H*)$_2$P), 1.2 (s, 4H,SC*H*$_2$CH$_2$), 0.9 (m, 2H, SCH$_2$CH$_2$). ^{31}P NMR (CD_2Cl_2): δ 90.8, 79.8 at 20 °C, 97.0, 88.5, 80.9 at -80 °C. IR (CH_2Cl_2): ν_{CO} = 1888, 1868 cm^{-1}. FD-MS: m/z = 1066.6, ([$Fe_2(S_2C_3H_6)(CO)_2(dppv)_2$]). Anal. Calcd for $C_{57}H_{50}Fe_2O_2P_4S_2$ (found): C, 64.18 (63.42); H, 4.72 (4.65).

Reaction of 1 with $AlBr_3$. A J-Young NMR tube was charged with 15.0 mg (0.0142 mmol) of **1** and 4.0 mg (0.0142 mmol) of $AlBr_3$. The tube was evacuated and cooled to 78K to allow ~2 mL of CD_2Cl_2 to be distilled onto the mixture. The solution was allowed to warm up in a -40 °C bath. NMR data was then collected at -20 °C. ^{31}P NMR (CD_2Cl_2, -20 °C): δ 91.7, 91.2, 90.6, 83.0.

Reaction of 2 with $AlBr_3$. A J-Young NMR tube was charged with 15.0 mg (0.0141 mmol) of **2** and 4.0 mg (0.0142 mmol) of $AlBr_3$. The tube was evacuated and cooled to 78K to allow ~2 mL of CD_2Cl_2 to be distilled onto the mixture. The solution

was allowed to warm up in a -40 °C bath. NMR data was then collected at -20 °C. ^{31}P NMR (CD_2Cl_2, -20 °C): δ 100.4, 92.3, 86.7, 69.3.

Reactions of 1 with $B(C_6F_5)_3$. A J-Young NMR tube was charged with 6.0 mg (0.0057 mmol) of **1** and 3.0 mg (0.0057 mmol) of $B(C_6F_5)_3$. The tube was evacuated and cooled to 78K to allow ~1 mL of CD_2Cl_2 to be distilled onto the mixture. The solution was allowed to warm up in a -40 °C bath. NMR data was then collected at -20 °C.

Reaction of 2 with $B(C_6F_5)_3$. A J-Young NMR tube was charged with 6.0 mg (0.0056 mmol) of **2** and 3.0 mg (0.0057 mmol) of $B(C_6F_5)_3$. The tube was evacuated and cooled to 78K to allow ~1 mL of CD_2Cl_2 to be distilled onto the mixture. The solution was allowed to warm up in a -40 °C bath. NMR data was then collected at -20 °C.

Reaction of 1 and 2 with $H(OEt_2)_2BAr^F_4$. A J-Young NMR tube was charged with 8.0 mg (0.0076 mmol) of **1** and 8.0 mg (0.0075 mmol) of **2**. The tube was evacuated and cooled to 78K to allow ~1 mL of CD_2Cl_2 to be distilled onto the mixture. The solution was allowed to warm to room temperature and the contents dissolved. The mixture was then cooled to 78K and 7.6 mg (0.0075 mmol) of solid $H(OEt_2)_2BAr^F_4$ placed on top of the frozen solution. The J-Young tube was evacuated and allowed to warm to room temperature. The ^1H NMR and ^{31}P NMR spectrum obtained after 30 min and 24 h were identical, indicating a mixture of unreacted **1**, **2** and $\mathbf{1}H^+$, $\mathbf{2}H^+$.
^{31}P NMR at t = 30 min: δ 93.1, 90.8 (**1** and **2**), 90.5, 90.4 ($[Fe_2(S_2C_2H_4)(\mu\text{-}H)(CO)_2(dppv)_2]^+$, $\mathbf{1}H^+$): 88.9, 87.9, 84.3, 82.7, 76.8 ($[Fe_2(S_2C_3H_6)(m\text{-}H)(CO)_2(dppv)_2]^+$, $\mathbf{2}H^+$).

Competition between 1 and 2 for $AlBr_3$. Treatment of 10 equiv of **1**, 1 equiv of **2**, with 2 equiv $AlBr_3$ resulted in quantitative conversion of **2**:

1·$AlBr_3$ + **2** → **1** + **2**·$AlBr_3$

K_{eq} was calculated with the following assumptions:

1) [**2**·$AlBr_3$] = 0.95 (we conservatives assume that we cannot detect 5% of the original 1 equiv).

2) [**1**] = 8.95 (1 equiv of a original 10 was consumed by $AlBr_3$, plus the 0.05 equiv left that did not react fully with **2**)

3) [**2**] = 0.05 (we can detect 95% conversion of this one equivalent)

4) [**1**·$AlBr_3$] = 1.05, see #2

K = [**2**·$AlBr_3$][**1**]/[**2**][**1**·$AlBr_3$] = (0.95)(8.95)/(0.05)(1.05) = 162

Check #1 [**2**·$AlBr_3$] + [**2**] = 1 (we started with 1 equiv **2**)

Check #2 [**1**] + [**1**·$AlBr_3$] = 10 (we started with 10 equiv **1**)

Check #3 [**2**·$AlBr_3$] + [**1**·$AlBr_3$] = 2 (we started with 2 equiv $AlBr_3$)

