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Electronic Supplementary Information (ESI)

Valorisation of Mixtures of Linear Alkenes using Cobalt-Mediated Isomerisation and Hydroformylation Chemistries

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1. General Considerations.

All syntheses were carried out using chemicals purchased from commercial sources unless otherwise cited. Air- and moisture-sensitive manipulations and hydroformylation reactions were performed under inert atmosphere, either in a N_2-filled glove box or with standard Schlenk techniques. Hazards: Carbon monoxide (CO) is a very toxic gas by inhalation and this reagent or metal carbonyl complexes were always used in well-ventilated hoods.

Glassware was dried in vacuo before use with a hot air gun. All solvents were dried and deoxygenated by using a Solvent Purification system (SPS). All solvents and reagents (liquids) have been degassed using freeze-pump-thaw cycles and stored at low temperature with activated molecular sieves (4 Å) under N_2 atmosphere prior to their use. NMR spectra were recorded at room temperature, unless otherwise cited, in 300 MHz, 400 MHz or 500 MHz spectrometers in CD_2Cl_2 and PhMe-d_8 unless otherwise noted. ^{1}H, $^{13}C\{^{1}H\}$ or $^{13}C\{^{1}H,^{31}P\}$-NMR chemical shifts were quoted in ppm relative to the residual solvent peaks. $^{31}P\{^{1}H\}$-NMR chemical shifts were quoted in ppm relative to 85% phosphoric acid in water. IR spectra were recorded using Attenuate Total Reflection (ATR) techniques unless otherwise cited. High-resolution mass spectra (HRMS) were recorded by matrix-assisted laser desorption/ionization (MALDI) or ESI ionization methods.

2. General Structural Comments on X-Ray Crystals.

2.1. X-Ray Crystals of [Co(H)(CO)$_2$(Xantphos)] (complex C1).

Crystals of the complex **C1** were grown by solvent diffusion, using toluene and *n*-pentane at –20 °C under inert atmosphere. The measured crystals were prepared under inert conditions and immersed in perfluoropolyether as protecting oil for manipulation.

Crystal structure determination for the complex **C1** was carried out using a Rigaku diffractometer equipped with a Pilatus 200K area detector, a Rigaku MicroMax-007HF microfocus rotating anode with MoK_α radiation, confocal Max Flux optics and an Oxford Cryosystems low temperature device Cryostream 700 plus (T = –173 °C). Full-sphere data collection was used with ω and φ scans. *Programs used:* Data collection and reduction with CrysAlisPro[1] V/60A and absorption correction with Scale3 Abspack scaling algorithm.[2] Crystal structure solution was achieved using the computer program SHELXT.[3] Visualization was performed with the program SHELXle.[4] Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXL 2015.[5] All non-hydrogen atoms were refined including anisotropic displacement parameters.

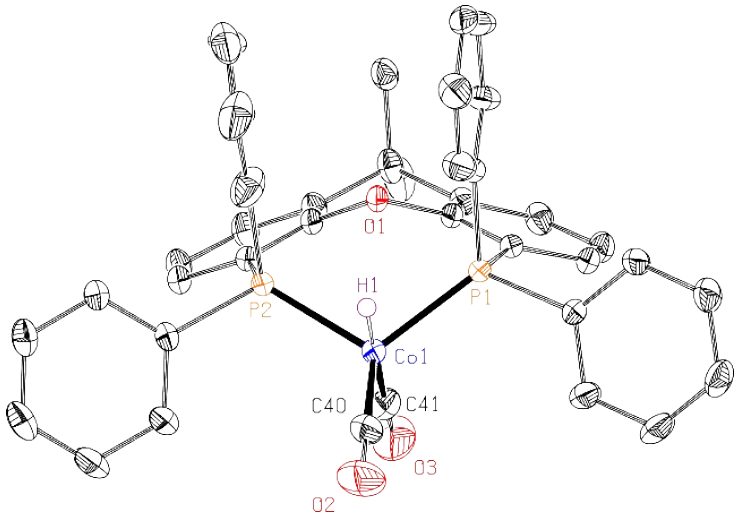


Figure 1 ORTEP drawing (thermal ellipsoids drawn at a 50% probability level) showing the structure of the complex **C1**. Colour Scheme: C: black, Hydride: violet, Co: blue, O: red, P: orange.

Comments to the crystal structure of complex **C1**: The asymmetric unit contains one molecule of the metal complex, one molecule of toluene and 0.5 molecules of pentane. The toluene molecule is disordered in three orientations with a ratio of 65:25:10. The half pentane molecule is disordered in two orientations and shared with the neighbouring asymmetric unit. The hydrogen atom attached to the cobalt atom was localized from the residual electron density and refined free on its position. The Co–H distance is of 1.50(2) Å, which is in the range for the expected distance for this type of bonds (a search in the CCDC for similar structures gave distances in the range 1.39-1.58 Å).

Table 1 Crystal data and structural parameters for the complex **C1**.

Compound	**Complex C1**
Formula	$C_{50}H_{47}CoO_3P_2$
Solvent	Toluene/Pentane
Formula weight	822.75
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	*P2*(1)/n
a (Å)	9.9652(3)
b (Å)	18.3490(5)
c (Å)	23.3602(9)
α (°)	90
β (°)	96.462(3)
γ (°)	90
Volume (Å^3)	4244.3(2)
Θ	4
ρ (g·cm^{-3})	1.288
μ (mm^{-1})	0.522
θmax (°)	34.798
Reflect. collected	76515
Unique reflect.	17442 [R(int) = 0.0548]
Absorpt. correction	Multi-scan
Parameters/restrains	678/739
R1/wR2 [I>2σ(I)]	0.0512/0.1233
R1/wR2 (all data)	0.1079/0.1468
Goodness-of-fit (F^2)	1.009
Peak/hole (e/Å^{-3})	0.986/–0.643

2.2. X-Ray Crystals of $[Co_2(CO)_6(Xantphos)]$ (Complex C2).

Crystals of the complex **C2** were grown by solvent diffusion, using toluene and *n*-pentane under inert atmosphere. The measured crystals were prepared under inert conditions and immersed in perfluoropolyether as protecting oil for manipulation.

A yellow prism-like specimen of $C_{45}H_{32}Co_2O_7P_2$, approximate dimensions 0.060 mm x 0.149 mm x 0.348 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å).

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 63484 reflections to a maximum θ angle of 30.55° (0.70 Å resolution), of which 11551 were independent (average redundancy 5.496, completeness = 99.2%, Rint = 3.56%, Rsig = 2.51%) and 10051 (87.01%) were greater than 2σ(F2). The final cell constants of a = 10.8578(8) Å, b = 11.6947(9) Å, c = 17.4282(13) Å, α = 106.744(3)°, β = 95.840(3)°, γ = 112.496(3)°, volume = 1900.9(3) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the Multi-Scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6883 and 0.7461.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, $C_{45}H_{32}Co_2O_7P_2$. The final anisotropic full-matrix least-squares refinement on F2 with 507 variables converged at R1 = 2.92%, for the observed data and wR2 = 7.82% for all data. The goodness-of-fit was 1.034. The largest peak in the final difference electron density synthesis was 1.113 e/$Å^3$ and the largest hole was -0.724 e/$Å^3$ with an RMS deviation of 0.069 e/$Å^3$. On the basis of the final model, the calculated density was 1.510 g/cm^3 and F(000), 884 e.

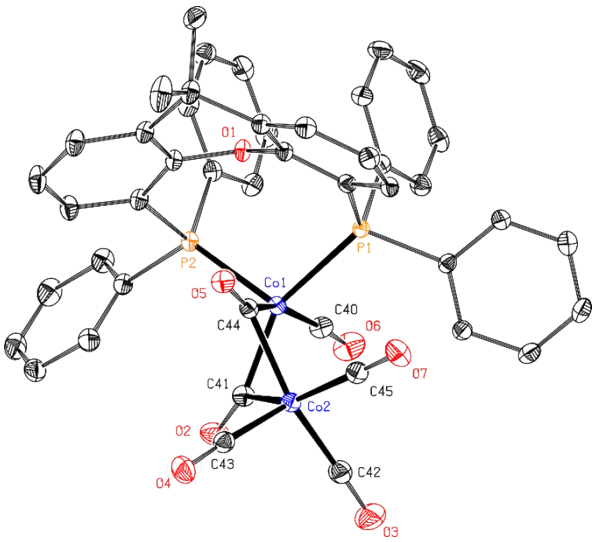


Figure 2 ORTEP drawing (thermal ellipsoids drawn at a 50% probability level) showing the structure of complex **C2**. Colour Scheme: C: black, Co: blue, O: red, P: orange.

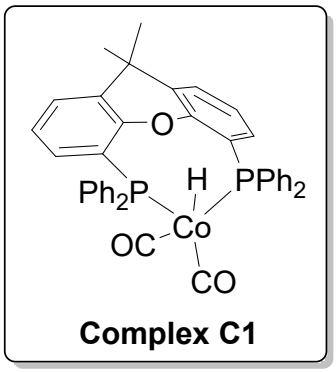
Comments to the crystal structure of complex **C2**: The asymmetric unit contains one molecule of the metal complex.

Table 2 Crystal data and structural parameters for the complex **C2**.

Compound	Complex C2
Formula	$C_{45}H_{32}Co_2O_7P_2$
Solvent	Toluene/Pentane
Formula weight	864.50
Temperature (K)	100(2)
Crystal system	Triclinic
Space group	P -1
a (Å)	10.8578(8)
b (Å)	11.6947(9)
c (Å)	17.4282(13)
α (°)	106.744(3)
β (°)	95.840(3)
γ (°)	112.496(3)
Volume (Å^3)	1900.9(3)
Θ	2
ρ (g·cm^{-3})	1.510
μ (mm^{-1})	1.011
θmax (°)	30.548
Reflect. collected	63484
Unique reflect.	11551 [R(int) = 0.0356]
Absorpt. correction	Semi-empirical from equivalents
Parameters/restrains	507/0
R1/wR2 [I>2σ(I)]	0.0292/0.0719
R1/wR2 (all data)	0.0375/0.0782
Goodness-of-fit (F^2)	1.034
Peak/hole (e/Å^{-3})	-0.724

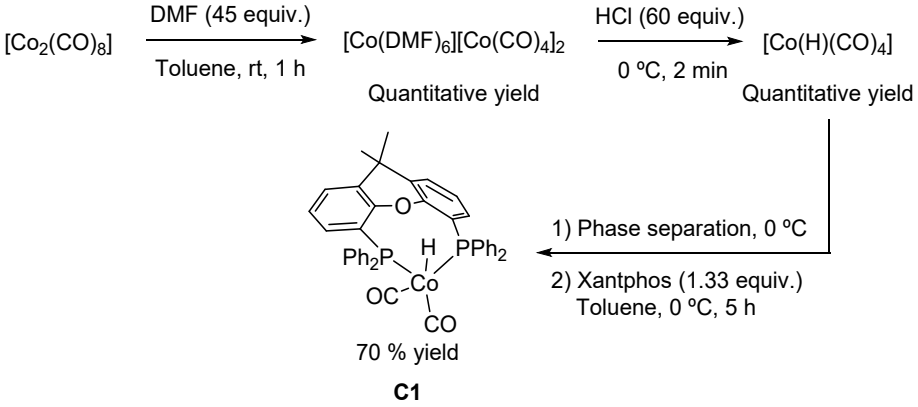
3. Synthesis of metal complexes C1 and C2.

