

SUPPORTING INFORMATION

Isolation, dynamic NMR study and X-ray characterisation of a bis sulfonium zirconocene-ate dimer.

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Experimental Section

General Remarks: Experiments were conducted under a dry argon atmosphere with standard Schlenk techniques. Solvents were freshly distilled under argon from solutions of NaK_{2.8}/benzophenone (pentane, THF), NaK_{2.8} (toluene, C₆D₆, toluene-*d*₈), or CaH₂ (CH₂Cl₂, CD₂Cl₂). Reagents were purchased from commercial suppliers and used without further purification, except for the thiols which were distilled and stored under an argon atmosphere. Diphenylphosphinoacetylene⁽¹⁾ and dimethylzirconocene⁽²⁾ were prepared according to literature procedures. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker DRX-500 spectrometer by the C.S.M. (Centre de Spectrométrie Moléculaire) of the Université de Bourgogne. Chemical shifts are reported in ppm relative to SiMe₄ (¹H; ¹³C) or H₃PO₄ (³¹P). ¹³C NMR assignments were confirmed by inverse gradient δ ¹H-¹³C HMQC and δ ¹H-¹³C HMBC. Combustion analyses were performed by the analytical service of L.S.E.O. of the Université de Bourgogne.

Preparation of complexes **1a,b**

To a solution of dimethylzirconocene (1.20 g; 4.8 mmol) in toluene (20 mL) was added diphenylphosphinoacetylene (1.00 g; 4.8 mmol) followed by a stoichiometric amount of phenyl-methanethiol (for **1a**: 0.56 mL; 4.8 mmol) or (4-methoxy-phenyl)-methanethiol (for **1b**: 0.67 mL; 4.8 mmol). The resulting solution was stirred for 2 h at room temperature then it was heated at 90 °C for 10 h. A beige solid precipitated during the reaction. The mixture was cooled to room temperature and was concentrated in *vacuo*, then pentane (40 mL) was added. The resulting solid product was washed with 5 X 10 mL of pentane and *vacuum* dried.

1a (both diastereomers): yield 1.62 g (61 %), beige powder

¹H NMR (500 MHz, 300 K, toluene-*d*₈): δ 4.47, 4.56 (broad s, 2H, CHPh), 5.56, 5.71, 5.94, 6.08 (s, 10H, Cp), 6.78, 6.85 (dd, 2H, $J_{HP} = 15.6$ Hz, $J_{HH} = 2.3$ Hz, =CH), 6.95-7.31 (H_{arom}), 7.44 (m, H_{arom}), 7.88 (t, H_{arom}), 7.92 (t, H_{arom}) ppm.

¹³C {¹H} NMR (125 MHz, 300 K, CD₂Cl₂): δ 66.2, 67.8 (d, $J_{CP} = 11.0$ Hz, CHPh), 110.2, 110.5, 110.9, 111.3 (d, $J_{CP} = 3.6$ Hz, Cp), 127.7 (s, C_{arom}), 127.8 (d, $J_{CP} = 7.6$ Hz, C_{arom}), 128.0 (s, C_{arom}), 128.5-129.3 (m, C_{arom}), 133.2 (s, C_{arom}), 133.4-133.6 (m, C_{arom}), 133.7 (s, C_{arom}),

134.9, 135.2 (d, $J_{CP} = 17.2$ Hz, C_{arom}), 135.0, 135.1 (d, $J_{CP} = 19.0$ Hz, $iPPh_2$), 144.7, 145.1 (s, iPh), 154.2, 155.1 (d, $J_{CP} = 9.2$ Hz, $=CH$), 180.8, 181.8 (d, $J_{CP} = 92.2$ Hz, $PC=$) ppm.

$^{31}P\{^1H\}$ NMR (202 MHz, 300 K, toluene- d_8): δ -1.4, -1.1 (s) ppm.

Anal. Calcd. for $C_{62}H_{54}P_2S_2Zr_2$: C, 67.23; H, 4.91; S, 5.79 %. Found: C, 67.19; H, 5.08; S, 5.75 %.