$\Delta G = - RT\ln K = -(8.3 \text{ J/deg})(253)\ln(162)$

$\Delta G > -10.9$

II. Selected Spectra

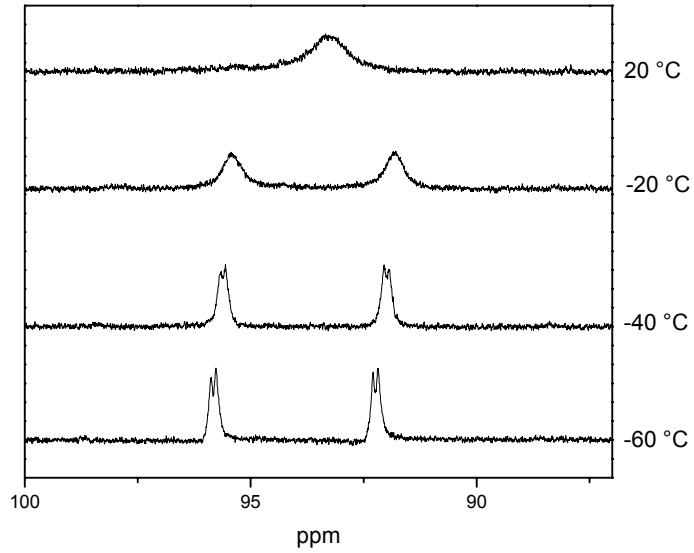

Figure 1S. 202 MHz ^{31}P NMR spectrum of $Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$ (CD_2Cl_2) recorded at various temperatures.

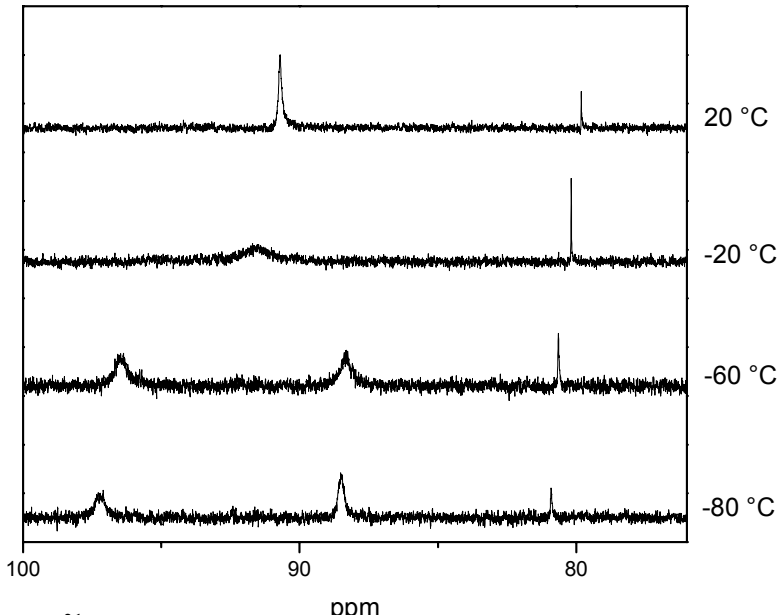

Figure 2S. 202 MHz ^{31}P NMR spectrum of $Fe_2(S_2C_3H_6)(CO)_2(dppv)_2$ (CD_2Cl_2) recorded at various temperatures.

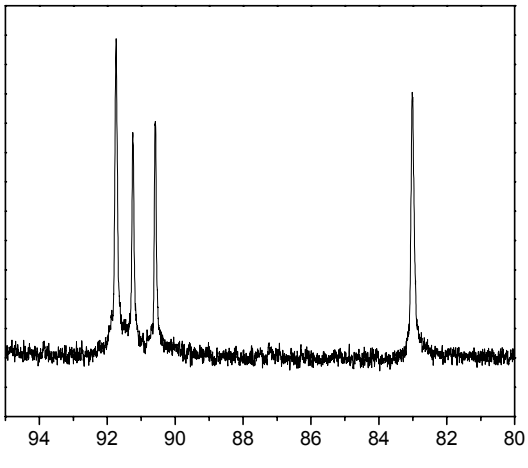

Figure 3S. 202 MHz ^{31}P NMR spectrum of a 1:1 mixture of $AlBr_3$ + $Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$ (CD_2Cl_2) at -20 °C.

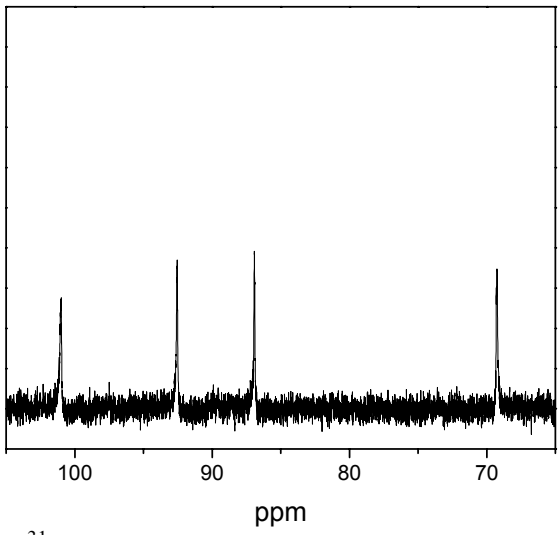

Figure 4S. 202 MHz ^{31}P NMR spectrum of a 1:1 mixture of $AlBr_3$ + $Fe_2(S_2C_3H_6)(CO)_2(dppv)_2$ (CD_2Cl_2) at -20 °C.