3.1. Synthesis of [Co(H)(CO)$_2$(Xantphos)] (complex C1).



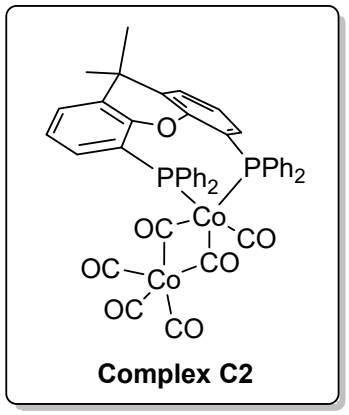
Complex C1

Complex C1: The preparation of the complex **C1** was performed by modifying a reported procedure in the literature.[6] Under argon atmosphere, [$Co_2(CO)_8$] (94.8 mg, 0.25 mmol) was dissolved in anhydrous toluene (1.7 mL) in a 2 mL vial with stirring and anhydrous DMF (869 µL, 11.20 mmol) was added to the previous solution. After formation of a pink precipitate (*ca.* 1 h), the reaction mixture was cooled down to 0 °C and aqueous HCl (2.5 mL, 6 M, 15.00 mmol) was added at once. After stirring for 2 minutes, two phases were formed: the aqueous phase (pink) and the organic phase (yellow). The organic phase was separated under argon atmosphere at 0 °C and dried over $MgSO_4$ and a solution of Xantphos (202 mg, 0.33 mmol) in anhydrous toluene (3.7 mL) was added. The reaction proceeded by CO bubbling, which led to the formation of a yellow precipitate. After 5 h stirring at 0 °C, the crude mixture was stored in the freezer under N_2 for 2 h. The liquid and precipitate were separated, the precipitate was washed with anhydrous *n*-pentane (5 mL) and solid was dried under vacuum. The complex **C1** was obtained as a yellow solid (161 mg, 70% yield). IR (neat, cm^{-1}) $\bar{\upsilon}$ 3057, 2956, 2928, 2861, 1917 ($\bar{\upsilon}_{CO}$), 1910 ($\bar{\upsilon}_{CO}$), 1586, 1479, 1433, 1404, 1358, 1307, 1227, 1180, 1154, 1118, 1091, 1068, 1026, 999, 794, 779, 748, 689, 655, 536, 509, 469, 441. ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 7.48 (dd, J = 7.9, 1.2 Hz, 2H), 7.36 (bs, 8H), 7.28–7.25 (m, 4H), 7.18 (t, J = 7.4 Hz, 8H), 7.02 (t, J = 7.7 Hz, 2H), 6.36–6.33 (m, 2H), 1.69 (s, 6H), –11.23 (t, J = 23.3 Hz, 1H) ppm. ^{13}C{^{1}H,^{31}P}-NMR (126 MHz, CD_2Cl_2) δ 209.3 (2 C, *C*O), 155.9 (2 C, *Carom*O), 136.3 (4 C, *Carom*P), 135.5 (2 C, *Carom*C(CH_3)$_2$), 133.6 (8 C, *Carom*H), 129.7 (2 C, *Carom*H), 129.5 (4 C, *Carom*H), 128.3 (8 C, *Carom*H), 127.5 (2 C, *Carom*P), 126.2 (2 C, *Carom*H), 124.0 (2 C, *Carom*H), 37.0 (2 C, *C*H_3), 27.1 (1 C, *C*(CH_3)$_2$) ppm. ^{31}P{^{1}H}-NMR (202 MHz, CD_2Cl_2) δ 43.4 ppm. HRMS (MALDI) *m/z* [M–2CO–H] calcd for $C_{39}H_{32}CoOP_2$ 637.1255, found 637.1270.



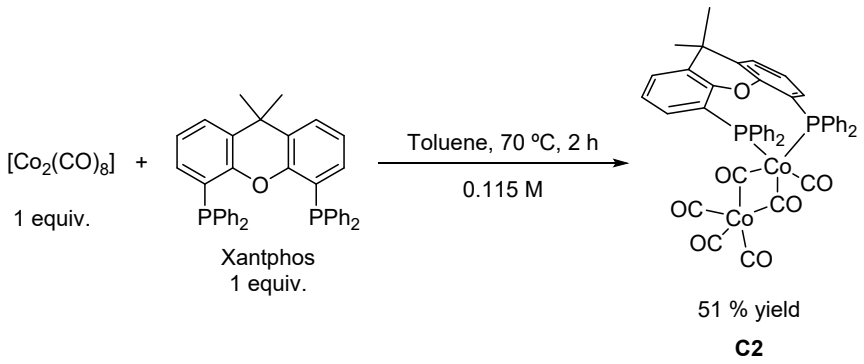
Scheme 1 Synthesis of **C1**.

3.2. Synthesis of $[Co_2(CO)_6(Xantphos)]$ (complex C2).



Complex C2

Complex C2: In a glove box filled with nitrogen, $[Co_2(CO)_8]$ (220 μmol, 83.8 mg) and Xantphos (220 μmol, 134.3 mg) were added into a 10 mL in a flame dried 10 mL ace pressure tube with a magnetic stirrer in 1.9 mL of anhydrous and deoxygenated toluene having a concentration of 0.115 M respect of the Xantphos. The reaction mixture was stirred at 70 ºC for 2 hours under nitrogen atmosphere. Following the reaction mixture was kept in the glove box and 5 mL of anhydrous and deoxygenated *n*-pentane was added into the glass tube, which led to the formation of a red orange precipitate. The vial was kept in the glove box for 48 hours to favour the precipitation of the product. Then, the liquid and precipitate were separated, the precipitate was washed twice with anhydrous *n*-pentane (2x5 mL) and solid was dried under vacuum. The complex **C2** was obtained as a red-orange solid (97 mg, 51 % yield). IR (neat, cm^{-1}) $\bar{\upsilon}$ 2955.64, 2043.39 ($\bar{\upsilon}_{CO}$), 1963.32 ($\bar{\upsilon}_{CO}$), 1940.02 ($\bar{\upsilon}_{CO}$), 1880.43 ($\bar{\upsilon}_{CO}$), 1815.43, 1785.57, 1479.34, 1433.32, 1405.48, 123-9.7, 1093.39, 747.79, 735.73, 686.25, 622.59, 603.46, 575.93. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 7.62 (d, J = 7.3 Hz, 2H), 7.26 (bs, 12 H), 7.17 (bs, 10 H), 6,61 (bs, 2H), 1.72 (s, 6 H). $^{13}C\{^{1}H\}$-NMR (126 MHz, CD_2Cl_2) 155.22 (2 C, *Carom*O), 133.23 (4 C, *Carom*P), 132.89, 130.87, 129.58, 128.10, 128.06, 128.02, 126.91, 124.52, 118.54, 118.25, 36.28 (2 C, CH_3). $^{31}P\{^{1}H\}$-NMR (202 MHz, CD_2Cl_2) δ 32.29. HRMS (ESI^+) *m/z* [M–5CO–Co] calcd for $C_{40}H_{32}CoO_2P_2$ 665.1210, found 665.1213.



Scheme 2 Synthesis of **C2**.

4. General procedure for the cobalt-catalyzed hydroformylation.

Essays for screening catalysts:

In a glove box filled with nitrogen, Xantphos (*ca.* 2.7 μmol in 360 μL of toluene) and [$Co_2(CO)_8$] (*ca.* 2.7 μmol in 360 μL of toluene), [Co(H)$(CO)_2$(Xantphos)] (**C1**) (*ca.* 2.3 μmol in 65 μL of toluene) or [$Co_2(CO)_6$(Xantphos)] (**C2**) (*ca.* 2.3 μmol in 65 μL of toluene) were added into a 2 mL vial equipped with a magnetic stirrer. Substrate (the corresponding octene, heptene or hexene or mixtures thereof; *ca.* 230 μmol), dodecane (*ca.* 69 μmol) and additional toluene were charged to provide the desired final solution having a 0.26 M concentration of substrate(s). The vial was transferred into an autoclave and taken out of the glove box. The autoclave was purged three times with syngas (1:1 H_2/CO ratio without stirring, at a pressure not higher than 10 bar) and, finally, the autoclave was pressurized with syngas to the desired pressure. The reaction mixture was stirred at the selected temperature (metallic block) for the selected reaction time. The reaction was cooled down to room temperature (ice bath) and the pressure was carefully released in a well-ventilated hood. Conversion, chemo- and regio-selectivity of the products arising from hydroformylation reaction conditions were determined by GC analysis on an achiral stationary phase (HP-5) using dodecane as the internal standard (IS).

Hydroformylation at the preparative scale (S/C = 500):

In a glove box filled with nitrogen, [$Co_2(CO)_6$(Xantphos)] (**C2**) (43.6 mg, 0.0505 mmol) was placed in a 25 mL autoclave with a magnetic stirrer. Oct-1-ene (**1a**) (4.0 mL, 25.2 mmol) and toluene (10.4 mL) were added to provide the desired final solution, giving a 1.8 M concentration of oct-1-ene. The autoclave was purged three times with syngas (1:1 H_2/CO ratio without stirring, at a pressure not higher than 10 bar) and, finally, the autoclave was pressurised with syngas to 40 bar. The autoclave was connected to a five-litre steel reservoir filled with syngas to ensure that pressure was high enough during the whole hydroformylation process. The reservoir was isolated from the reactor by a valve, and the pressure inside the autoclave was restored to 40 bar by opening the valve when the pressure inside the autoclave dropped by 10% and closing it afterwards. The reaction mixture was stirred at 140 °C for 21 h. The reaction was cooled down to room temperature (ice bath) and the pressure was carefully released in a well-ventilated hood. The reaction mixture was distilled under reduced pressure to obtain the corresponding mixture of aldehydes (fraction 1, b.p. = 35-45 ºC, 25-30 mbar, 8.84 g, 2.3 mmol of aldehydes and fraction 2, b.p. = 75-80 ºC, 25-30 mbar, 1.57 g, 11.0 mmol of aldehydes; 53% overall yield).

Hydroformylation at the preparative scale (S/C = 1000):

In a glove box filled with nitrogen, [$Co_2(CO)_6$(Xantphos)] (**C2**) (21.8 mg, 0.0252 mmol) was placed in a 25 mL autoclave with a magnetic stirrer. Oct-1-ene (**1a**) (4.0 mL, 25.2 mmol) and toluene (10.4 mL) were added to provide the desired final solution, giving a 1.8 M concentration of oct-1-ene. The hydroformylation process was carried out as indicated above for S/C = 500. The reaction mixture was distilled under reduced pressure to obtain the corresponding mixture of aldehydes (fraction 1, b.p. = 40-45 ºC, 25-30 mbar,

8.40 g, 1.72 mmol of aldehydes and fraction 2, b.p. = 75-80 ºC, 25 mbar, 2.16 g, 11.0 mmol of aldehydes; 51% overall yield).