1b (both diastereomers): yield 1.88 g (67 %), beige powder.

1H NMR (500 MHz, 300 K, C_6D_6): δ 3.28, 3.34 (s, 6H, OMe), 4.52, 4.63 (broad s, 2H, $CHPh$), 5.70, 5.79, 6.00, 6.16 (s, 10H, Cp), 6.79, 6.87 (dd, 2H, $J_{HP} = 15.4$ Hz, $J_{HH} = 2.3$ Hz, $=CH$), 6.92-7.34 (H_{arom}), 7.51 (m, H_{arom}), 7.99 (t, H_{arom}) ppm.

$^{13}C\{^1H\}$ NMR (125 MHz, 300 K, CD_2Cl_2):* δ 55.6, 55.7 (s, OMe), 65.7, 67.1 (d, $J_{CP} = 11.5$ Hz, $CHPh$), 110.2, 110.5, 110.9, 111.3 (d, $J_{CP} = 2.3$ Hz, Cp), 128.2 (d, $J_{CP} = 13.8$ Hz, C_{arom}), 128.6 (s, C_{arom}), 128.9-129.3 (m, C_{arom}), 129.6, 129.9 (d, $J_{CP} = 19.1$ Hz, C_{arom}), 133.2-133.7 (m, C_{arom}), 134.3 (s, C_{quat}), 134.8-135.3 (m, C_{arom}), 154.7, 155.5 (d, $J_{CP} = 9.2$ Hz, $=CH$) ppm.

* Some of the ^{13}C NMR signals are not visible due to very low solubility in common deuterated solvents.

$^{31}P\{^1H\}$ NMR (202 MHz, 300 K, C_6D_6): δ -0.4, -0.3 (s) ppm.

Anal. Calcd. for $C_{64}H_{58}O_2P_2S_2Zr_2$: C, 65.83; H, 5.01; S, 5.49 %. Found: C, 65.87; H, 4.87; S, 5.13 %.

Preparation of mixture of complexes **1a**, **1b** and **1c**

To a solution of **1a** (0.08 g ; 0.07 mmol) in toluene (5 mL) was added a solution of **1b** (0.08 g ; 0.07 mmol) in toluene (5 mL). The resulting solution was heated at 90 °C for some hours (or stirred at room temperature several days), then was *vacuum* dried.

Scrambling experiment: To a solution of dimethylzirconocene (0.48 g; 1.9 mmol) in toluene (20 mL) was added diphenylphosphinoacetylene (0.40 g; 1.9 mmol) followed by half equivalent of each of the thiols (phenyl-methanethiol: 0.11 mL; 0.95 mmol, and (4-methoxyphenyl)-methanethiol: 0.13 mL; 0.95 mmol). The resulting solution was stirred for 2 h at room temperature then it was heated at 90 °C for 10 h. A beige solid precipitated during the reaction. The mixture was cooled to room temperature, concentrated in *vacuo* and pentane (40 mL) was added. The resulting solid product was washed with 5 X 10 mL of pentane and was *vacuum* dried.

Characteristic NMR resonances:

^1H NMR (500 MHz, 300 K, C_6D_6): δ 3.27, 3.34 (s, OMe, **1b**), 3.27, 3.33 (s, OMe, **1c**), 4.47, 4.59 (broad s, CHPh , **1a**), 4.49, 4.51, 4.61, 4.62 (broad s, CHPh , **1c**), 4.52, 4.63 (broad s, CHPh , **1b**), 5.63, 5.73, 5.97, 6.13 (s, Cp, **1a**), 5.65, 5.69, 5.75, 5.79, 5.98, 5.99, 6.14, 6.15 (s, Cp, **1c**), 5.71, 5.80, 6.00, 6.17 (s, Cp, **1b**) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 300 K, C_6D_6): δ -0.59, -0.48 (s, **1a**), -0.54, -0.50, -0.42, -0.29 (s, **1c**), -0.37, -0.27 (s, **1b**) ppm.