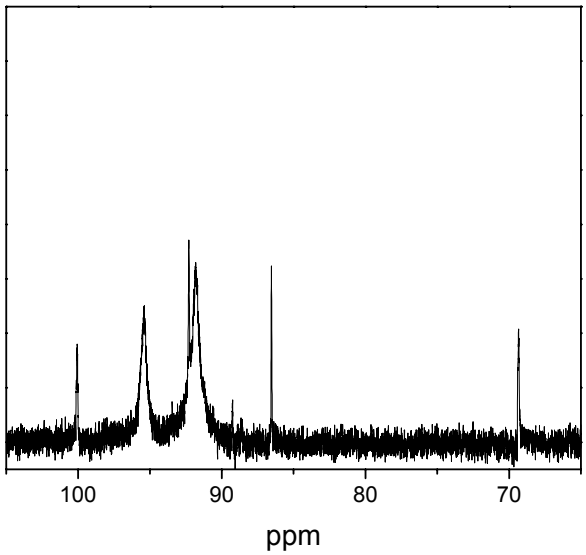

Figure 5S. 202 MHz ^{31}P NMR spectrum of a 1:1 mixture of $Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$ + $Fe_2(S_2C_3H_6)(CO)_2(dppv)_2$ with 1 equiv. of $B(C_6F_5)_3$ at -20 °C.

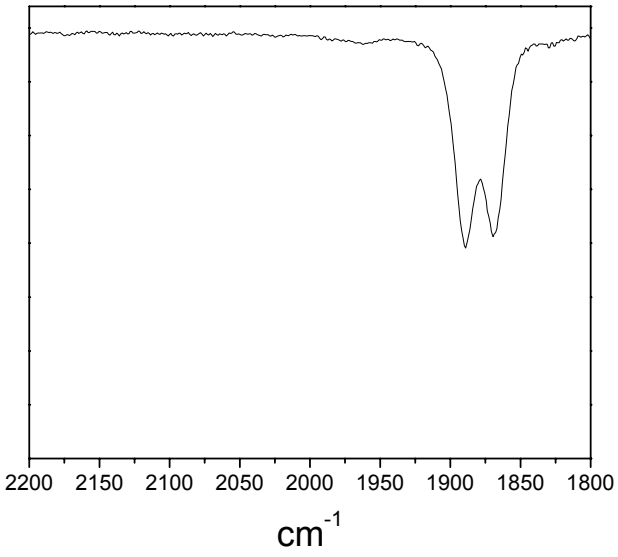

Figure 6S. IR spectrum of $Fe_2(S_2C_3H_6)(CO)_2(dppv)_2$ in CH_2Cl_2.

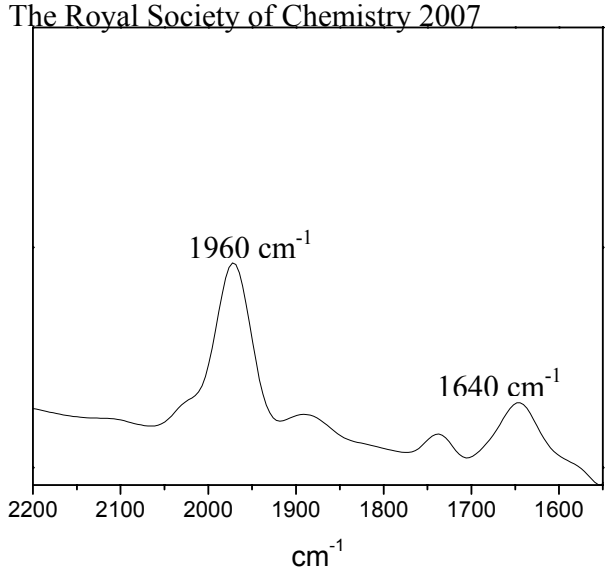

Figure 7S. IR spectrum of $Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$ and $AlBr_3$ in CH_2Cl_2 at –30 °C.

III. Computational work

DFT calculations were carried out using the pure B-P86 functional [A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822] along with a valence triple-ζ basis set plus polarization functions on all atoms [A. Schafer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829]. Stationary points of the energy hypersurface were located using energy gradient techniques and full vibrational analysis has been carried out to further characterize each stationary point.

1. *Prototypical input parameters (i.e. "control" file) used for RI-DFT energy minimization calculations (for keyword meaning, please refer to any TURBOMOLE manual which is freely available on-line; only the bottom line is explicitly described since it concerns the energy convergence criterion)*
2.

CONTROL file

```
$title
$operating system unix
$symmetry c1
$coord    file=coord
$user-defined bonds    file=coord
$atoms
fe 1,20
  basis =fe def-TZVP
  jbas  =fe def-TZVP
p  2,8,21,25
  basis =p def-TZVP
  jbas  =p def-TZVP
h  3-5,9-11,14-15,17-18,22-24,26-28
  basis =h def-TZVP
  jbas  =h def-TZVP
c  6,13,16,29
  basis =c def-TZVP
  jbas  =c def-TZVP
o  7,30
  basis =o def-TZVP
  jbas  =o def-TZVP
s  12,19
  basis =s def-TZVP
  jbas  =s def-TZVP
```

```
al 31
   basis =al def-TZVP
   jbas  =al def-TZVP
br 32-34
   basis =br def-TZVP
   jbas  =br def-TZVP
$pople   AO
$basis    file=basis
$rundimensions
   dim(fock,dens)=161136
   natoms=34
   nshell=256
   nbf(CAO)=566
   nbf(AO)=538
   dim(trafo[SAO<-->AO/CAO])=622
   rhfshells=1
$scfmo    file=mos
$closed shells
 a       1-159                                  ( 2 )
$scfiterlimit     3000
$thize     0.10000000E-04
$thime        5
$scfintunit
 unit=30       size=0        file=twoint
$scfdiis   start=0.5
$drvopt
   cartesian  on
   basis      off
   global     off
   hessian    on
   dipole     on
   nuclear polarizability
$interconversion  off
   qconv=1.d-7
   maxiter=25
$optimize
   internal   off
   cartesian  on
   global     off
   basis      off   logarithm
$coordinateupdate
   dqmax=0.3
   interpolate  on
   statistics    5
$forceupdate
   ahlrichs numgeo=142  mingeo=3 maxgeo=4 modus=<g|dq> dynamic fail=0.3
```

```
  threig=0.005  reseig=0.005  thrbig=3.0  scale=1.00  damping=0.0
$forceinit off
  diag=default
$energy    file=energy
$grad    file=gradient
$forceapprox    file=forceapprox
$lock off
$dft
  functional b-p
  gridsize   m3
$scfdamp   start=1.000  step=0.050  min=0.050
$ricore      70
$ridft
$jbas file=auxbasis
$scforbitalshift closedshell=0.4
$scfconv    6  (it means that SCF convergence criterion will be 10-6 for the energy.
Gradient are evaluated only if the integer in $scfconv is > 6)
```