4.1. Determination of the conversion, chemoselectivity and regioselectivity in hydroformylation reaction mixtures.

Conversion, chemo- and regio-selectivity of the products arising from hydroformylation reaction conditions were determined by GC analysis on an achiral stationary phase (HP-5) using dodecane as the internal standard. The conversion was determined using the response factor of the starting material. The selectivity was determined from area % data of the GC analysis.

GC analysis conditions for hydroformylation reaction mixtures of oct-1-ene, (*Z*)-oct-2-ene, (*E*)-oct-2-ene, (*E*)-oct-3-ene, (*E*)-oct-4-ene and (*Z*)-oct-4-ene: Conversion, chemo- and regio-selectivity in the mixtures arising from hydroformylation reaction conditions were determined by GC-FID analysis with a HP-5 column (5% phenyl methyl siloxane; 30 m x 320 µm x 0.25 µm). Flow rate: 2.3 mL/min. Temperature program: 35 °C for 5 min, then up to 150 °C at 20 °C/min and 10 min at 150 °C, then up to 320 °C at 20 °C/min and 5 min at 320 ºC. Retention times: 5.2 min for oct-1-ene, 5.3 min for (*E*)-oct-4-ene, 5.4 min for octane, 5.6 min for (*E*)-oct-3-ene, 5.7 min for (*Z*)-oct-4-ene, 5.9 min for (*E*)-oct-2-ene, 6.1 min for (*Z*)-oct-2-ene, 9.5 min for **2d** (2-propylhexanal), 9.6 min for **2c** (2-ethylheptanal), 9.7 min for **2b** (2-methyloctanal), 10.2 min for **2a** (nonanal) , 10.7 min for **3d** (2-propyl-hexan-1-ol), 10.8 min for **3c** (2-ethyl-heptan-1-ol), 10.9 min for **3b** (2-methyl-octan-1-ol), 11.1 min for the IS (dodecane), 11.3 min for **3a** (nonan-1-ol).

GC analysis conditions for hydroformylation reaction mixtures of hept-1-ene, (*Z*)-hept-2-ene, (*E*)-hept-2-ene, (*E*)-hept-3-ene: Conversion, chemo- and regio-selectivity in the mixtures arising from hydroformylation reaction conditions were determined by GC-FID analysis with a HP-5 column (5% phenyl methyl siloxane; 30 m x 320 µm x 0.25 µm). Flow rate: 2.6 mL/min. Temperature program: 40 °C for 5 min, then up to 150 °C at 20 °C/min and 10 min at 150 °C, then up to 275 °C at 20 °C/min and 5 min at 275 °C. Retention times: 2.74 min for hept-1-ene, 2.06 min for (*E*)-hept-3-ene, 2.89 min for heptane, 2.95 min for (*E*)-hept-2-ene, 3.07 min for (*Z*)-hept-2-ene, 7.88 min for 2-propylpentanal, 7.98 min for 2-ethylhexanal, 8.09 min for 2-methylheptanal, 8.60 min for octanal, 10.39 min for the IS (dodecane).

GC analysis conditions for hydroformylation reaction mixtures of hex-1-ene, (*Z*)-hex-2-ene, (*E*)-hex-2-ene, (*E*)-hex-3-ene, (*Z*)-hex-3-ene: Conversion, chemo- and regio-selectivity in the mixtures arising from hydroformylation reaction conditions were determined by GC-FID analysis with a HP-5 column (5% phenyl methyl siloxane; 30 m x 320 µm x 0.25 µm). Flow rate: 2.6 mL/min. Temperature program: 40 °C for 5 min, then up to 150 °C at 20 °C/min and 10 min at 150 °C, then up to 275 °C at 20 °C/min and 5 min at 275 °C. Retention times: 1.95 min for hex-1-ene, 1.99 min for hexane, 2.03 min for (*E*)-hex-2-ene, (*Z*)-hex-3-ene, (*E*)-hex-3-ene, 2.09 min for (*Z*)-hex-2-ene), 6.38 min for 2-ethylpentanal, 6.52 min for 2-methylhexanal, 7.24 min for heptanal, 10.39 min for the IS (dodecane).

4.2. Selected GC chromatograms.

Representative example of a GC chromatogram of the mixtures derived from oct-1-ene or its isomers under cobalt-catalysed hydroformylation reaction conditions.

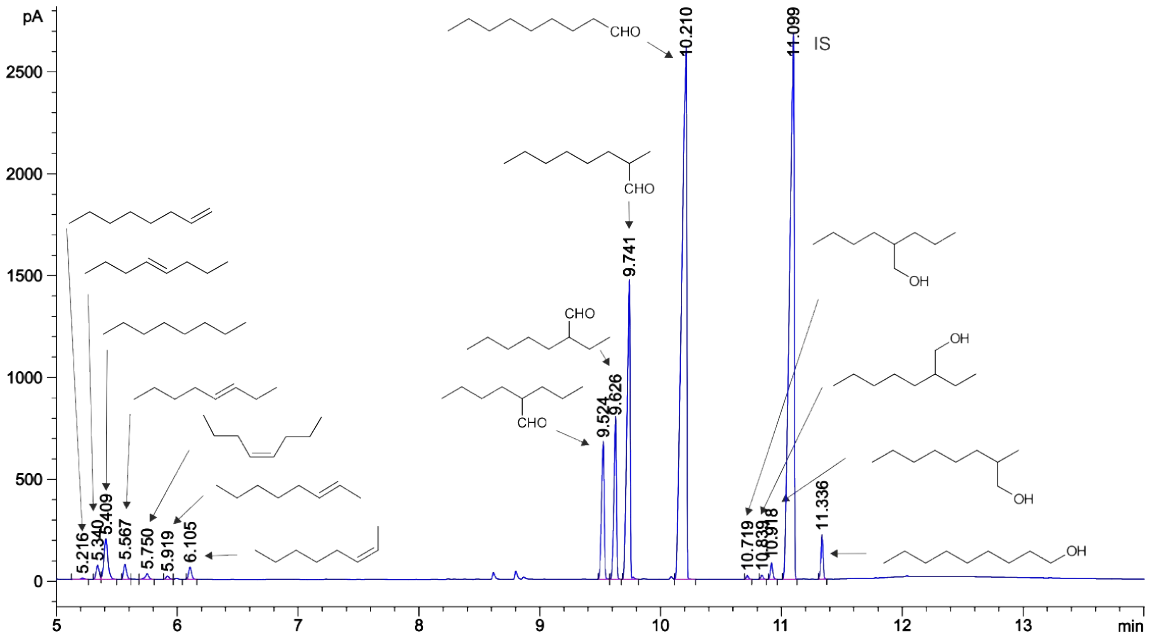


Figure 3 GC chromatogram of the mixtures derived from octenes after hydroformylation catalysis.

Representative example of a GC chromatogram of the mixtures derived from hept-1-ene or its isomers under cobalt-catalysed hydroformylation reaction conditions.

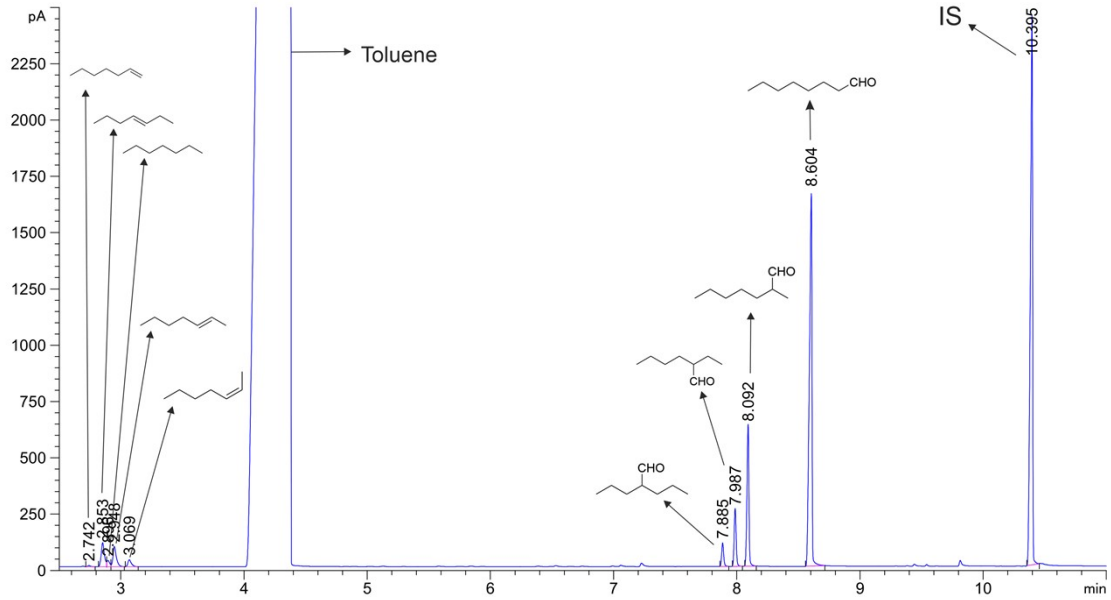


Figure 4 GC chromatogram of mixtures derived from heptenes after hydroformylation catalysis.

Representative example of a GC chromatogram of the mixtures derived from hex-1-ene or its isomers under cobalt-catalysed hydroformylation reaction conditions.

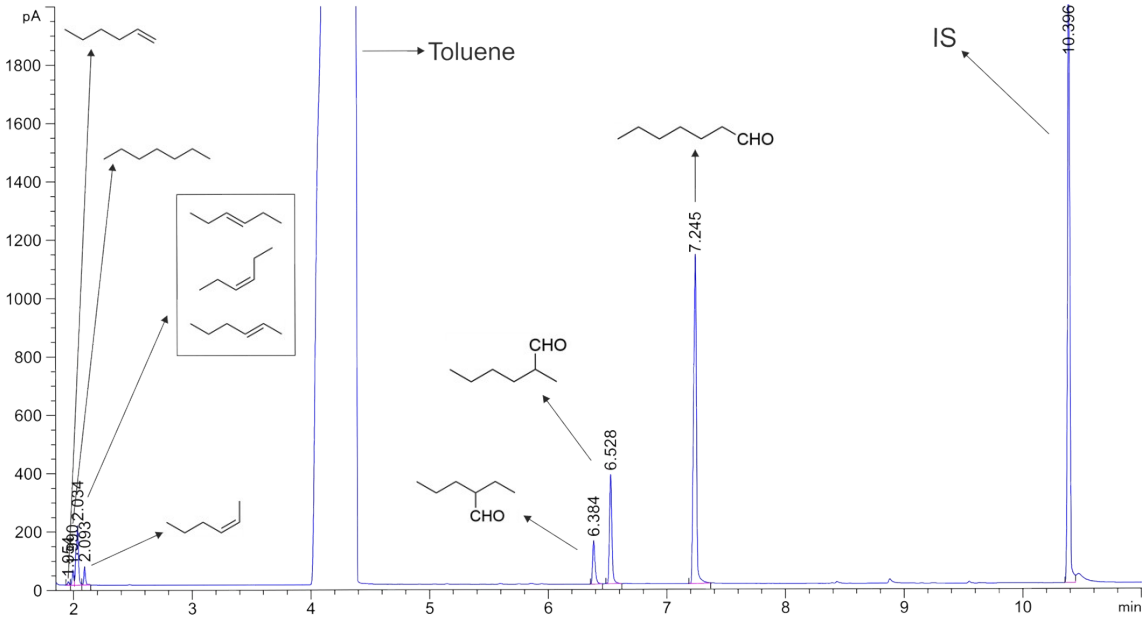
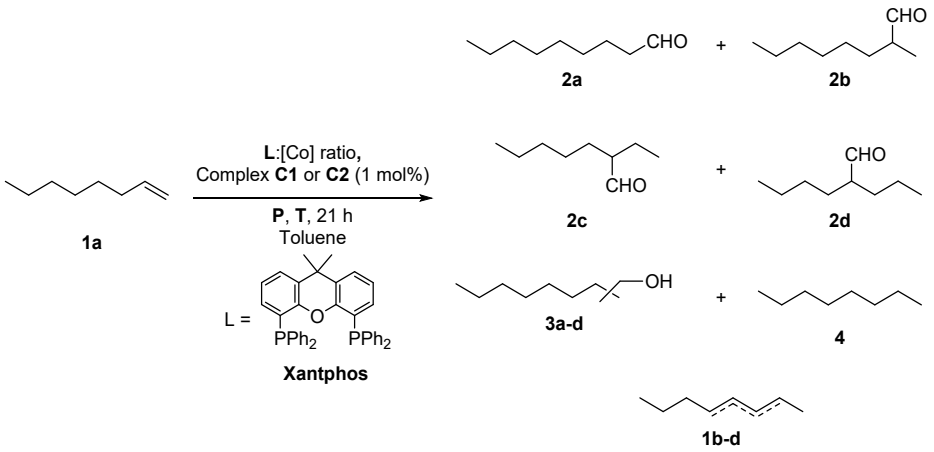


Figure 5 GC chromatogram of mixtures derived from hexenes after hydroformylation catalysis.

5. Complete set of results for cobalt-catalysed hydroformylation.

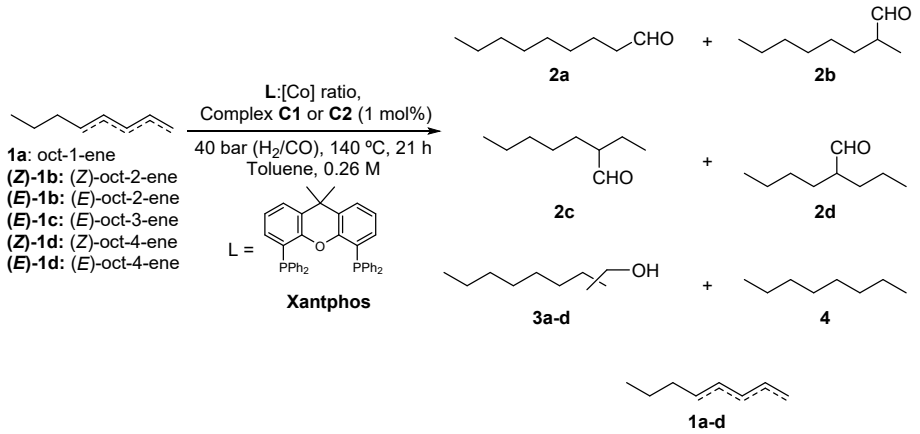
Table 3 Complete set of results of cobalt-catalysed hydroformylation of oct-1-ene.



Entry	T (°C)	Pressure (H_2/CO) (bar)	L:[Co] ratio[a], C1 or C2	[ ] (M)	Conv. (%)[a]	Selectivity[b]				Regioselectivity[b]
						2a–d (%)	3a–d (%)	4 (%)	1b-d (%)	2a/2b (2a/2b/2c/2d)
1	90	40 (1:1)	1:1	0.26	17	11	0	24	65	81:19 (75:18:4:3)
2	110	40 (1:1)	1:1	0.26	50	58	1	7	34	80:20 (73:18:5:4)
3	140	40 (1:1)	1:1	0.26	>99	79	13	4	4	73:27 (62:23:8:7)
4	160	40 (1:1)	1:1	0.26	>99	79	12	5	4	70:30 (56:24:11:9)
5	140	40 (1:3)	1:1	0.26	52	59	0	8	33	76:24 (68:21:6:5)
6	140	40 (3:1)	1:1	0.26	99	48	13	10	29	76:24 (67:21:7:5)
7	140	40 (1:1)	0.25:1	0.26	98	80	17	0	3	79:21 (70:19:6:5)
8	140	40 (1:1)	0:1	0.26	>99	71	25	2	2	77:23 (66:19:8:7)
9	140	40 (1:1)	0.5:1	0.26	>99	85	11	2	2	76:24 (65:21:8:6)
10	140	40 (1:1)	2:1	0.26	51	37	1	13	49	72:28 (64:26:6:4)
11	140	40 (1:1)	**C1**	0.26	99	73	2	10	15	74:26 (64:22:8:6)
12	140	40 (1:1)	0.5:1	0.1	>99	85	5	3	7	75:25 (63:21:9:7)
13	140	40 (1:1)	0.5:1	0.5	>99	80	15	3	2	74:26 (61:21:10:8)
14	140	40 (1:1)	0.5:1	1	>99	67	31	0	2	69:31 (51:23:14:12)
15	140	40 (1:1)	**C2**	0.26	>99	89	2	4	5	78:22 (69:19:7:5)

The hydroformylations were performed in a parallel autoclave. Reaction conditions: [alkene] = 0.26 M; reaction time = 21 h; stirring rate = 800 rpm; H_2/CO in a 1:1 ratio, unless otherwise cited. [a] **L**:[Co] Molar ratio between **L** and cobalt centres in $[Co_2(CO)_8]$. [b] Conversion, regioselectivity and product distribution were determined by GC analysis on an achiral stationary phase (HP-5). Selectivities were calculated as mol of compound into mol of converted substrate.

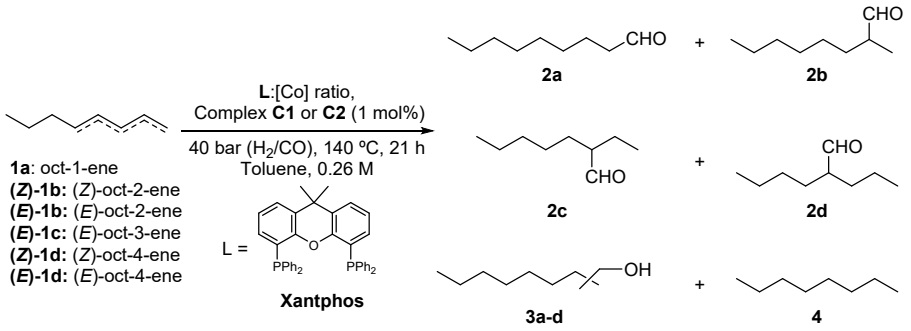
Table 4 Complete set of results of cobalt-catalysed hydroformylation of octenes.



Entry	Substrate	T (°C)	Pressure (H_2/CO) (bar)	L:[Co] ratio[a], C1 or C2	Conv. (%)[a]	Selectivity[b]				Regioselectivity[b]
						2a–d (%)	3a–d (%)	4 (%)	1a-d (%)	2a/2b (2a/2b/2c/2d)
1	(*Z*)-Oct-2-ene	140	40 (1:1)	0.5:1	99	89	4	4	3	74:26 (62:22:9:7)
2		140	40 (1:1)	**C1**	99	55	1	11	33	74:26 (63:22:8:7)
3	(*E*)-Oct-2-ene	140	40 (1:1)	0.5:1	>99	86	3	5	6	75:25 (62:22:9:7)
4		140	40 (1:1)	**C1**	>99	57	1	11	31	74:26 (63:22:8:7)
5	(*E*)-Oct-3-ene	140	40 (1:1)	0.5:1	99	91	4	3	2	74:26 (60:21:10:9)
6		140	40 (1:1)	**C1**	94	74	1	16	9	73:27 (60:22:9:9)
7	(*Z*)-Oct-4-ene	140	40 (1:1)	0.5:1	>99	91	3	4	2	74:26 (59:21:10:10)
8		140	40 (1:1)	**C1**	98	62	1	15	22	74:26 (61:21:9:9)
9	(*E*)-Oct-4-ene	140	40 (1:1)	0.5:1	99	89	3	5	3	75:25 (60:21:9:10)
10		140	40 (1:1)	**C1**	79	68	0	19	13	74:26 (60:21:9:10)

The hydroformylations were performed in a parallel autoclave. Reaction conditions: [alkene] = 0.26 M; reaction time = 21 h; stirring rate = 800 rpm; H_2/CO in a 1:1 ratio, unless otherwise cited. [a] **L**:[Co] Molar ratio between **L** and cobalt centres in $[Co_2(CO)_8]$. [b] Conversion, regioselectivity and product distribution were determined by GC analysis on an achiral stationary phase (HP-5). Selectivities were calculated as mol of compound into mol of converted substrate.

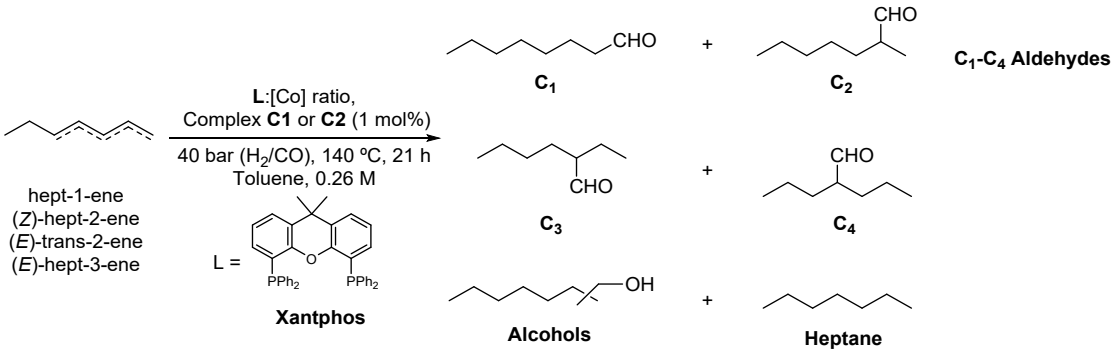
Table 5 Complete set of results of cobalt-catalysed hydroformylation of a mixture of octenes.



Entry	Substrate	T (°C)	Pressure (H_2/CO) (bar)	L:[Co] ratio[a], C1 or C2	Selectivity[b]				Regioselectivity[b]
					2a–d (%)	3a–d (%)	4 (%)	1a-d (%)	2a/2b (2a/2b/2c/2d)
1	Octene mixture	140	40 (1:1)	0.5:1	91	3	3	3	74:26 (62:21:9:8)
2		140	40 (1:1)	**C1**	60	1	14	25	74:26 (62:21:9:8)
3		140	40 (1:1)	**C2**	83	1	7	9	77:23 (66:19:8:7)

The hydroformylations were performed in a parallel autoclave. Reaction conditions: [alkene] = 0.26 M; reaction time = 21 h; stirring rate = 800 rpm; H_2/CO in a 1:1 ratio, unless otherwise cited. [a] **L**:[Co] Molar ratio between **L** and cobalt centres in $[Co_2(CO)_8]$. [b] regioselectivity and product distribution were determined by GC analysis on an achiral stationary phase (HP-5). Selectivities were calculated as mol of compound into mol of converted substrate.

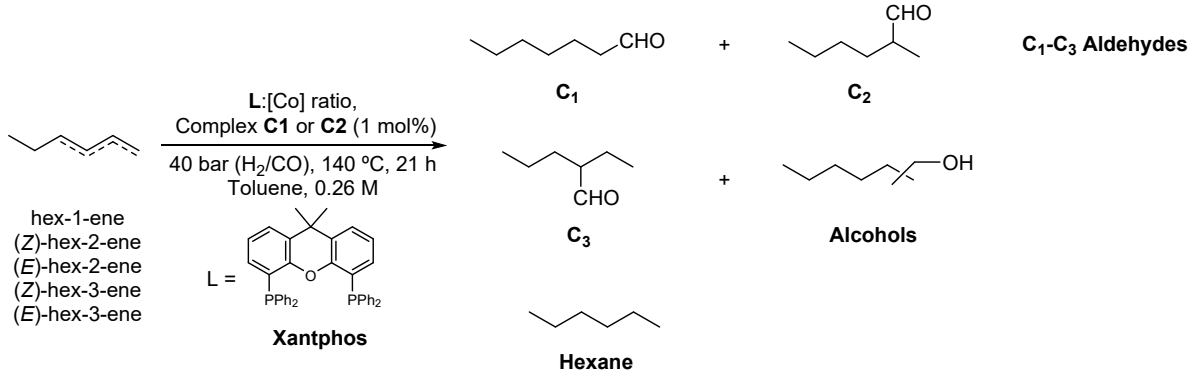
Table 6 Complete set of results of cobalt-catalysed hydroformylation of a mixture of heptenes.



Entry	Substrate	T (°C)	Pressure (H_2/CO) (bar)	L:[Co] ratio[a], C1 or C2	Selectivity[b]				Regioselectivity[b]
					Aldehydes (%)	Alcohols (%)	Heptane (%)	Alkenes (%)	C_1/C_2 ($C_1/C_2/C_3/C_4$)
1	Heptene mixture	140	40 (1:1)	0.5:1	87	1	1	11	77:23 (69:20:8:3)
2		140	40 (1:1)	**C1**	33	0	0	67	77:23 (69:20:8:3)
3		140	40 (1:1)	**C2**	85	2	1	12	78:22 (70:19:8:3)

The hydroformylations were performed in a parallel autoclave. Reaction conditions: [alkene] = 0.26 M; reaction time = 21 h; stirring rate = 800 rpm; H_2/CO in a 1:1 ratio, unless otherwise cited. [a] **L**:[Co] Molar ratio between **L** and cobalt centres in $[Co_2(CO)_8]$. [b] regioselectivity and product distribution were determined by GC analysis on an achiral stationary phase (HP-5). Selectivities were calculated as mol of compound into mol of converted substrate.

Table 7 Complete set of results of cobalt-catalysed hydroformylation of a mixture of hexenes.



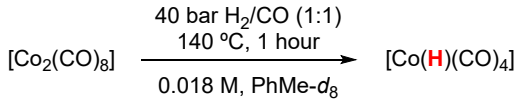
Entry	Substrate	T (°C)	Pressure (H_2/CO) (bar)	L:[Co] ratio[a], C1 or C2	Selectivity[b]				Regioselectivity[b]
					Aldehydes (%)	Alcohols (%)	Hexane (%)	Alkenes (%)	C_1/C_2 ($C_1/C_2/C_3$)
1	Hexenes Mixture	140	40 (1:1)	0.5:1	85	1	2	12	78:22 (72:20:8)
2		140	40 (1:1)	**C1**	36	0	1	63	77:23 (71:21:8)
3		140	40 (1:1)	**C2**	82	3	2	13	79:21 (73:19:8)

The hydroformylations were performed in a parallel autoclave. Reaction conditions: [alkene] = 0.26 M; reaction time = 21 h; stirring rate = 800 rpm; H_2/CO in a 1:1 ratio, unless otherwise cited. [a] **L**:[Co] Molar ratio between **L** and cobalt centres in $[Co_2(CO)_8]$. [b] Regioselectivity and product distribution were determined by GC analysis on an achiral stationary phase (HP-5). Selectivities were calculated as mol of compound into mol of converted substrate.

6. NMR pressure experiments.

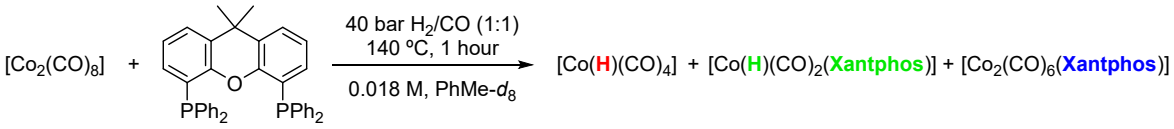
General procedure: The corresponding solutions of cobalt catalysts/complexes were placed in an autoclave and pressurized and heated under the stated conditions in each case. After that, the autoclave was depressurized. The autoclave was opened in the glove box and *ca.* 0.6-0.7 mL of the solution were quickly placed in an NMR tube which was immediately closed with a septum. The required NMR experiments were run from this point within a few minutes (< 15 min.).

a. $[Co_2(CO)_8]$ (10.75 mg, 31.44 µmol) was dissolved in 1.75 mL of deuterated toluene (0.018 M). The solution was pressurised at 40 bar of H_2/CO (1:1) in an autoclave. The autoclave was heated 140 ºC for 1 hour. ^{1}H-NMR (126 MHz, PhMe-d_8) δ –11.59 (singlet) ppm. HRMS ESI-MS (negative mode) *m/z*: $[M–H]^-$ calcd. for C_4CoO_4 170.9129, found 170.9245.



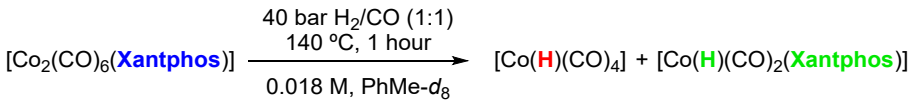
Scheme 3 Treatment of $[Co_2(CO)_8]$ with H_2/CO.

b. $[Co_2(CO)_8]$ (11.02 mg, 31.9 µmol) and Xantphos (18.80 mg, 31.9 µmol) were dissolved in 1.79 mL of deuterated toluene (0.018 M). The mixture was pressurized at 40 bar of H_2/CO (1:1) in an autoclave. The autoclave was heated 140 ºC for 1 hour. ^{1}H-NMR (126 MHz, PhMe-d_8) δ –10.86 (t, J = 28.2 Hz) and –11.47 (s) ppm. ^{31}P{^{1}H}-NMR (202 MHz, PhMe-d_8) δ 32.47, 41.65 ppm. HRMS ESI-MS (negative mode) *m/z*: $[M–H]^-$ calcd. for C_4CoO_4 170.9129, found 170.9295. For the HRMS ESI-MS spectra of **C1**, see section 3.1.



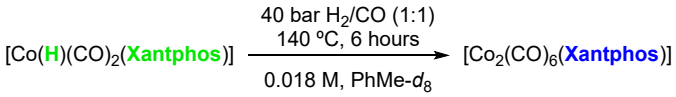
Scheme 4 Treatment of a mixture of $[Co_2(CO)_8]$ and Xantphos with H_2/CO.

c. $[Co_2(CO)_6(Xantphos)]$ (**C2**) (16 mg, 18.51 µmol) was dissolved in 1.03 mL of deuterated toluene (0.018 M). The solution was pressurized at 40 bar of H_2/CO (1:1) in an autoclave. The autoclave was heated 140 ºC for 1 hour. ^{1}H-NMR (126 MHz, PhMe-d_8) δ –10.86 (triplet, J = 28.1 Hz) and –11.58 (singlet) ppm. ^{31}P{^{1}H}-NMR (202 MHz, PhMe-d_8) δ 32.47 and 41.67 ppm. HRMS ESI-MS (negative mode) *m/z*: $[M–H]^-$ calcd. for C_4O_4Co 170.9129, found 170.9298. For the HRMS ESI-MS spectra of **C1**, see section 3.1.



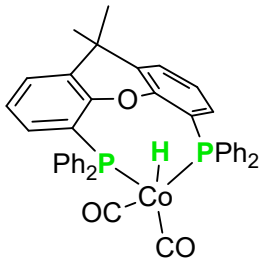
Scheme 5 Treatment of $[Co_2(CO)_6(Xantphos)]$ (**C2**) with H_2/CO.

d. $[Co(H)(CO)_2(Xantphos)]$ (**C1**) (12.85 mg, 18.51 µmol) was dissolved in 1.03 mL of deuterated toluene (0.018 M). The solution was pressurized at 40 bar of H_2/CO (1:1) in an autoclave. The autoclave was heated 140 ºC for 6 hours. ^{1}H-NMR (126 MHz, PhMe-d_8) δ –10.86 (triplet, J = 28.1 Hz). ^{31}P{^{1}H}-NMR (202 MHz, PhMe-d_8) δ 32.47 and 41.67 ppm.



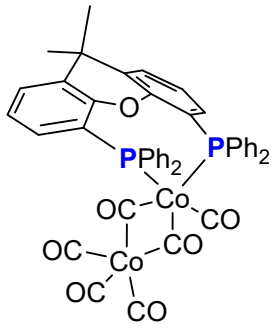
Scheme 6 Treatment of $[Co(H)(CO)_2(Xantphos)]$ (**C1**) with H_2/CO.

e. Complex **C1** $[Co(H)(CO)_2(Xantphos)]$ in deuterated toluene. ^{1}H-NMR (126 MHz, PhMe-d_8) δ –10.86 (t, J = 28.3 Hz). ^{31}P{^{1}H} NMR (202 MHz, PhMe-d_8) δ 41.69 ppm.



$[Co(H)(CO)_2(Xantphos)]$
Complex **C1**

f. Complex **C2** $[Co_2(CO)_6(Xantphos)]$ in deuterated toluene. ^{31}P{^{1}H}-NMR (202 MHz, PhMe-d_8) δ 32.30 ppm.



$[Co_2(CO)_6(Xantphos)]$
Complex **C2**

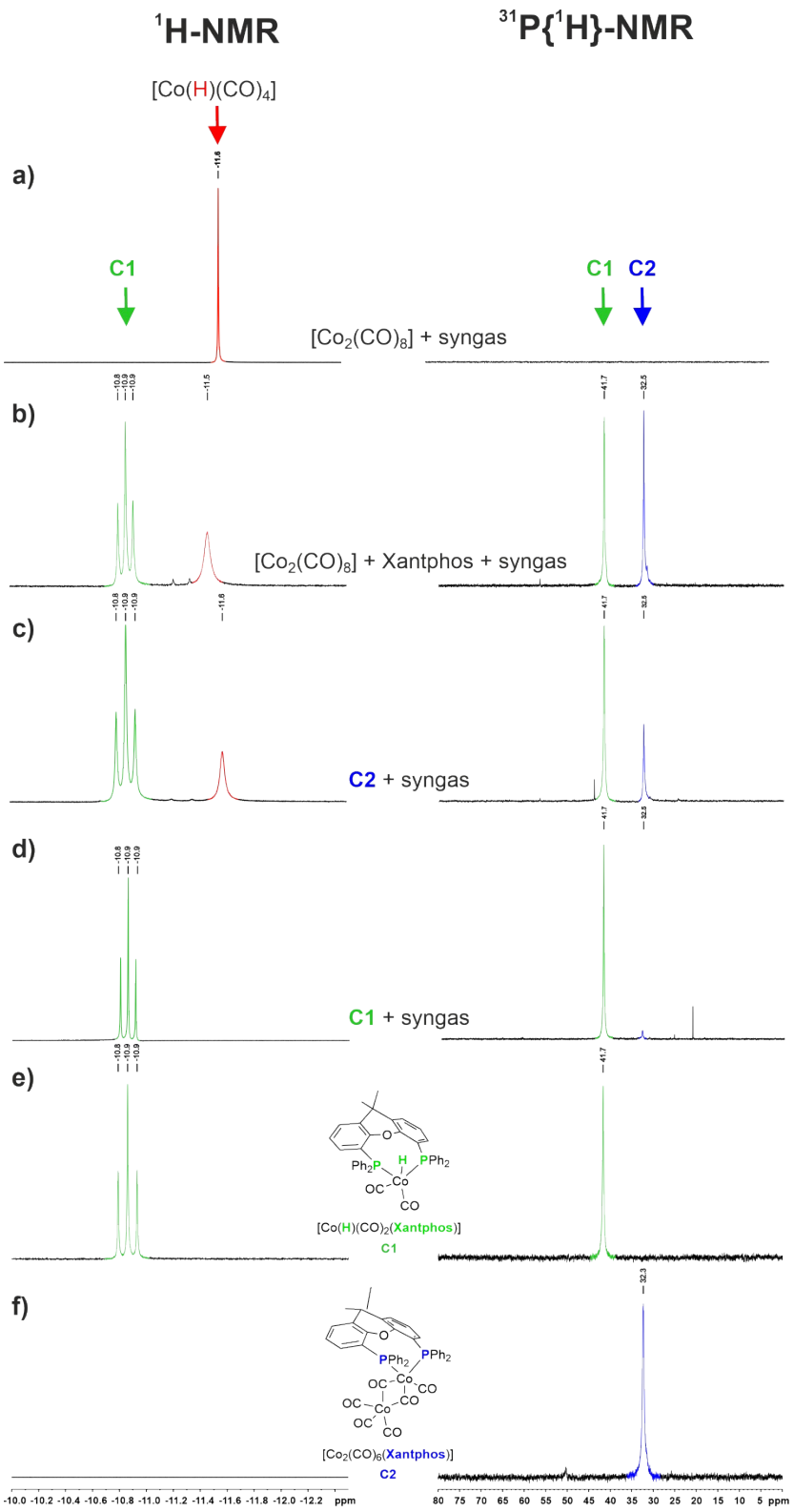


Figure 6 Regions of the ^{1}H-NMR and ^{31}P{^{1}H}-NMR spectra **a)** Spectra of [$Co_2(CO)_8$] after treatment with 40 bar of H_2/CO (1:1) at 140 ºC for 1 hour in PhMe-d_8; **b)** Spectra of [$Co_2(CO)_8$] and Xantphos after treatment with 40 bar of H_2/CO (1:1) at 140 ºC for 1 hour in PhMe-d_8; **c)** Spectra of **C2** after treatment with 40 bar of H_2/CO (1:1) at 140 ºC for 1 hour in PhMe-d_8; **d)** Spectra of **C1** after treatment with 40 bar of H_2/CO (1:1) at 140 ºC for 6 hours in PhMe-d_8; **e)** Spectra of [Co(H)$(CO)_2$(Xantphos)] in PhMe-d_8 under N_2. **f)** Spectra of [$Co_2(CO)_6$(Xantphos)] in PhMe-d_8 under N_2.

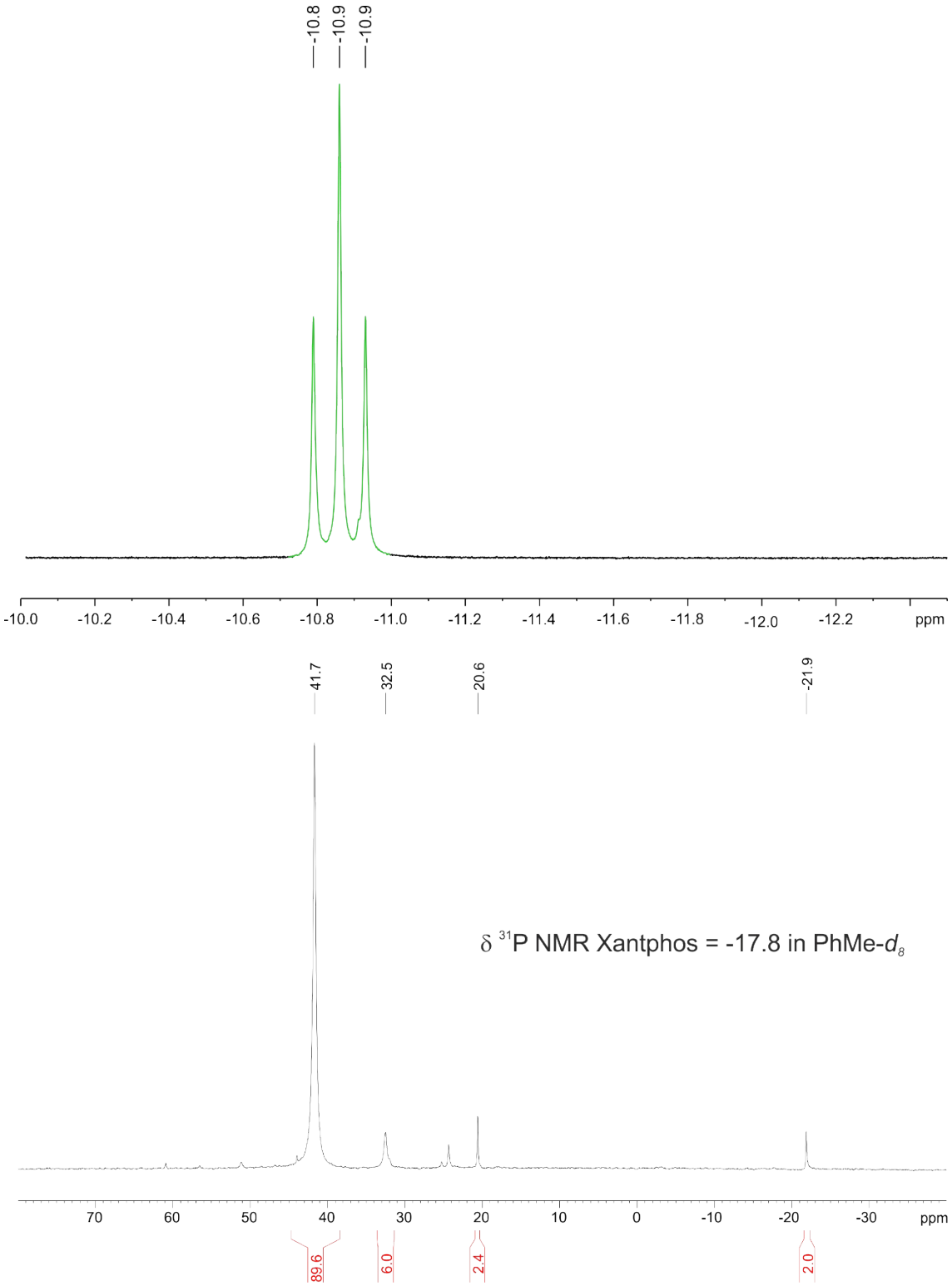


Figure 7 Hydride region in ^{1}H-NMR (top) and ^{31}P{^{1}H}-NMR spectrum (bottom) of [Co(H)(CO)$_2$(Xantphos)] **(C1)** after being under 40 bar of H_2/CO (1:1), 140 ºC for 21 h in PhMe-d_8.

7. Reaction progress monitoring

The progress of the hydroformylation of an equimolar mixture of octenes was monitored by running independent hydroformylations at different reactions times and analysing the composition of the resulting reaction mixtures. Reaction conditions: 1 mol% **C2**, 140 °C, 40 bar H_2/CO 1:1, toluene, 43.3 mM in oct-1-ene, (*E*)-oct-2-ene, (*Z*)-oct-2-ene, (*E*)-oct-3-ene, (*E*)-oct-4-ene and (*Z*)-oct-4-ene. Results are expressed in mol%.

Time (h)	1-octene	4-*E*-Octene	3-*E*- and 4-*Z*-Octene	2-*E*-Octene	2-*Z*-Octene	C_4-CHO	C_3-CHO	C_2-CHO	C_1-CHO	C_4-CH_2OH	C_3-CH_2OH	C_2-CH_2OH	C_1-CH_2OH
0.0	16.67	16.67	33.33	16.67	16.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.5	15.10	16.80	33.00	17.50	16.60	0.11	0.12	0.30	0.51	0.00	0.00	0.00	0.00
1.5	3.80	15.60	26.40	18.70	10.70	1.90	2.10	5.40	15.60	0.00	0.00	0.00	0.00
3.0	0.60	13.60	19.60	15.80	5.30	3.50	3.80	9.60	28.10	0.00	0.00	0.00	0.00
6.0	0.30	6.20	12.60	7.30	2.30	5.50	6.20	15.50	44.00	0.00	0.00	0.00	0.00
12.0	0.10	1.20	4.10	1.40	0.50	7.10	7.90	19.00	58.60	0.00	0.00	0.00	0.00
15.0	0.20	2.10	5.10	2.30	0.70	6.69	7.32	17.53	58.14	0.00	0.00	0.00	0.00
21.0	0.00	0.10	2.00	0.10	0.10	7.80	8.60	19.10	58.90	0.20	0.20	0.80	2.20

8. Spectroscopic Data

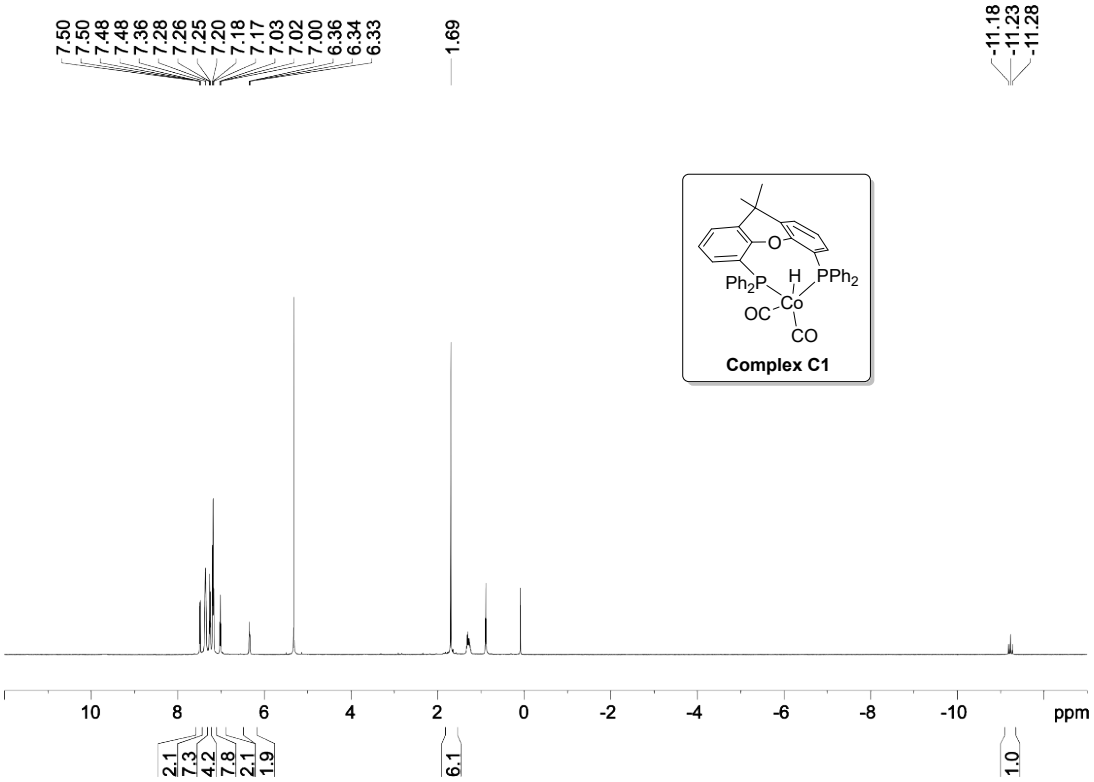


Figure 8 ^{1}H-NMR spectrum (500 MHz, CD_2Cl_2) of complex **C1**.

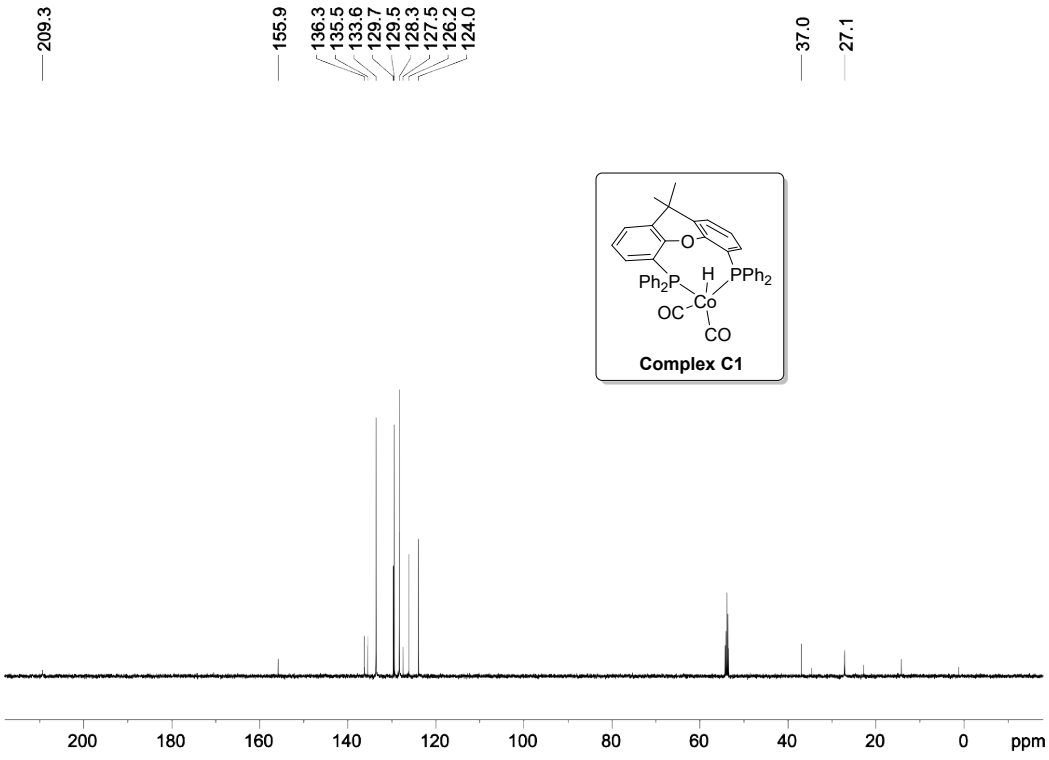


Figure 9 $^{13}C\{^{1}H,^{31}P\}$-NMR spectrum (126 MHz, CD_2Cl_2) of **2**.

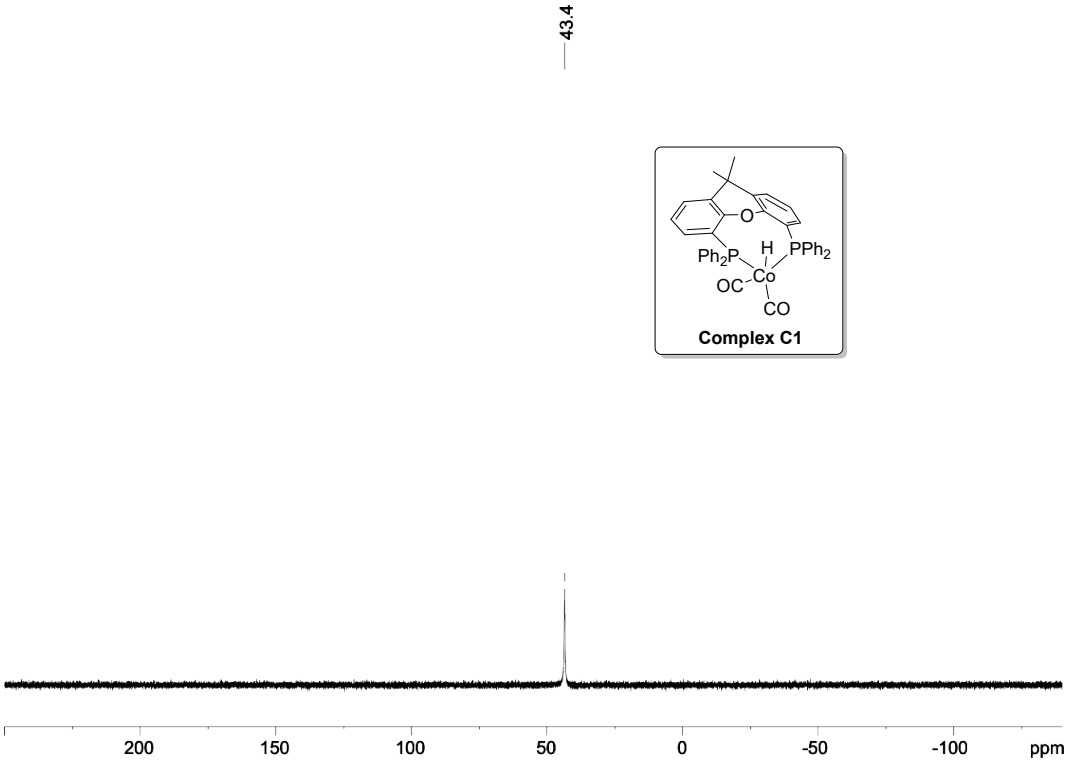


Figure 10 $^{31}P\{^{1}H\}$-NMR spectrum (202 MHz, CD_2Cl_2) of complex **C1**.

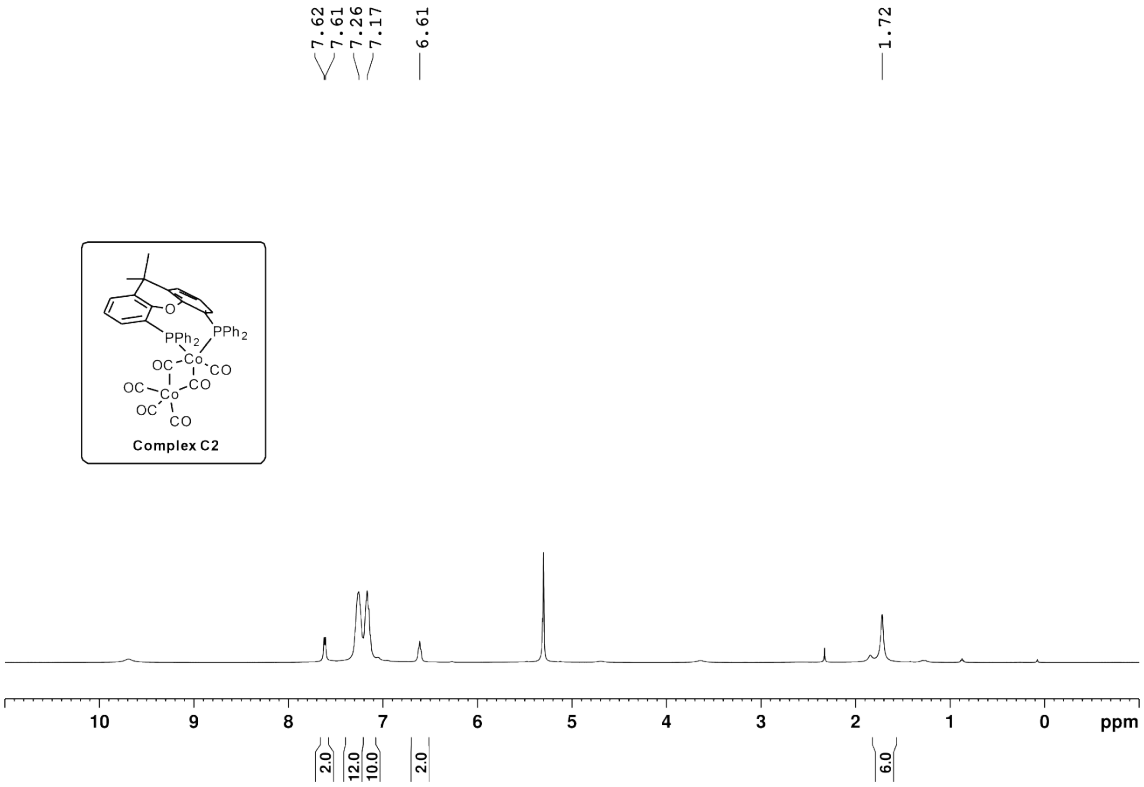


Figure 11 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of complex **C2**.

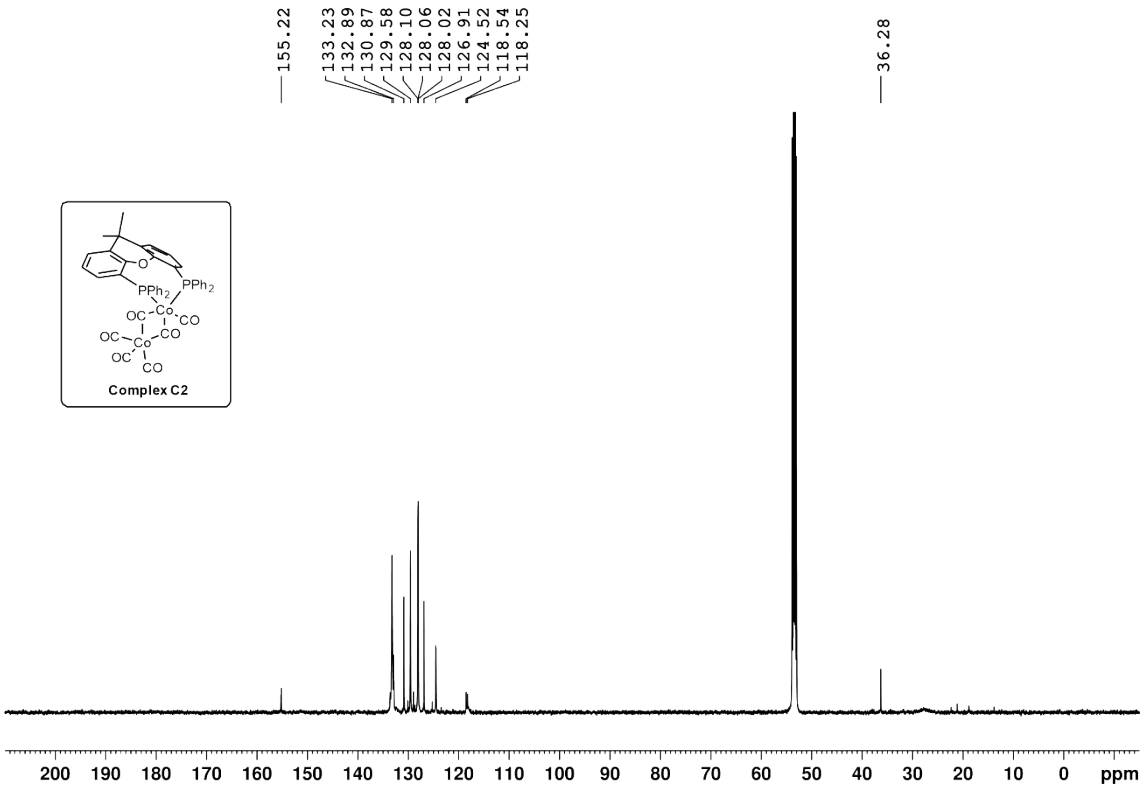


Figure 12 $^{13}C\{^{1}H\}$-NMR spectrum (126 MHz, CD_2Cl_2) of complex **C2**.

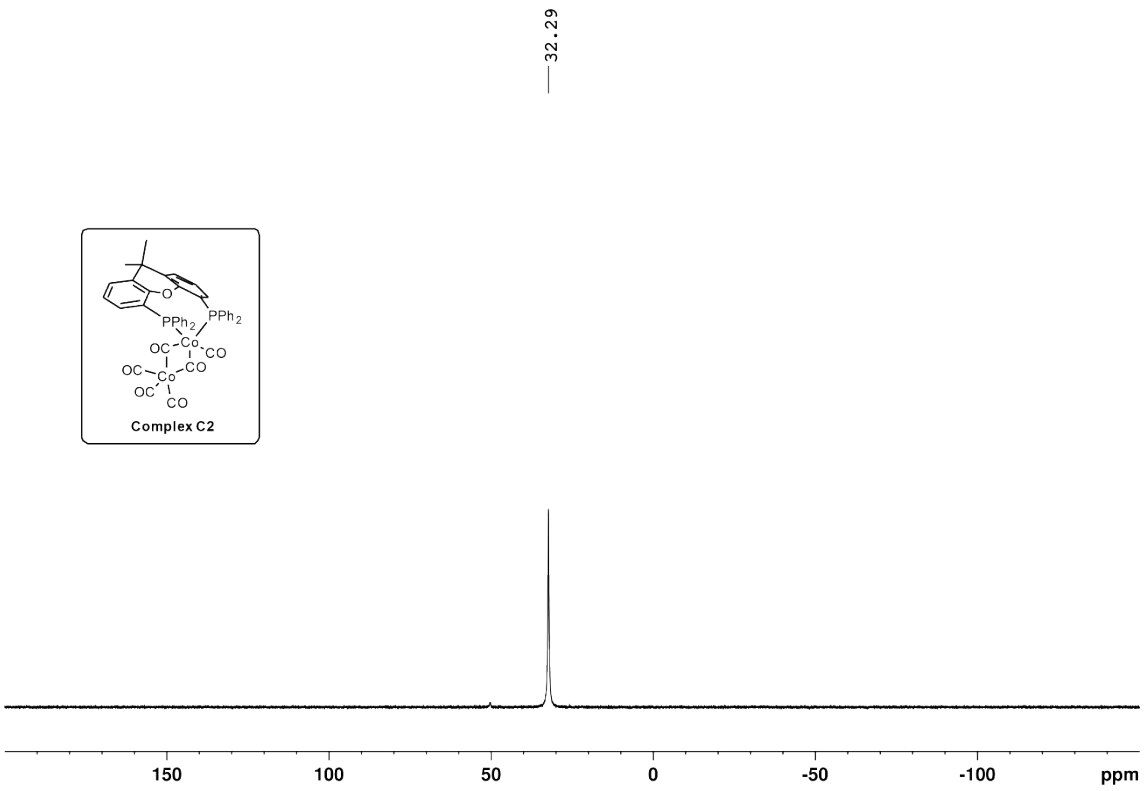


Figure 13 $^{31}P\{^{1}H\}$-NMR spectrum (202 MHz, CD_2Cl_2) of complex **C2**.

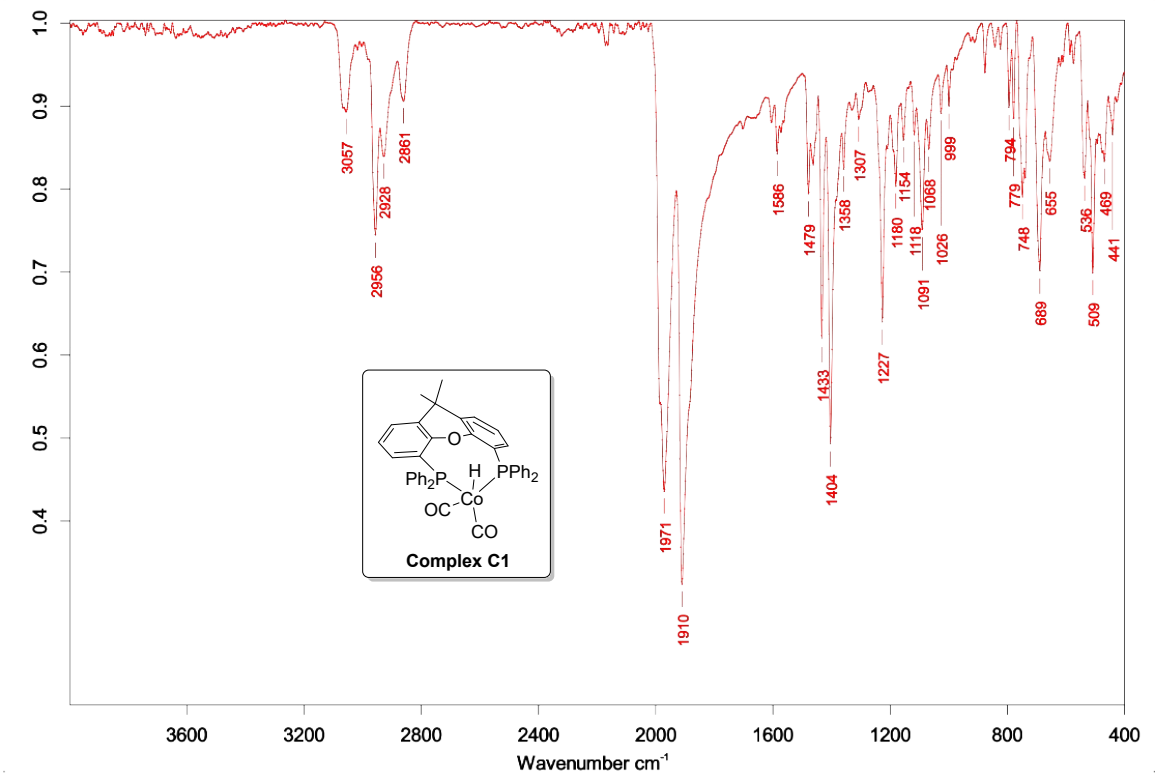


Figure 14 IR spectrum of complex complex **C1**.

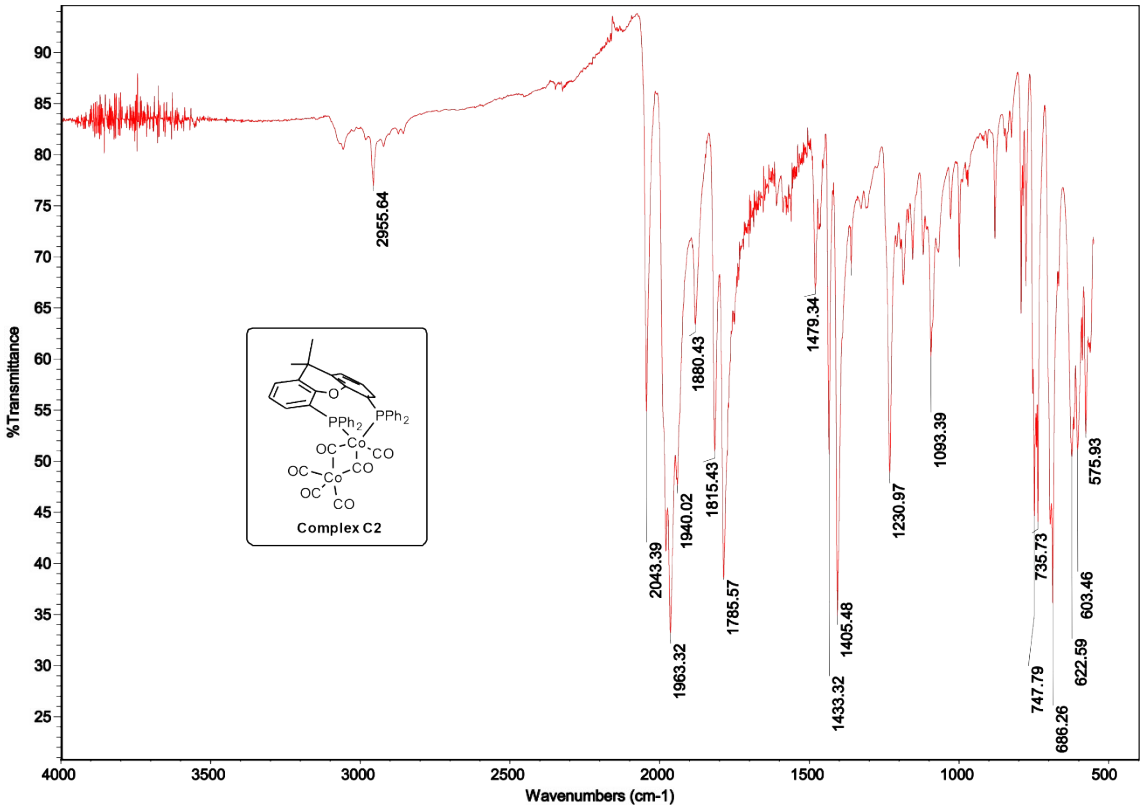


Figure 15 IR spectrum of complex **C2**.

9. Bibliography

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2) Empirical absorption correction using spherical harmonics as implemented in Scale3 Abspack scaling algorithm, CrysAlisPro 1.171.39.12b (Rigaku OD, 2015).

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