Preparation of complexes **2a,b**

To a suspension of the appropriate bis-zirconocene-ate complex (for **2a**: 0.25 g; 0.23 mmol of **1a**, and for **2b**: 0.25 g; 0.21 mmol of **1b**) in THF (15 mL), was added at room temperature, a large excess of a solution of borane methyl sulfide complex in THF ($\text{C} = 2 \text{ mol.L}^{-1}$) (for **2a,b**: 2 mL; 4 mmol). The reaction mixture was stirred for 2 h, and then evaporated to dryness. The resulting solid was washed by 3 X 10 mL of pentane and *vacuum* dried.

2a: yield 0.23 g (86 %), white powder.

^1H NMR (500 MHz, 300 K, C_6D_6): δ 0.10 (broad s, BH_3), 2.10 (broad s, BH_3), 4.12 (dd, 1H, $J_{\text{HP}} = 5.5 \text{ Hz}$, $J_{\text{HH}} = 1.9 \text{ Hz}$, CHPh), 5.45, 6.00 (s, 5H, Cp), 6.78 (dd, 1H, $J_{\text{HP}} = 27.0 \text{ Hz}$, $J_{\text{HH}} = 1.9 \text{ Hz}$, =CH), 6.82-7.32 (m, H_{arom}), 7.62 (m, H_{arom}), 8.38 (m, H_{arom}) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 300 K, C_6D_6): δ 64.3 (d, $J_{\text{PC}} = 27.6 \text{ Hz}$, CHPh), 108.5, 110.8 (s, Cp), 127.6, 128.8 (s, C_{arom}), 129.3 (d, $J_{\text{PC}} = 9.2 \text{ Hz}$, C_{arom}), 129.4 (s, C_{arom}), 130.4, 131.5 (d, $J_{\text{PC}} = 2.2 \text{ Hz}$, C_{arom}), 133.1, 134.3 (d, $J_{\text{PC}} = 8.6 \text{ Hz}$, C_{arom}), 144.5 (s, *iPh*), 159.4 (d, $J_{\text{PC}} = 6.3 \text{ Hz}$, =CH), 172.4 (d, $J_{\text{PC}} = 22.3 \text{ Hz}$, PC=) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 300 K, C_6D_6): δ 27.0 (m) ppm.

MS(EI) m/z 566 [$\text{M}^{+\bullet} - \text{BH}_3$].

Anal. Calcd. for $\text{C}_{31}\text{H}_{33}\text{B}_2\text{PSZr}$: C, 64.03; H, 5.72; S, 5.51 %. Found: C, 63.58; H, 5.84; S, 5.18 %.

2b: yield 0.23 g (88 %), white powder.

^1H NMR (500 MHz, 300 K, C_6D_6): δ 0.13 (broad s, BH_3), 2.03 (broad s, BH_3), 3.23 (s, 3H, OMe), 4.15 (dd, 1H, $J_{\text{HP}} = 5.0 \text{ Hz}$, $J_{\text{HH}} = 1.8 \text{ Hz}$, CHPh), 5.47, 6.01 (s, 5H, Cp), 6.66-6.68 (m, H_{arom}), 6.79 (dd, 1H, $J_{\text{HP}} = 27.1 \text{ Hz}$, $J_{\text{HH}} = 1.8 \text{ Hz}$, =CH), 6.83-7.24 (m, H_{arom}), 7.64 (m, H_{arom}), 8.39 (m, H_{arom}) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 300 K, C_6D_6): δ 55.2 (s, OMe), 64.2 (d, $J_{\text{PC}} = 26.9$ Hz, CHPh), 108.6, 110.9 (s, Cp), 128.9 (s, *m*Ph), 128.9, 129.4 (d, $J_{\text{PC}} = 9.6$ Hz, *o*PPh₂), 130.5 (d, $J_{\text{PC}} = 2.0$ Hz, *p*PPh₂), 131.5 (d, $J_{\text{PC}} = 57.6$ Hz, *i*PPh₂), 131.6 (s, *o*Ph), 133.2 (d, $J_{\text{PC}} = 8.6$ Hz, *m*PPh₂), 134.0 (d, $J_{\text{PC}} = 44.1$ Hz, *i*PPh₂), 134.5 (d, $J_{\text{PC}} = 8.6$ Hz, *m*PPh₂), 136.8 (s, *i*Ph), 160.0 (s, *i*PhOMe), 160.0 (d, $J_{\text{PC}} = 6.7$ Hz, =CH), 171.9 (d, $J_{\text{PC}} = 22.1$ Hz, PC=) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 300 K, C_6D_6) δ 27.1 (m) ppm.