2. *Coordinates (XYZ) of the optimized structures (stationary point of the PES, subsequently characterized as minima) discussed throughout the paper.*

$Fe_2(S_2C_2H_4)(PH_3)_4(CO)(COAlBr_3)$, C_2 isomer

Fe	2.3696026	-0.9736454	5.1077132
P	4.4774859	-1.1021984	5.6811228
H	5.2238358	-2.3129245	5.4849079
H	4.9064458	-0.8857876	7.0356450
H	5.4541164	-0.2345092	5.0867321
C	2.6486488	-1.1305777	3.3854557
O	2.8272155	-1.2194496	2.2310896
P	2.1969703	1.2155506	4.8908955
H	3.3633141	2.0544842	4.8302371
H	1.4970190	1.9705587	5.8850265
H	1.5491304	1.7716788	3.7438503
S	1.3149971	-0.8374118	7.1270886
C	1.8228351	-2.3941090	8.0203919

H	2.7456714	-2.1491650	8.5643043
H	1.0416115	-2.5957937	8.7652371
C	2.0175526	-3.5684518	7.0666740
H	3.0520572	-3.9377038	7.0769397
H	1.3612743	-4.4136056	7.3152497
S	1.6508985	-3.1068321	5.2959834
Fe	-0.0603916	-1.5748993	5.4744330
P	-1.5704988	-2.7352556	6.6008807
H	-2.7334305	-3.2596627	5.9518847
H	-2.2510858	-2.1276603	7.7005680
H	-1.2078295	-3.9456497	7.2823827
P	-0.6679242	-2.1057649	3.4114440
H	0.1736312	-2.9711982	2.6466331
H	-1.9101969	-2.7819254	3.1688570
H	-0.8378352	-1.0802405	2.4328934
C	-0.9293217	-0.1283179	5.3680134
O	-1.5596132	0.9026895	5.2568014
Al	-3.3930959	1.5458429	5.2799695
Br	-3.5237344	2.7258591	3.3131628
Br	-3.4991468	2.7624645	7.2242128
Br	-4.5916945	-0.4414051	5.2983825

$Fe_2(S_2C_2H_4)(PH_3)_4(CO)(COAlBr_3)$, μ-CO isomer

C	2.6091709	-1.0927167	3.3662791
O	2.9656029	-1.2156245	2.2655898
Fe	2.1130561	-0.9217995	5.0414649
S	1.4806643	-3.1545271	5.2728757
C	2.0961227	-3.6224300	6.9703515
C	2.1046954	-2.4485409	7.9438667
S	1.2116827	-0.9531513	7.2759429

Fe	-0.2290019	-1.6983513	5.6768574
P	-1.6955127	-2.9750588	4.6696397
P	4.2311830	-1.0901902	5.7371145
P	2.1535033	1.3024357	5.0505216
C	0.1588242	-0.6848737	4.3329453
O	-0.2168463	-0.0189796	3.3441563
Al	-1.4423756	0.9494831	2.3251933
Br	-0.8560334	0.5428577	0.1395508
P	-1.8219883	-0.4406805	6.5198915
Br	-1.0944548	3.1231341	3.0697368
Br	-3.5666311	0.1651852	2.8784428
H	4.6675054	-0.4876865	6.9649427
H	5.2467426	-0.5111096	4.9121909
H	1.1005012	1.9822094	5.7353160
H	3.2487768	2.0238134	5.6303562
H	2.0820079	2.0123031	3.8160618
H	4.8952768	-2.3470891	5.9260177
H	3.1289156	-2.1313197	8.1847802
H	1.6083724	-2.7025075	8.8903995
H	1.4264445	-4.4231725	7.3101141
H	3.0992834	-4.0543538	6.8465906
H	-2.8810225	-1.0428339	7.2822741
H	-1.4826955	0.5692177	7.4763500
H	-2.6547917	0.3457325	5.6617912
H	-2.9979816	-3.2105994	5.2260371
H	-2.1478997	-2.6482540	3.3504845
H	-1.3599003	-4.3458439	4.4311518

$Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$ (**1**)

C	4.065879	-0.568241	2.192765

C	4.720728	0.024211	1.098793
C	6.101616	-0.172497	0.945850
C	6.808326	-0.964059	1.856163
C	6.146697	-1.568587	2.929566
C	4.773823	-1.363118	3.098341
P	3.716915	1.058983	-0.093511
C	2.228083	-0.052025	-0.247267
C	1.025208	0.523145	-0.341839
P	0.961859	2.378954	-0.261282
C	-0.596356	2.624220	0.738271
C	-1.778525	1.926175	0.431051
C	-2.927407	2.099763	1.205594
C	-2.911656	2.978917	2.294541
C	-1.744012	3.680975	2.601939
C	-0.589388	3.502036	1.830939
Fe	2.929952	3.095287	0.436478
C	2.752810	2.621628	2.108400
O	2.624699	2.340163	3.242525
Fe	4.731130	4.965957	0.671601
S	2.499920	5.269786	0.987042
C	1.845374	5.950843	-0.628023
C	2.671686	5.473353	-1.811020
S	3.919292	4.174868	-1.306346
P	5.323765	5.485355	2.760413
C	6.720660	6.710321	2.609252
C	6.926219	7.276529	1.414229
P	5.726707	6.835647	0.063178
C	4.893318	8.512290	-0.086011
C	5.475513	9.592365	-0.772364
C	4.861353	10.848322	-0.767412
C	3.662851	11.044021	-0.072781

