

## Phosphinoquinoline supported Co<sup>II</sup>, Ni<sup>II</sup>, and Fe<sup>II</sup> complexes: divergent behaviour upon reduction

Pauline Schiltz,<sup>a</sup> Nicolas Casaretto,<sup>a</sup> Sophie Bourcier,<sup>a</sup> Audrey. Auffrant,<sup>\*a</sup> Corinne Gosmini,<sup>\*a</sup>

Laboratoire de Chimie Moléculaire (LCM), CNRS, Ecole Polytechnique, Institut Polytechnique de Paris,  
Route de Saclay, 91120 Palaiseau, France

### Table of content

1. NMR spectra .....	2
2. X-Ray data.....	7

## 1. NMR spectra

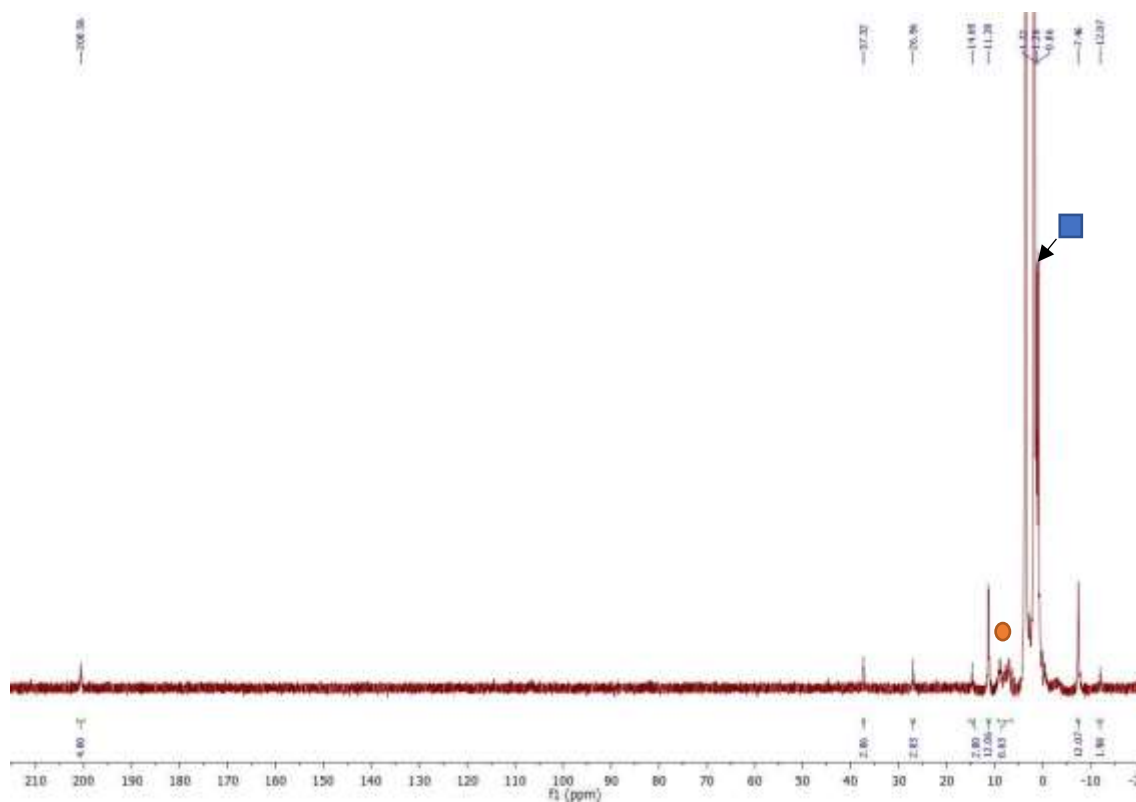


Figure S1  $^1\text{H}$  NMR spectrum of  $[\text{Co}(\text{L}^h)\text{Br}](\text{CoBr}_3)$  in  $\text{THF-d}_8$  (free ligand (16 %, ●), pentane (■ masked by a THF resonance))