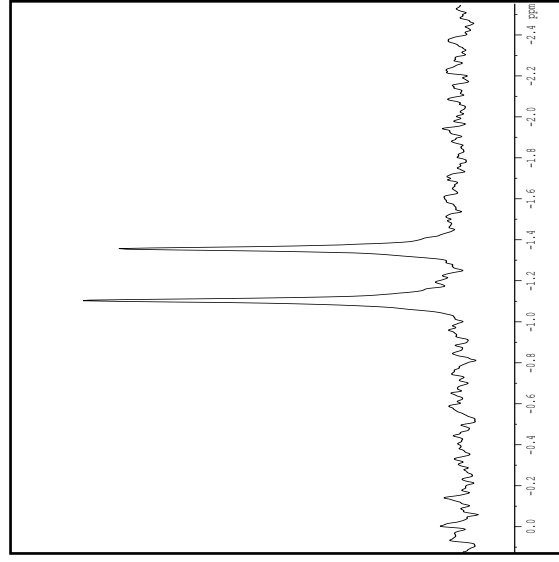
MS(EI) m/z 596 [$\text{M}^{+\bullet} - \text{BH}_3$].

Anal. Calcd. for $\text{C}_{32}\text{H}_{35}\text{B}_2\text{OPSZr}$: C, 62.85; H, 6.18; S, 5.24 %. Found: C, 63.12; H, 6.01; S, 5.08 %.

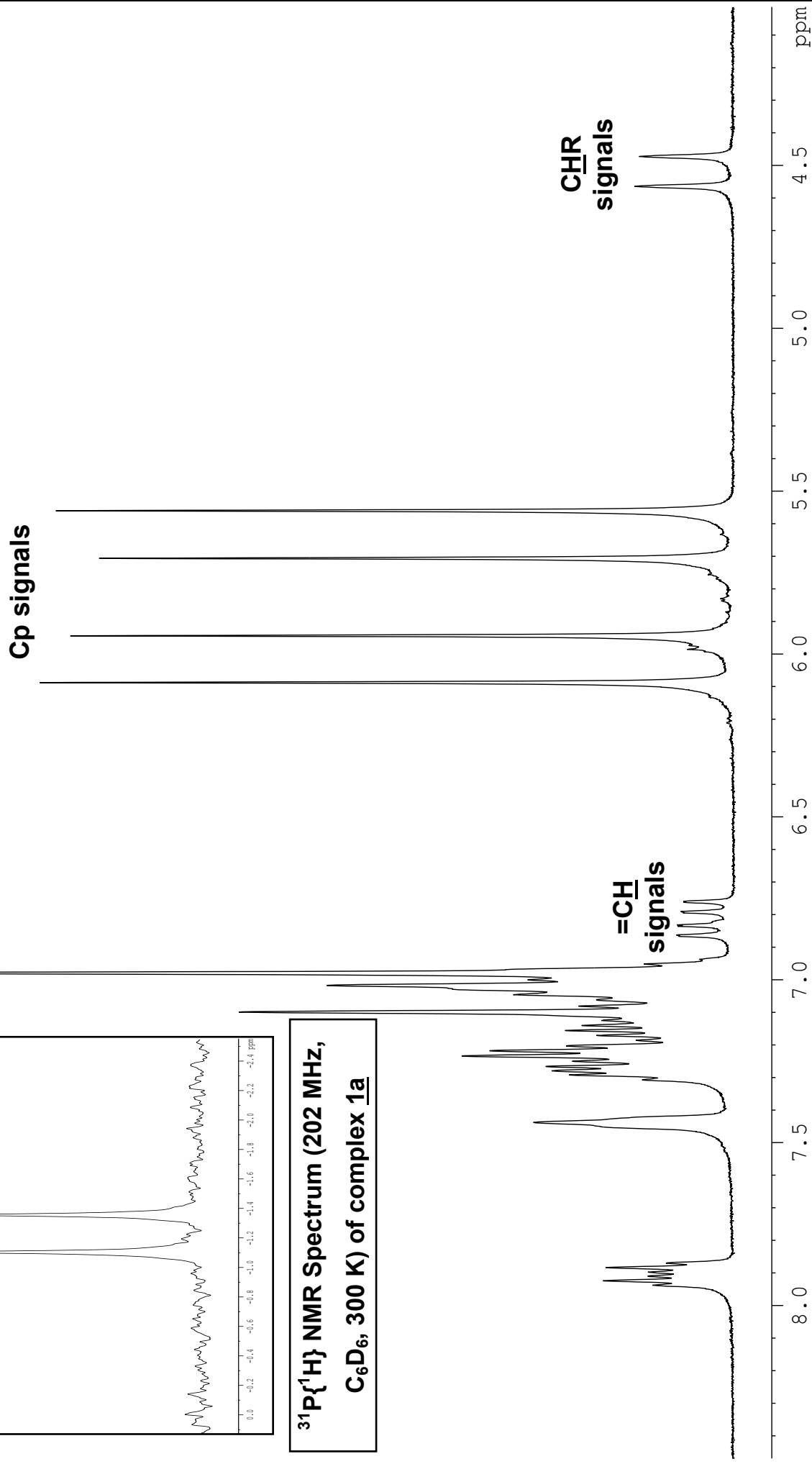
References:

1. Charrier, C., Simonnin, M. P., Chodkiewicz, W., and Cadiot, P. (1964) *Compt. Rend.* **258**, 1537-1540.
2. Samuel, E., and Rausch, M. D. (1973) *J. Am. Chem. Soc.* **95**, 6263-6267.

**^1H NMR Spectrum (500 MHz,
Tol- d_8 , 300 K) of complex 1a**

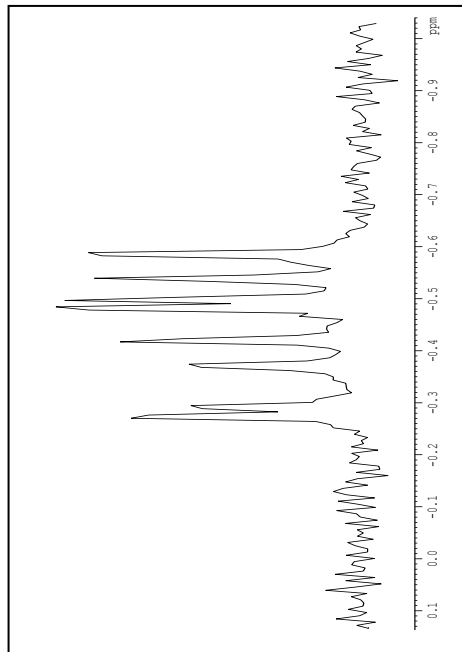
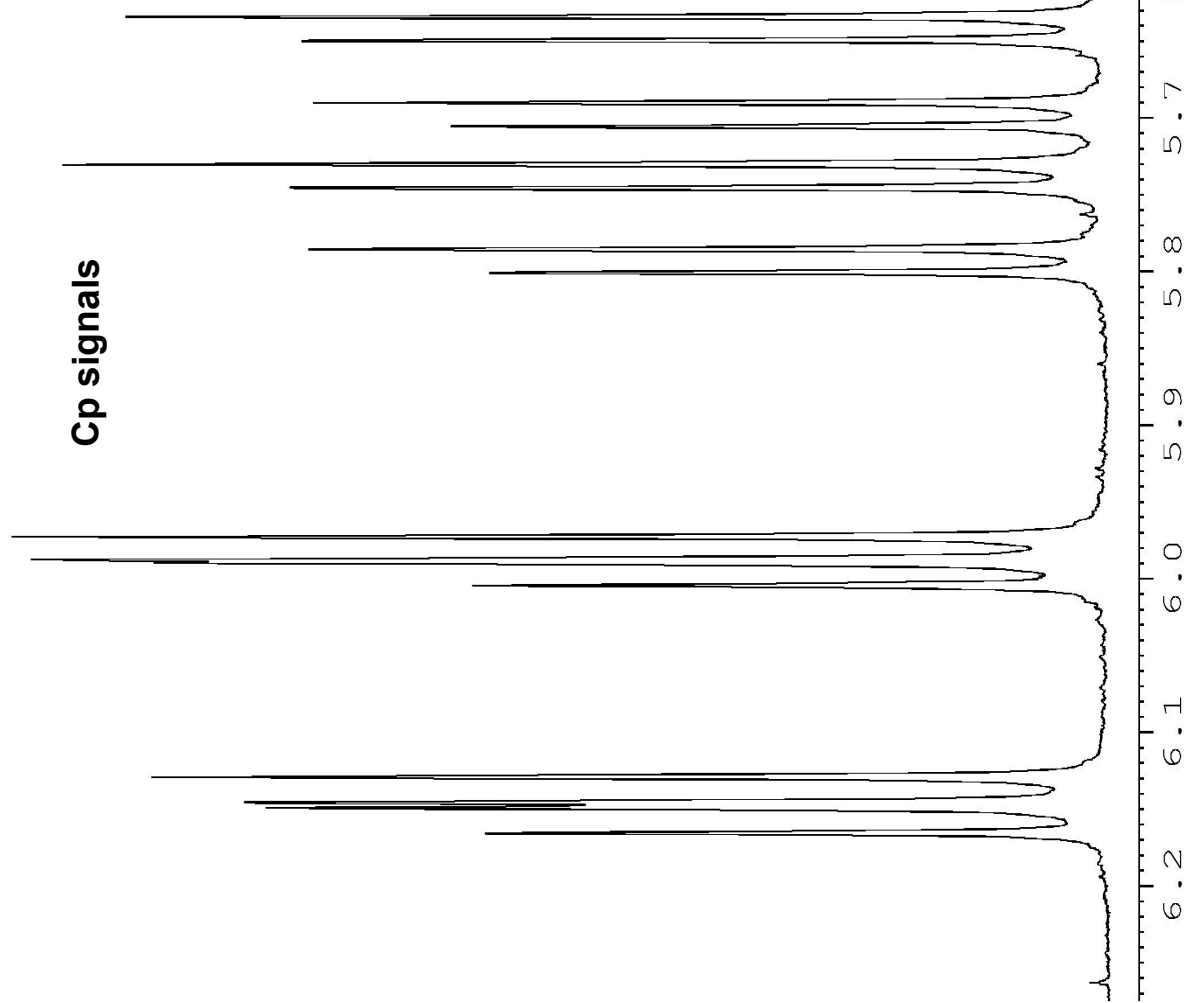


**$^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum (202 MHz,
 C_6D_6 , 300 K) of complex 1a**



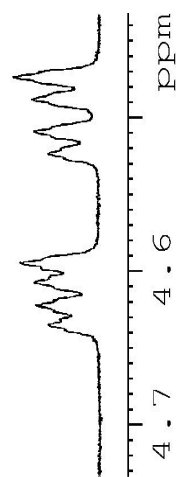
^1H NMR Spectrum (500 MHz, C_6D_6 , 300 K) of the mixture of complexes : 1a, 1b and 1c

Cp signals



$^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum (202 MHz, C_6D_6 , 300 K) of the mixture of complexes : 1a, 1b and 1c

CHR signals



Temperature dependant ^1H NMR Spectrum (500 MHz,
Tol- d_8) of the mixture of complexes : 1a, 1b and 1c