C	3.083598	9.977759	0.621243
C	3.694751	8.719814	0.614060
C	6.066600	4.269385	3.969085
C	6.093571	2.902035	3.674367
C	6.645200	1.995082	4.586396
C	7.176190	2.448561	5.795653
C	7.149236	3.815052	6.099169
C	6.593290	4.719753	5.193384
C	4.161491	6.392251	3.904900
C	3.197904	5.653148	4.612645
C	2.297290	6.300772	5.460931
C	2.344658	7.690994	5.613329
C	3.297096	8.431521	4.908761
C	4.199348	7.786792	4.054686
C	6.181186	4.011272	0.525794
O	7.169447	3.381665	0.413221
C	6.798560	6.795805	-1.454082
C	6.250933	7.072801	-2.718661
C	7.026516	6.950886	-3.873269
C	8.360534	6.539003	-3.783299
C	8.909983	6.246059	-2.531983
C	8.134188	6.369064	-1.374376
C	0.360763	2.772523	-1.991931
C	-0.731545	3.621066	-2.236553
C	-1.080673	3.971109	-3.545815
C	-0.347678	3.475077	-4.627464
C	0.742174	2.628869	-4.392460
C	1.098391	2.286331	-3.086291
C	4.583628	0.697204	-1.714534
C	4.117174	-0.293457	-2.596204
C	4.778217	-0.546443	-3.801884

C	5.917883	0.185121	-4.145560
C	6.389401	1.172516	-3.276853
C	5.725472	1.432161	-2.074510
H	0.322741	4.051112	2.070740
H	-1.725031	4.369772	3.448610
H	-3.809762	3.115012	2.899997
H	-3.836994	1.548875	0.957772
H	-1.810959	1.253040	-0.427913
H	1.966065	1.645336	-2.919504
H	1.324896	2.238765	-5.228920
H	-0.621911	3.746941	-5.648328
H	-1.932065	4.632452	-3.718108
H	-1.320806	4.005664	-1.402640
H	0.107846	-0.061260	-0.456832
H	2.357183	-1.138683	-0.263817
H	6.105583	2.213700	-1.419076
H	7.273768	1.757232	-3.535751
H	6.434287	-0.011816	-5.086951
H	4.399154	-1.320952	-4.471761
H	3.228075	-0.875676	-2.352099
H	2.995840	-0.412500	2.340083
H	4.248768	-1.821346	3.938434
H	6.698759	-2.195436	3.632249
H	7.881084	-1.111999	1.719049
H	6.631406	0.280405	0.107948
H	2.048429	5.016691	-2.591446
H	3.245890	6.292576	-2.263156
H	0.802296	5.615300	-0.697355
H	1.848790	7.045753	-0.539907
H	6.552664	5.779949	5.452334
H	7.554830	4.175947	7.046416

H	7.604987	1.739534	6.506447
H	6.650475	0.931502	4.344244
H	5.670497	2.544337	2.735414
H	3.156514	4.567345	4.508944
H	1.556534	5.714614	6.007812
H	1.642688	8.194287	6.280638
H	3.344929	9.516194	5.023704
H	4.938003	8.375498	3.508389
H	7.336931	6.949885	3.481137
H	7.710086	8.020583	1.241294
H	6.410484	9.453107	-1.317211
H	5.323911	11.677873	-1.306043
H	3.184811	12.025531	-0.069866
H	2.152179	10.121592	1.171846
H	3.248103	7.890882	1.167738
H	8.570812	6.119601	-0.405587
H	9.947845	5.917072	-2.453271
H	8.966949	6.443672	-4.685727
H	6.586272	7.175909	-4.846489
H	5.213485	7.401666	-2.803832

$Fe_2(S_2C_3H_6)(CO)_2(dppv)_2$ (**2**)

C	4.093252	-0.527702	2.219760
C	4.743272	0.049433	1.114494
C	6.120750	-0.164246	0.950735
C	6.827884	-0.956741	1.859932
C	6.170174	-1.545870	2.944310
C	4.801321	-1.323996	3.124148
P	3.729554	1.069716	-0.086013

C	2.252042	-0.059269	-0.209346
C	1.041079	0.498767	-0.300432
P	0.950027	2.355074	-0.268945
C	-0.603193	2.597663	0.741376
C	-1.786054	1.897898	0.439863
C	-2.928384	2.063193	1.225598
C	-2.905455	2.934180	2.320921
C	-1.737291	3.637497	2.622346
C	-0.589304	3.468279	1.839546
Fe	2.911774	3.122634	0.408403
C	2.727509	2.642530	2.079291
O	2.594767	2.352269	3.210920
Fe	4.685857	5.037035	0.634863
S	2.446363	5.282956	1.022789
C	1.517921	6.167825	-0.336823
C	2.309626	6.476626	-1.596528
C	2.837445	5.251781	-2.324597
S	3.965038	4.130832	-1.350571
P	5.268453	5.526360	2.743805
C	6.684005	6.730916	2.620098
C	6.916975	7.300976	1.432374
P	5.719872	6.907854	0.065161
C	4.953636	8.622005	-0.047984
C	5.563951	9.684999	-0.734600
C	4.996344	10.962789	-0.709959
C	3.820358	11.197836	0.009526
C	3.213974	10.147662	0.705855
C	3.775728	8.867980	0.674673
C	5.995773	4.287171	3.938242
C	6.026469	2.925544	3.620155
C	6.574003	2.003933	4.519839