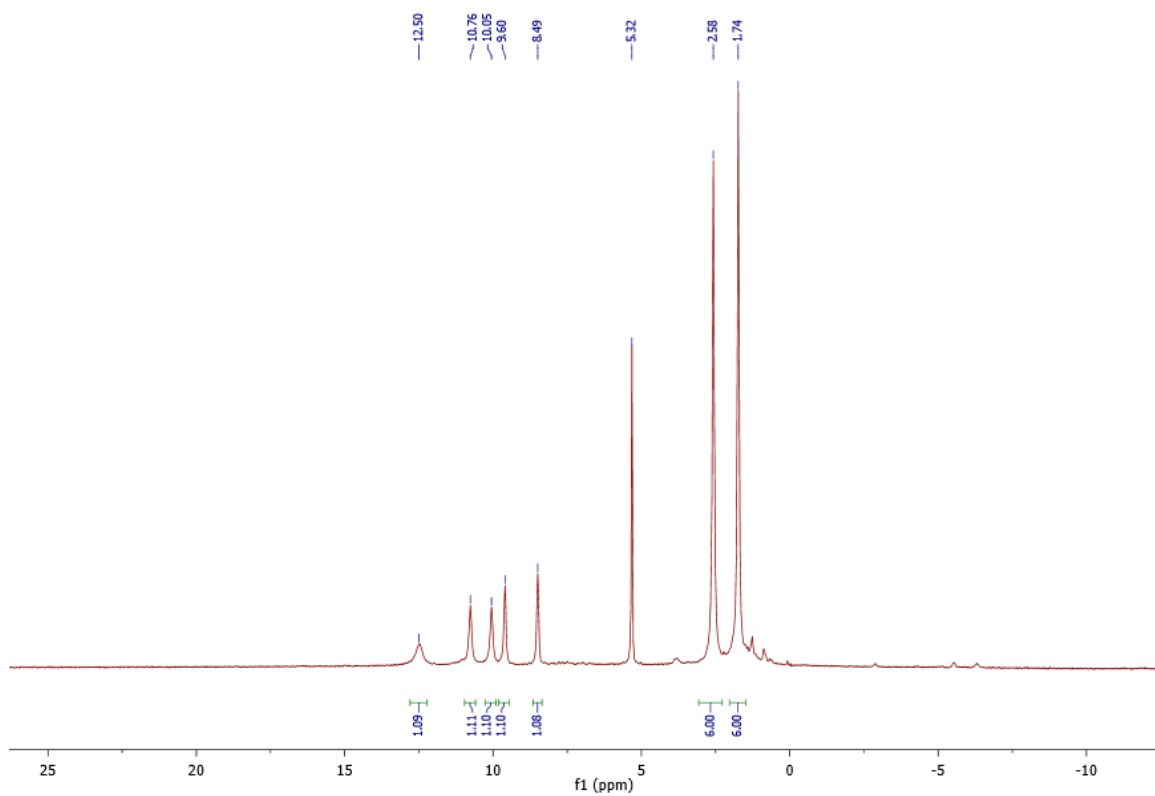


Figure S2:  $^1\text{H}$  NMR spectrum of  $[\text{NiLBr}_2]$  in  $\text{CD}_2\text{Cl}_2$

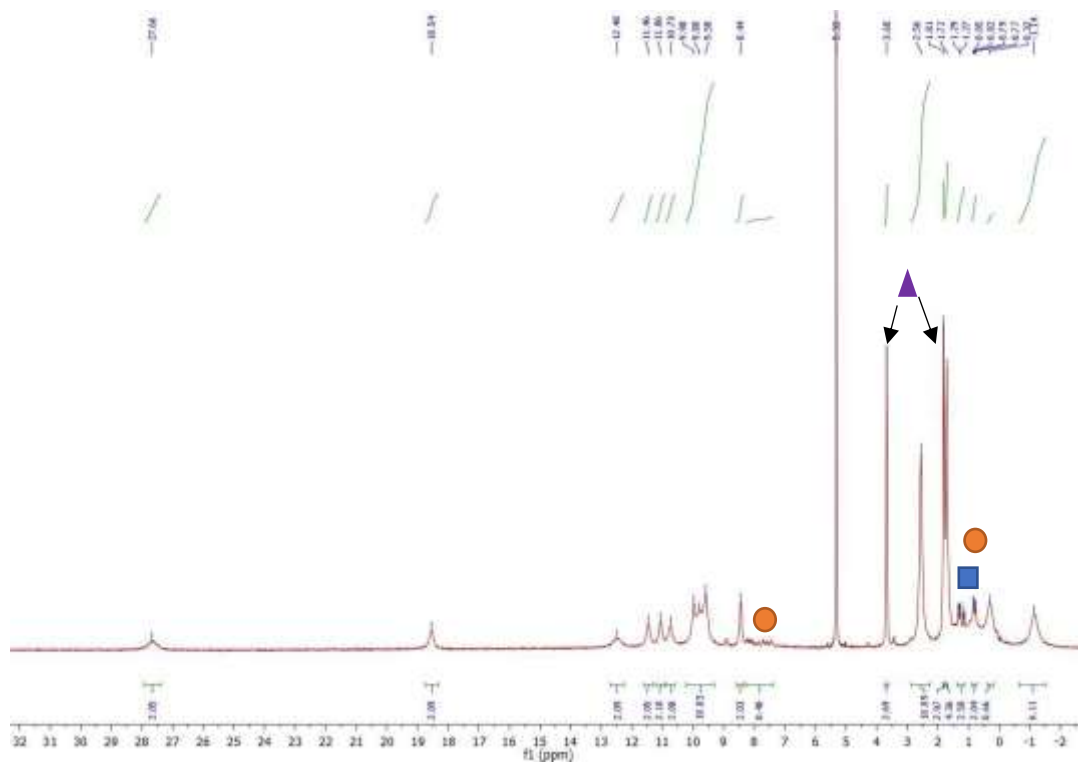


Figure S3:  $^1\text{H}$  NMR spectrum of  $[\text{NiL}_2\text{Br}](\text{Br})$  in  $\text{CD}_2\text{Cl}_2$  (free ligand (10%,  $\bullet$ ), THF ( $\blacktriangle$ , 67%), pentane ( $\blacksquare$ ).

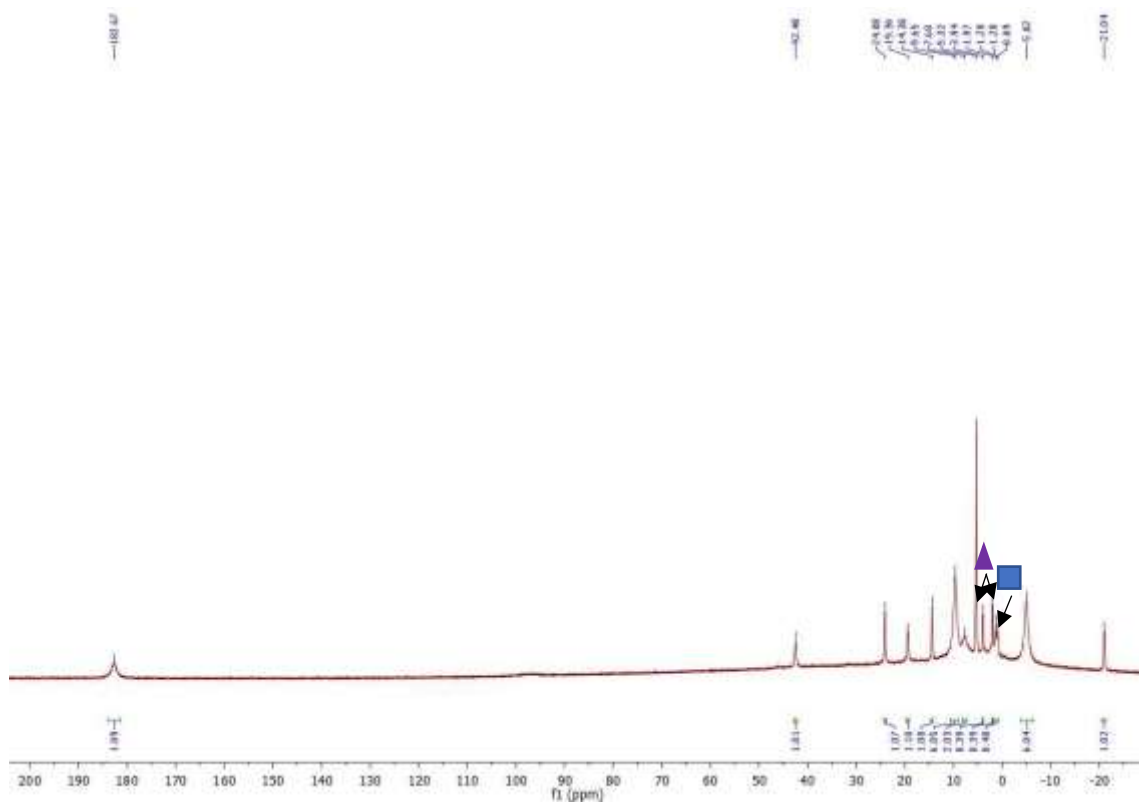


Figure S4:  $^1\text{H}$  NMR spectrum of  $[\text{FeLBr}_2]$  in  $\text{CD}_2\text{Cl}_2$  THF ( $\blacktriangle$  10%), pentane ( $\blacksquare$  4%)

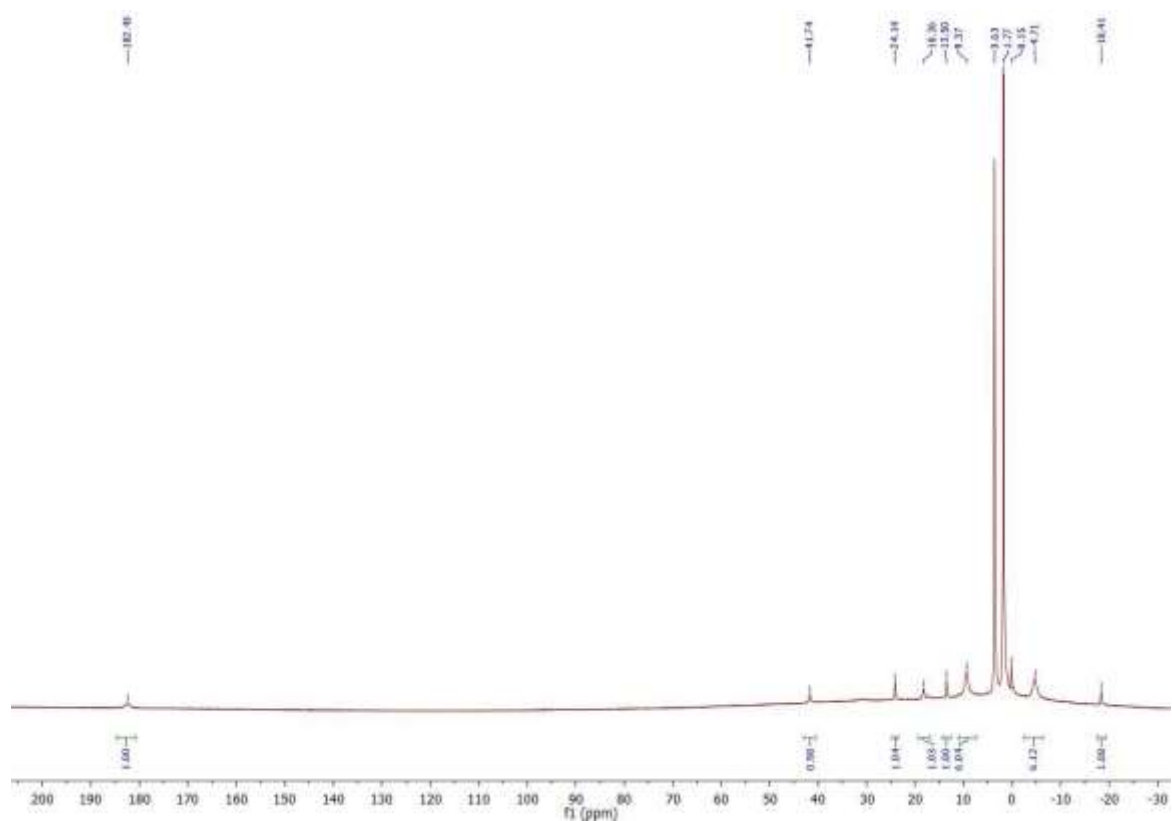


Figure S5:  $^1\text{H}$  NMR spectrum of  $[\text{FeLBr}_2]$  in  $\text{THF-d}_8$

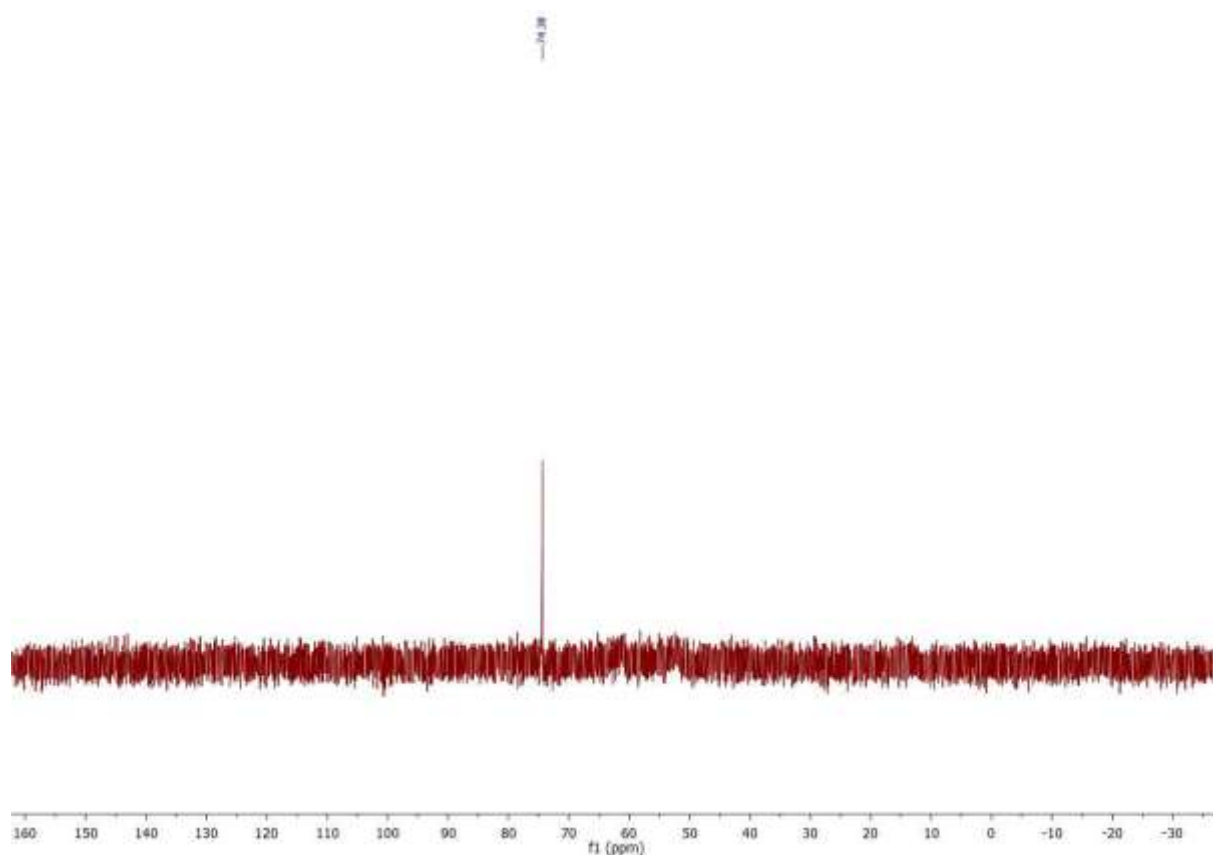


Figure S6:  $^{31}\text{P}$  NMR $\{^1\text{H}\}$  spectrum in  $\text{THF-d}_8$  of the crude mixture of the reduction of  $[\text{FeLBr}_2]$  by  $\text{KC}_8$  (2 equiv.)

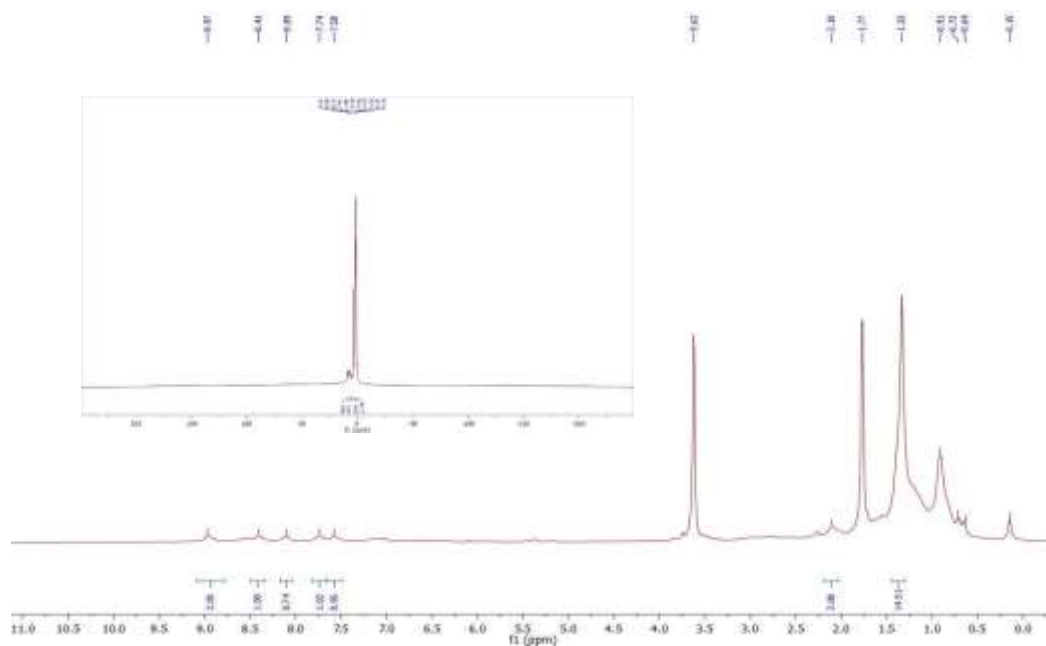


Figure S7:  $^1\text{H}$  NMR spectrum in  $\text{THF-d}_8$  spectrum of the crude mixture of the reduction of  $[\text{FeLBr}_2]$  by  $\text{KC}_8$  (2 equiv.).

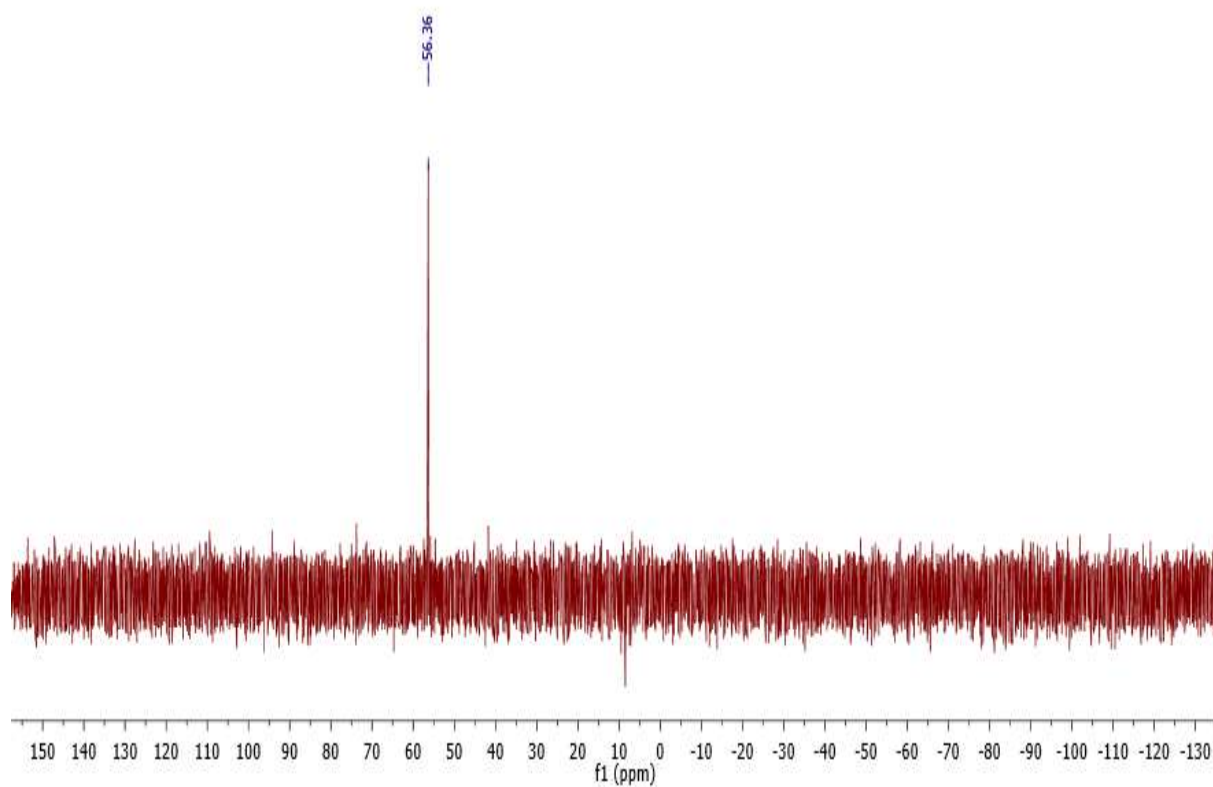


Figure S8:  $^{31}\text{P}$  NMR spectrum of  $[\text{NiL}_3]$  in  $\text{THF-d}_8$



## 2. X-Ray data

*Table S1: Crystallography data*

<b>Compound</b>	<b>[Co(L<sup>II</sup>)Br](CoBr<sub>3</sub>)</b>	<b>[Co L<sub>2</sub>Br]</b>	<b>[NiLBr<sub>2</sub>]</b>
Molecular formula	C <sub>31</sub> H <sub>40</sub> Br <sub>4</sub> Cl <sub>2</sub> Co <sub>2</sub> N <sub>2</sub> P <sub>2</sub>	C <sub>15</sub> H <sub>20</sub> Br <sub>0.5</sub> Co <sub>0.5</sub> NP	C <sub>30</sub> H <sub>40</sub> Br <sub>4</sub> N <sub>2</sub> Ni <sub>2</sub> P <sub>2</sub>
Molecular weight	1010.99	314.71	927.64
Space group	P-1	Fddd	P-1
T (K)	150.0	150.0	150
V(Å <sup>3</sup> )	1888.6(5)	11910.1(17)	1655.34(14)
a(Å)	11.6902(18)	21.7708(17)	10.6093(5)
b(Å)	13.315(2)	22.4926(19)	10.7482(5)
c(Å)	14.484(2)	24.322(2)	15.4756(8)
α(°)	109.871(4)	90	108.104(3)
β(°)	100.733(4)	90	98.410(3)
γ(°)	109.062(4)	90	91.115(3)
Z	2	32	2
d(g·cm <sup>-3</sup> )	1.778	1.404	1.861
F(000)	996.0	5216.0	920.0
θ <sub>max</sub>	25.677	28.279	28.451
Rflns measd	33540	54844	87583
Unique data	7180	3697	8344
Rint	0.0874	0.1139	0.0953
wR2	0.1399	0.0643	0.0645
R1	0.0580	0.0322	0.0341
GoF	1.030	1.011	1.051
CCDC number	2284773	2284774	2284775

*Table S2: Crystallography data*

<b>Compound</b>	<b>[Ni L<sub>2</sub>Br](Br)</b>	<b>[FeLBr<sub>2</sub>]</b>	<b>[NiL<sub>3</sub>]</b>
Molecular formula	C <sub>31</sub> H <sub>42</sub> Br <sub>2</sub> Cl <sub>2</sub> N <sub>2</sub> NiP <sub>2</sub>	C <sub>15</sub> H <sub>20</sub> Br <sub>2</sub> FeNP	C <sub>45</sub> H <sub>60</sub> N <sub>3</sub> Ni <sub>3</sub> P <sub>3</sub>
Molecular weight	794.03	460.96	912.00
Space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c	P6 <sub>3</sub>
T (K)	150	150	149.9
V(Å <sup>3</sup> )	3442.2(13)	1761.8(2)	2384.3(7)
a(Å)	11.482(2)	10.4908(8)	15.101(2)
b(Å)	20.260(5)	12.7615(9)	15.101(2)
c(Å)	15.511(3)	13.1600(12)	12.0727(17)
α(°)	90	90	90
β(°)	107.439(5)	90.251(5)	90
γ(°)	90	90	120
Z	4	4	2
d(g·cm <sup>-3</sup> )	1.532	1.738	1.270
F(000)	1616.0	912.0	960.0
θ <sub>max</sub>	25.681	26.372	25.68
Rflns measd	61917	24863	24516
Unique data	6529	3598	2997
Rint	0.1693	0.0983	0.1513
wR2	0.0853	0.0909	0.0995
R1	0.0473	0.0443	0.0489
GoF	1.008	1.016	0.901
CCDC number	2284776	2284777	2284778



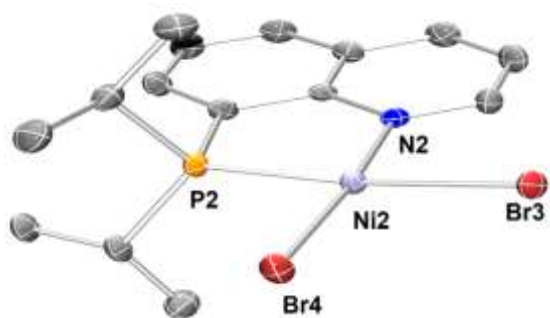


Figure S11: Ortep plot of the second molecule of **[NiLBr<sub>2</sub>]** with thermal ellipsoids (drawn at the 50% probability level). The cation, the H atoms and one CH<sub>2</sub>Cl<sub>2</sub> molecule were omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1-N1 1.940(4); Co1-N2 1.933(7); Co1-P1 2.244(2); Co1-P2 2.270(2); Co1-Br1 2.532(2); C1-C10 1.479(9); P1-Co1-N1 83.4(2); P1-Co1-N2 85.0(2); P1-Co1-P2 108.49(9); N1-Co1-N2 80.8(3); N1-Co1-Br1 88.2(2); P1-Co1-Br1 98.21(7); N2-Co1-Br1 97.2(2); P2-Co1-Br1 98.95(7).