C	7.096017	2.436754	5.740175
C	7.065101	3.797675	6.067562
C	6.513745	4.717144	5.173810
C	4.113071	6.427705	3.898054
C	3.141082	5.689987	4.595713
C	2.249521	6.336241	5.454749
C	2.312317	7.723723	5.625421
C	3.271883	8.463163	4.929246
C	4.166711	7.819413	4.066739
C	6.138465	4.085018	0.503657
O	7.125682	3.452986	0.398767
C	6.807436	6.862996	-1.441061
C	6.276482	7.149680	-2.710689
C	7.064051	7.020642	-3.856499
C	8.391934	6.591683	-3.752112
C	8.924086	6.290263	-2.495659
C	8.136996	6.421554	-1.346655
C	0.306628	2.669952	-2.000130
C	-0.754372	3.555313	-2.254520
C	-1.137484	3.848011	-3.568053
C	-0.470118	3.258134	-4.645232
C	0.588787	2.376403	-4.401020
C	0.977913	2.088942	-3.090617
C	4.593964	0.690558	-1.701567
C	4.104126	-0.279100	-2.593179
C	4.767902	-0.545849	-3.794473
C	5.931277	0.154018	-4.124622
C	6.423941	1.123383	-3.247452
C	5.758838	1.395937	-2.048700
H	3.145129	7.143641	-1.339613
H	1.660099	7.044446	-2.289135

H	0.322543	4.020448	2.074774
H	-1.712161	4.319204	3.474414
H	-3.798784	3.062699	2.935076
H	-3.838925	1.512174	0.981998
H	-1.824498	1.230345	-0.423328
H	1.819686	1.416236	-2.917421
H	1.120173	1.913266	-5.234246
H	-0.772078	3.484072	-5.669425
H	-1.964590	4.537525	-3.747432
H	-1.294642	4.012036	-1.423670
H	0.129011	-0.098380	-0.390396
H	2.395700	-1.144381	-0.204566
H	6.155103	2.163540	-1.386330
H	7.326688	1.683594	-3.497007
H	6.450595	-0.054823	-5.061788
H	4.373536	-1.307227	-4.470428
H	3.197130	-0.836943	-2.356894
H	3.026556	-0.360173	2.376957
H	4.278877	-1.771167	3.971810
H	6.721712	-2.172031	3.648024
H	7.897618	-1.117686	1.713527
H	6.647744	0.275140	0.104065
H	2.016186	4.614555	-2.679997
H	3.430540	5.553504	-3.199873
H	0.635424	5.551844	-0.562797
H	1.163174	7.099415	0.127371
H	6.469223	5.772690	5.450622
H	7.463709	4.142653	7.023707
H	7.519280	1.714619	6.441147
H	6.582722	0.944766	4.259847
H	5.608739	2.583456	2.673102

H	3.088310	4.606143	4.477964
H	1.503100	5.750963	5.995116
H	1.617612	8.225811	6.301330
H	3.331705	9.545655	5.058849
H	4.913128	8.407077	3.530048
H	7.293092	6.950866	3.502005
H	7.717070	8.031344	1.274961
H	6.482455	9.515721	-1.298254
H	5.477812	11.777793	-1.254131
H	3.379090	12.196195	0.027441
H	2.298645	10.321784	1.274570
H	3.300455	8.047017	1.216829
H	8.559449	6.164815	-0.373511
H	9.956560	5.947388	-2.406261
H	9.006943	6.489155	-4.647844
H	6.637957	7.252211	-4.834594
H	5.242501	7.487223	-2.805420

1-AlBr3 adduct (μ-CO isomer)

C	4.811004	6.125373	5.655030
C	4.550765	5.178402	4.648562
C	3.771264	4.056435	4.947279
C	3.257774	3.875215	6.235494
C	3.525041	4.813922	7.233663
C	4.303063	5.940441	6.941780
P	5.277279	5.407908	2.951218
C	4.826365	7.194658	2.631387
C	3.533113	7.656612	2.935677
C	3.166513	8.975010	2.652004

C	4.084253	9.851479	2.062687
C	5.370934	9.398750	1.755501
C	5.739542	8.078263	2.033174
Fe	4.954197	3.922313	1.342065
P	7.087919	4.313400	0.842487
C	7.897115	5.019165	2.356114
C	7.088275	5.534744	3.285083
Fe	2.961958	2.388418	0.628137
S	2.746264	4.515620	1.433701
C	2.496147	5.595477	-0.070412
C	3.194410	5.018939	-1.290775
S	4.297302	3.572132	-0.849468
P	0.971850	2.151755	-0.351329
C	0.767859	0.360919	-0.776635
C	1.852203	-0.417415	-0.720857
P	3.471413	0.336925	-0.213889
C	4.133827	-1.113921	0.760456
C	5.205439	-1.899124	0.308611
C	5.583812	-3.046406	1.011580
C	4.899992	-3.422685	2.168731
C	3.837065	-2.641389	2.628187
C	3.456126	-1.492866	1.931828
C	-0.600948	2.478225	0.601423
C	-1.832766	1.981034	0.136207
C	-3.008342	2.213237	0.852484
C	-2.971801	2.952322	2.040124
C	-1.755664	3.458428	2.502768
C	-0.574950	3.220314	1.790147
C	0.557347	2.937469	-1.998934
C	-0.389539	3.968298	-2.114880
C	-0.626476	4.575645	-3.352389

C	0.076894	4.161088	-4.486890
C	1.025134	3.137834	-4.377814
C	1.268468	2.533268	-3.142414
C	2.352170	1.712956	2.124691
O	1.917115	1.320397	3.137466
C	5.182000	2.480139	2.197999
O	5.497725	1.507621	2.883473
Al	6.218905	0.735874	4.455142
Br	7.483364	2.403554	5.459124
C	4.434966	0.213770	-1.803074
C	3.871466	-0.330501	-2.968816
C	4.617871	-0.417161	-4.148652
C	5.939384	0.033856	-4.175868
C	6.506794	0.575774	-3.019154
C	5.761057	0.674083	-1.842037
C	8.262664	2.937565	0.407965
C	8.684618	2.709747	-0.912363
C	9.574668	1.669311	-1.196821
C	10.035816	0.835296	-0.173156
C	9.606315	1.047315	1.139884
C	8.725765	2.092987	1.430194
C	7.608483	5.632085	-0.384913
C	8.967665	5.918632	-0.608854
C	9.339757	6.963480	-1.457718
C	8.360582	7.732320	-2.098067
C	7.009358	7.457640	-1.874640
C	6.638148	6.417785	-1.015293
Br	4.417809	0.050765	5.729167
Br	7.556656	-1.009733	3.738941
H	0.370735	3.618954	2.158770
H	-1.717677	4.037113	3.427210

H	-3.890738	3.132509	2.600711
H	-3.955210	1.816471	0.481784
H	-1.885529	1.423283	-0.800285
H	2.027383	1.752694	-3.067112
H	1.583715	2.811789	-5.256825
H	-0.112122	4.633346	-5.452273
H	-1.367858	5.373204	-3.428560
H	-0.954040	4.292247	-1.239491
H	-0.212014	-0.026874	-1.067206
H	1.815236	-1.488623	-0.940638
H	6.221268	1.106972	-0.952131
H	7.537703	0.929170	-3.025259
H	6.525498	-0.036454	-5.093869
H	4.165045	-0.846348	-5.044485
H	2.844031	-0.695518	-2.963681
H	2.625919	-0.898755	2.312354
H	3.309348	-2.912677	3.543421
H	5.203485	-4.313653	2.720516
H	6.424933	-3.642345	0.653133
H	5.746559	-1.624781	-0.596507
H	2.476682	4.639567	-2.026758
H	3.827156	5.762100	-1.794170
H	1.410114	5.683590	-0.220416
H	2.886313	6.582214	0.212464
H	9.741519	5.318266	-0.127642
H	10.397806	7.177134	-1.620882
H	8.652775	8.544555	-2.766053
H	6.239550	8.056669	-2.364549
H	5.587324	6.210871	-0.815935
H	8.336070	3.358376	-1.717284
H	9.915871	1.515128	-2.222765

H	10.729181	0.023016	-0.397988
H	9.943330	0.396016	1.946820
H	8.410484	2.252458	2.464053
H	8.987492	5.037110	2.437455
H	7.453007	6.010818	4.198698
H	2.815178	6.985516	3.409551
H	2.160986	9.319894	2.900434
H	3.799451	10.883359	1.850216
H	6.096773	10.075704	1.301256
H	6.746458	7.738925	1.787871
H	3.568253	3.314938	4.175103
H	2.666443	2.985543	6.454026
H	3.133140	4.667167	8.241645
H	4.517264	6.676246	7.719267
H	5.401942	7.016504	5.433293

2-AlBr3 adduct (μ-CO isomer)

C	4.823647	6.143623	5.683021
C	4.556228	5.201060	4.674473
C	3.783145	4.075299	4.976811
C	3.282130	3.887705	6.268992
C	3.554094	4.824047	7.268146
C	4.327277	5.952939	6.973663
P	5.266587	5.443554	2.971174
C	4.826125	7.236513	2.669452
C	3.546009	7.712987	3.003133
C	3.184436	9.032281	2.718107
C	4.095756	9.895952	2.100298
C	5.371641	9.430142	1.769104

C	5.734052	8.107997	2.046437
Fe	4.916572	4.012656	1.320168
P	7.065919	4.361138	0.831773
C	7.880253	5.053893	2.347896
C	7.080047	5.559338	3.289543
Fe	2.964102	2.392082	0.645657
S	2.671048	4.478910	1.570436
C	1.987647	5.690484	0.331724
C	3.404436	4.985052	-1.668584
C	2.966594	6.114696	-0.747731
H	3.841343	6.572996	-0.258826
H	2.495311	6.902715	-1.363589
S	4.310119	3.561444	-0.869587
P	0.970228	2.134245	-0.344466
C	0.778968	0.338378	-0.749838
C	1.868521	-0.432122	-0.696417
P	3.488199	0.331198	-0.207974
C	4.155679	-1.121505	0.762730
C	5.226452	-1.904739	0.305566
C	5.603552	-3.057642	0.999706
C	4.919552	-3.442394	2.154032
C	3.857081	-2.663784	2.618496
C	3.477302	-1.509452	1.930849
C	-0.613371	2.447349	0.598203
C	-1.841237	1.972152	0.099548
C	-3.024948	2.182095	0.809105
C	-3.001138	2.874414	2.025098
C	-1.788989	3.355260	2.522916
C	-0.600062	3.140662	1.816330
C	0.552673	2.889617	-2.006159
C	-0.389449	3.922642	-2.142475

C	-0.620989	4.511231	-3.390131
C	0.081496	4.074019	-4.516600
C	1.021824	3.045926	-4.388706
C	1.260608	2.461680	-3.142663
C	2.347965	1.680962	2.122887
O	1.903670	1.270603	3.123864
C	5.100527	2.530920	2.127618
O	5.461006	1.570307	2.813913
Al	6.188237	0.791222	4.375153
Br	7.459238	2.440286	5.404181
C	4.436538	0.198644	-1.804460
C	3.857537	-0.338250	-2.965804
C	4.592971	-0.434486	-4.151586
C	5.920013	-0.000113	-4.188708
C	6.502819	0.535829	-3.036768
C	5.767062	0.644883	-1.854090
C	8.227125	2.966565	0.412084
C	8.629169	2.716633	-0.910855
C	9.530659	1.684909	-1.189203
C	10.025283	0.881714	-0.156231
C	9.613751	1.113707	1.158828
C	8.719947	2.150388	1.442916
C	7.656799	5.653528	-0.397502
C	9.031050	5.913757	-0.554098
C	9.467025	6.933424	-1.402548
C	8.538385	7.705770	-2.110345
C	7.173098	7.452654	-1.961103
C	6.737965	6.434650	-1.104967
Br	4.397316	0.093993	5.659534
Br	7.524009	-0.952437	3.650784
H	0.341871	3.518418	2.216143

H	-1.759555	3.894412	3.471170
H	-3.926470	3.036895	2.580462
H	-3.968631	1.804621	0.411104
H	-1.883016	1.448352	-0.857034
H	2.015225	1.678520	-3.054407
H	1.578799	2.699767	-5.261037
H	-0.102576	4.531902	-5.489779
H	-1.356666	5.312565	-3.479703
H	-0.957326	4.262913	-1.275356
H	-0.201655	-0.056705	-1.027344
H	1.836487	-1.505053	-0.906876
H	6.238967	1.072619	-0.968243
H	7.537988	0.877092	-3.051136
H	6.498902	-0.080511	-5.110489
H	4.127106	-0.858796	-5.043232
H	2.826528	-0.692712	-2.952030
H	2.646166	-0.919640	2.315314
H	3.328050	-2.941357	3.531150
H	5.222430	-4.337388	2.699679
H	6.444478	-3.650864	0.636348
H	5.767911	-1.625285	-0.597626
H	2.544562	4.557000	-2.198977
H	4.107399	5.359961	-2.426768
H	1.080902	5.241996	-0.097776
H	1.687420	6.557083	0.937101
H	9.768099	5.309289	-0.022653
H	10.536247	7.123927	-1.513205
H	8.880558	8.501193	-2.774906
H	6.440699	8.049274	-2.508302
H	5.674734	6.242803	-0.974563
H	8.258733	3.344768	-1.721950

H	9.857757	1.515158	-2.217309
H	10.730759	0.078647	-0.376373
H	9.976913	0.485831	1.972852
H	8.420685	2.326992	2.478865
H	8.971065	5.069246	2.424164
H	7.454113	6.021630	4.206417
H	2.834828	7.051175	3.500669
H	2.188924	9.389214	2.989175
H	3.814224	10.927981	1.884632
H	6.093268	10.097226	1.293944
H	6.731632	7.756939	1.779759
H	3.573006	3.336442	4.204040
H	2.695788	2.995384	6.489878
H	3.170415	4.673395	8.278757
H	4.546622	6.686682	7.751565
H	5.411610	7.036325	5.460314

IV. X-ray Crystallography

Crystals were mounted using Paratone-N oil (Exxon) to a thin glass fiber. Data, collected at 198 K on a Siemens CCD diffractometer, were filtered to remove statistical outliers. The integration software (SAINT) was used to test for crystal decay as a bi-linear function of X-ray exposure time and sin(Θ). The data were solved using SHELXTL by Direct Methods; atomic positions were deduced from an E map or by an unweighted difference Fourier synthesis. H atom *U*'s were assigned as $1.2U_{eq}$ for adjacent C atoms. Non-H atoms were refined anisotropically. Successful convergence of the full-matrix least-squares refinement of F^2 was indicated by the maximum shift/error for the final cycle. Crystallographic data is listed in Table 1S.

Table 1S. Details of data collection and structure refinement for **1**.

Compound	**1**
Chemical formula	$C_{56}H_{48}Fe_2O_2P_4S_2$
Temperature (K)	193(2)
Crystal size (mm^3)	0.36 x 0.09 x 0.03
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.9417(7)
b (Å)	17.3546(10)
c (Å)	26.1713(15)
α (°)	90.0
β (°)	97.901 (2)
γ (°)	90.0
V ($Å^3$)	4922.5 (5)
Z	4
Density calcd (Mg m^{-3})	1.420
μ (Mo K_α, mm^{-1})	0.71073
max./min. trans'n	0.9750/0.7444
reflections meas'd/Indep.	21096/20391
data/restraints/parameters	20391/0/598
GOF on F^2	0.808
R_{int}	0.00[c]
R_1 [I > 2σ] (all data)[a]	0.0374 (0.0797)
WR_2 [I > 2σ] (all data)[b]	0.0506 (0.0569)
max. peak/hole ($e^-/Å^3$)	0.463/-0.433

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$

[b] $wR2 = \{[w(|F_o|-|F_c|)^2]/\Sigma[wF_o^2]\}^{1/2}$, where $w = 1/\sigma^2 (F_o)$

Structure of $Fe_2(S_2C_2H_4)(CO)_2(dppv)_2$, **1,** with thermal ellipsoid set at the 35% probability level: