Supporting Information

Unusual Reactivity of *cyclo*-(P_5Ph_5): Oxidative Addition at a Group 6 Metal Carbonyl and Insertion of Acetonitrile into a P–P Bond

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Experimental Procedures

General Remarks

All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried and freshly distilled under nitrogen and kept over molecular sieve 4 Å. The NMR spectra were recorded at 25 °C with a Bruker AVANCE DRX 400 spectrometer (^{1}H NMR: 400.13 MHz, ^{31}P NMR: 161.97 MHz). TMS was used as internal standard for ^{1}H NMR spectra. ^{31}P NMR: 85% H_3PO_4 was used as external standard. The chemical shifts and coupling constants were obtained with the simulation program SpinWorks 4.[1] Mass spectrometry measurements were carried out as ESI-MS with a BRUKER Daltonics FT-ICR-MS spectrometer (Type APEX II, 7 Tesla). IR spectra: KBr pellets were prepared in a nitrogen-filled glove box and the spectra were recorded on a PerkinElmer System 2000 FTIR spectrometer in the range 350-4000 cm^{-1}. Elemental analyses for C, H, and N were performed on a FlashEA1112 element analyser. In some cases, formation of carbides can result in a lower carbon content. Thermogravimetric (TG) and differential thermal analysis (DTA) curves, coupled with mass spectrometry, were obtained using a NETZSCH STA449F1 thermoanalyser in a dynamic argon atmosphere (heating rate 10 °C·min^{-1}, flow rate 25 mL·min^{-1}, aluminium oxide crucible, mass 20 mg, and temperature range from room temperature up to 900 °C).

Materials

$[Cr(CO)_y(MeCN)_x]$ (x = 1, y = 5; x = 2, y = 4), $[Mo(CO)_4(nbd)]$ (nbd = 2,5-norbornadiene),[2] $[W(CO)_4(MeCN)_2]$,[3] and *cyclo*-(P_5Ph_5)[4] were synthesised according to literature methods. *Cyclo*-(P_5Ph_5) (**1**) was recrystallised from hot toluene to obtain crystals of higher purity and quality. Compounds **Ia-c** were synthesised as previously reported.[5]

Synthesis of the Complexes

Synthesis of 1a

At room temperature, a solution of $[Cr(CO)_4(MeCN)_2]$ (0.276 g, 1.12 mmol) in toluene (20 mL) was added dropwise to a solution of *cyclo*-(P_5Ph_5) (0.36 g, 0.56 mmol) in toluene (20 mL). The colour of the solution changed from cream white through orange to brown during the addition. The reaction mixture was stirred at room temperature for 30 minutes and then refluxed overnight at 120 °C to give a reddish-brown mixture. The solvent was removed *in vacuo* and the resulting black solid was re-dissolved in CH_2Cl_2. Slow diffusion of Et_2O into this solution at 0 °C afforded **1a** as black crystals (387.9 mg, 68.2%): ^{1}H NMR (C_6D_6): δ = 8.2-6.6 (m, Ph): ^{31}P{^{1}H} NMR (C_6D_6): see Table S3; IR (KBr): $\tilde{\nu}$ = 1991 (s), 1953 (vs), 1938 (vs), 1906 (sh), 1880 cm^{-1} (sh) (CO); elemental anal. calcd (%) for $C_{38}H_{28}Cr_2NO_6P_5$ (853.46): C 53.48, H 3.31, N 1.64; found: C 52.13, H 3.14, N 1.52.

Synthesis of 1b

At room temperature, a solution of $[Mo(CO)_4(nbd)]$ (0.24 g, 0.74 mmol) in toluene (15 mL) was added dropwise to a solution of *cyclo*-(P_5Ph_5) (0.21 g, 0.37 mmol) in toluene (15 mL). 5 mL of MeCN were added to this solution. The color of the solution changed from cream white through orange to brown during the addition. The reaction mixture was stirred at room temperature for 30 minutes and then refluxed overnight at 120 °C to give a dark-brown mixture. The solvent was removed *in vacuo* and the resulting black solid was re-dissolved in CH_2Cl_2. Slow diffusion of *n*-hexane into this solution at 0 °C afforded **1b** as black crystals (353.1 mg, 96.5%): ^{1}H NMR (C_6D_6): δ = 8.2-6.6 (m, Ph): ^{31}P{^{1}H} NMR (C_6D_6): see Table S3; IR (KBr): $\tilde{\nu}$ = 2009 (s), 1969 (vs), 1954 (vs), 1920 (sh), 1890 cm^{-1} (sh) (CO); elemental anal. calcd (%) for $C_{38}H_{28}Mo_2NO_6P_5$ (941.34): C 48.48, H 3.00, N 1.49; found: C 47.95, H 2.90, N 1.41.

Synthesis of 1c

At room temperature, a solution of $[W(CO)_4(MeCN)_2]$ (0.28 g, 0.74 mmol) in toluene (15 mL) was added dropwise to a solution of *cyclo*-(P_5Ph_5) (0.21 g, 0.37 mmol) in toluene (15 mL). The color of the solution changed from cream white through orange to brown during the addition. The reaction mixture was stirred at room temperature for 30 minutes and then refluxed overnight at 120 °C to give a reddish-brown mixture. The solvent was removed *in vacuo* and the resulting black solid was re-dissolved in CH_2Cl_2. Slow diffusion of *n*-hexane into this solution at 0 °C afforded **1c** as greenish-black crystals (311.1 mg, 71.7%): ^{1}H NMR (C_6D_6): δ = 8.2-6.6 (m, Ph): ^{31}P{^{1}H} NMR (C_6D_6): see Table S3; IR (KBr): $\tilde{\nu}$ = 2074(w), 2005 (s), 1964 (vs), 1947 (vs), 1913 (sh), 1881 cm^{-1} (sh) (CO), 1581 (w) cm^{-1} (C=N); elemental anal. calcd (%) for $C_{38}H_{28}NO_6P_5W_2$ (1117.16): C 40.85, H 2.53, N 1.25; found: C 41.90, H 2.41, N 1.20.

The mass spectra of compounds **1a**-**c** in MeCN showed the molecular ion peak $[M]^+$ at *m/z* 853.46, 941.34 and 1117.97, respectively.

Synthesis of 2c

At room temperature, a solution of *cyclo*-(P_5Ph_5) (0.162 g; 0.3 mmol) in toluene (15 mL) was added dropwise to a solution of [$W(CO)_4(MeCN)_2$] (0.378 g, 1 mmol) in toluene (20 mL). The reaction mixture was stirred at room temperature for 30 minutes and then refluxed at 120 °C for 48 h to give a dark-brown mixture. The color of the reaction medium changed from pale-yellow to orange to red-brown and finally dark-brown. The solvent was reduced *in vacuo* to 8 mL and filtered. The mixture of **1c** and **2c** was separated by chromatography on SiO_2, eluting with CH_2Cl_2. Slow diffusion of *n*-hexane into the CH_2Cl_2 solution of fraction 1 at 0 °C afforded **2c** as greenish-black crystals (397.7 mg, 27.6%): ^{1}H NMR (C_6D_6): δ = 8.6-6.4 (m, Ph): $^{31}P\{^1H\}$ NMR (C_6D_6): see Table S3; IR (KBr): $\tilde{\nu}$ = 2073 (s), 2005 (s), 1976 (vs), 1940 (vs), 1923 (vs) cm^{-1} (CO), 1632 (w) cm^{-1} (C=N); Elemental anal. calcd (%) for $C_{43}H_{28}NO_{11}P_5W_3$ (1441.06): C 35.84, H 1.96, N 0.97; found: C 36.33, H 2.09, N 0.89.
In order to improve the synthesis of **2c**, [$W(CO)_4(MeCN)_2$] and *cyclo*-(P_5Ph_5) (ratio 3:1) were refluxed in toluene at 120 °C for 24 h and 48 h and in each case $^{31}P\{^1H\}$ NMR spectra showed that a mixture of **1c** and **2c** was obtained (Fig. S8). This mixture was separated by column chromatography. A $^{31}P\{^1H\}$ NMR analysis of the reaction mixture left in air overnight showed no change. Using a ratio of 3.5:1 and refluxing for 48 hours gave a mixture of **1c** and **2c** (according to $^{31}P\{^1H\}$ NMR analysis).

Synthesis of 2

Refluxing [$W(CO)_4(MeCN)_2$] and **1b** in a 1:1 ratio resulted in a complex **2**, which is isostructural with **2c**. An independent mixed occupancy was applied for every metal site in the model, which led to improved *R* values for the structure model of this complex. The refinement yielded the following occupancies for the metal sites:

M1: 60.703% W 39.297% Mo
M2: 55.116% W 44.887% Mo
M3: 90.569% W 09.431% Mo

A mixed Mo/W complex [M(μ-PMe_2)$(CO)_3(PMe_3)]_2$ (M = Mo and W in 1/4 ratio)[10] is also known.

Data Collection and Structure Refinement

X-ray data were collected with a GEMINI CCD diffractometer (Rigaku Inc.), λ(Mo-K_α) = 0.71073 Å, *T* = 130(2) K, empirical absorption corrections with SCALE3 ABSPACK.[6] All structures were solved by dual space methods with SIR-92.[7] Structure refinement was done with SHELXL-2016[8] by using full-matrix least-square routines against F^2. All hydrogen atoms were calculated on idealised positions. The pictures were generated with the program Mercury.[9] CCDC 1888485 (**1a**), CCDC 1888484 (**1b**), CCDC 1888482 (**1c**), CCDC 1888486 (**2**, Mo/W disordered) and CCDC 1888488 (**2c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

Results and Discussion

The structures of the complexes **1a-c** and **2c** are presented in Figs. S1-S3 and the crystallographic data summarised in Table S1. Selected bond lengths are presented in Table S2.

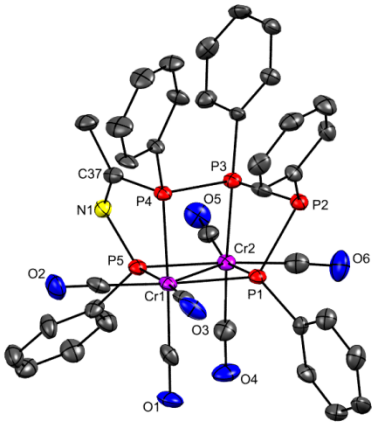


Figure S1. Molecular structure and atom-labelling scheme for **1a** with ellipsoids drawn at 50% probability level. H atoms are omitted for clarity.

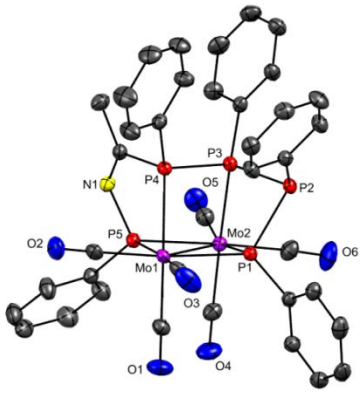


Figure S2. Molecular structure and atom-labelling scheme for **1b** with ellipsoids drawn at 50% probability level. H atoms are omitted for clarity.

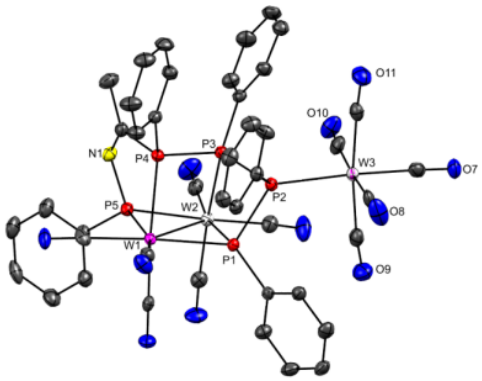


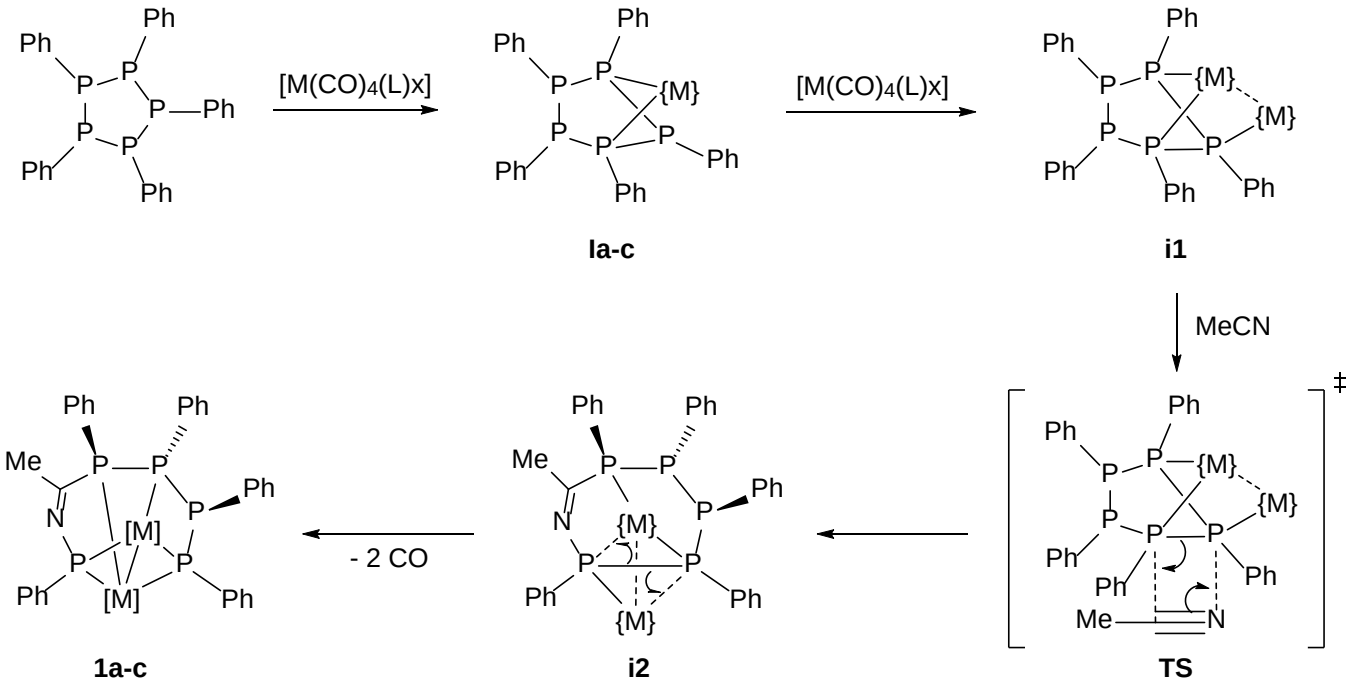
Figure S3. Molecular structure and atom-labelling scheme for **2** (Mo/W disordered, only the distribution with solely tungsten is shown) with ellipsoids drawn at 50% probability level. H atoms are omitted for clarity.

Table S1. Crystallographic data for complexes **1a**–**c** and **2c**, and **2**.

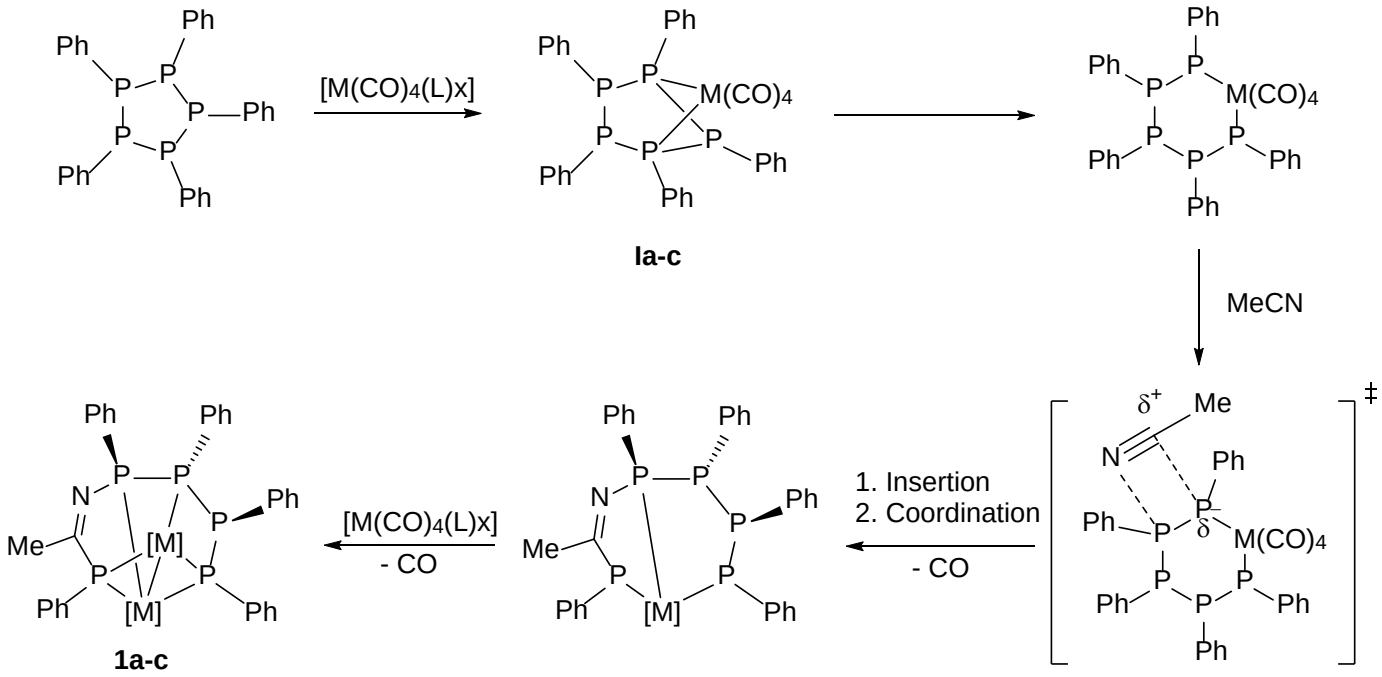
	1a	**1b**	**1c**	**2c**	**2**
Chemical formula	$C_{38}H_{28}Cr_2NO_6P_5$	$C_{38}H_{28}Mo_2NO_6P_5$	$C_{38}H_{28}NO_6P_5W_2$	$C_{43}H_{28}NO_{11}P_5W_3$	$C_{43}H_{28}Mo_{0.94}NO_{11}P_5W_{2.06}$
M_r	853.46	941.34	1117.16	1441.06	1358.76
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	130	130	130	130	130
a, b, c (Å)	9.762(6), 11.432(5), 17.325(1)	9.799(1), 11.495(2), 17.575(3)	9.8152(3), 11.4914(3), 17.537(5)	12.398(2) 24.739(4), 14.869(2)	12.399(2), 24.779(3), 14.873(2)
α, β, γ (°)	87.26(5), 86.91(5), 71.25(5)	86.67(1), 87.98(1), 71.85(1)	86.59(2), 87.75(2), 71.745(3)	97.46(2)	97.48(1)
V (Å^3)	1827.38(2)	1877.67(5)	1874.65(1)	4522.00(1)	4530.69(1)
Z	2	2	2	4	4
Radiation type	Mo-$K\alpha$	Mo-$K\alpha$	Mo-$K\alpha$	Mo-$K\alpha$	Mo-$K\alpha$
μ (mm^{-1})	0.86	0.93	6.39	7.85	5.72
Crystal size (mm)	0.07 × 0.05 × 0.05	0.2 × 0.2 × 0.1	0.1 × 0.03 × 0.03	0.1 × 0.1 × 0.08	0.08 × 0.04 × 0.02
T_{min}, T_{max}	0.978, 1	0.977, 1	0.763, 1	0.644, 1	0.922, 1
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12544, 6634, 3722	57840, 11464, 9736	37548, 11438, 9085	38747, 14794, 12747	50289, 15068, 11427
R_{int}	0.074	0.036	0.048	0.028	0.060
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.602	0.714	0.714	0.755	0.754
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.067, 0.137, 1.00	0.029, 0.065, 1.07	0.031, 0.057, 1.02	0.028, 0.057, 1.09	0.040, 0.060, 1.01
No. of reflections	6634	11464	11438	14794	15068
No. of parameters	470	470	470	569	572
No. of restraints	0	0	0	0	0
H atom treatment	H atom parameters constrained	H atom parameters constrained	H atom parameters constrained	H atom parameters constrained	H atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.07, −0.53	0.60, −0.51	1.26, −1.23	1.75, −1.5	1.50, −1.34

Table S2. Selected bond lengths (Å) and angles (°) for **1a**-**c** and **2c**.

Bond Length (Å); Bond Angle (°)	**1a** (M = Cr)	**1b** (M = Mo)	**1c** (M = W)	**2c** (M = W)
M(1)–M(2)	2.893(1)	3.0253(2)	3.0279(2)	3.0279(2)
P(1)–M(1)	2.315(2)	2.4538(5)	2.454(1)	2.4948(8)
P(1)–M(2)	2.337(2)	2.4668(5)	2.4675(9)	2.4758(8)
P(2)-M(3)				2.5274(8)
P(3)–M(2)	2.387(2)	2.5161(5)	2.5091(9)	2.5161(8)
P(4)–M(1)	2.323(2)	2.4688(5)	2.4629(9)	2.4986(8)
P(5)–M(1)	2.297(2)	2.4335(5)	2.4363(9)	2.4361(8)
P(5)–M(2)	2.303(2)	2.4412(5)	2.442(1)	2.4349(9)
P(1)–P(2)	2.204(2)	2.2028(7)	2.205(1)	2.210(1)
P(2)–P(3)	2.192(2)	2.2008(7)	2.202(1)	2.245(1)
P(3)–P(4)	2.219(2)	2.2245(6)	2.230(1)	2.224(1)
P(5)–N(1)	1.748(5)	1.743(2)	1.743(3)	1.719(3)
C(37)–P(4)	1.859(6)	1.880(2)	1.883(4)	1.889(3)
C(37)–N(1)	1.280(6)	1.276(2)	1.274(4)	1.266(4)
M(1)–P(1)–M(2)	76.90(6)	75.88(2)	75.94(3)	75.06(2)
M(1)–P(5)–M(2)	77.95(6)	76.72(2)	76.72(3)	76.87(2)
P(2)–P(3)–P(4)	105.1(1)	106.29(3)	106.22(5)	103.09(4)
P(3)–P(2)–P(1)	77.69(7)	80.22(2)	79.76(5)	80.34(4)
P(5)–M(1)–P(1)	102.98(7)	103.86(2)	103.81(3)	103.61(3)
P(5)–M(2)–P(1)	102.12(7)	103.24(2)	103.22(3)	104.22(3)
C(37)-N(1)-P(5)	115.7(4)	118.3(2)	118.3(3)	119.3(2)



Scheme S1. This mechanism for the formation of **1a**-**c** does not involve an oxidative insertion and is thus unlikely.



[M] = $M(CO)_3$

a: M = Cr, L = MeCN, x = 2
b: M = Mo, L = nbd, x = 1
c: M = W, L = MeCN, x = 2

Scheme S2. This mechanism for the formation of **1a-c** leads to the wrong constitutional isomer and thus is ruled out.

Table S3. $^{31}P\{^{1}H\}$ NMR data (δ (ppm) and *J* (Hz), standard deviations in brackets) of compounds **1a-c** in C_6D_6 at 25°C. Numbering scheme is given in scheme 1.

	1a	**1b**	**1c**	**2c**
	Chemical Shift (ppm)			
$\delta(P_A)$	343.09(1)	305.12(1)	260.10(1)	260.57(1)
$\delta(P_B)$	195.55(1)	145.56(1)	138.79(1)	116.97(1)
$\delta(P_C)$	162.80(1)	141.20(1)	96.92(1)	115.75(1)
$\delta(P_D)$	79.62(1)	62.07(1)	54.77(1)	90.28(1)
$\delta(P_E)$	7.27(1)	19.09(1)	24.27(1)	60.53(1)
	$J_{P\text{-}P}$ (Hz) and $J_{W\text{-}P}$ (Hz)			
$^{2}J(P_A,P_B)$	1.49(8)	10.21(3)	13.35(1)	
$^{2}J(P_A,P_C)$	89.69(7)	87.66(3)	103.05(1)	
$^{2}J(P_A,P_D)$	-0.00(7)	-0.00(3)	-0.03(9)	
$^{2}J(P_A,P_E)$	20.06(7)	14.65(5)	14.10(1)	
$^{2}J(P_B,P_C)$	10.99(8)	10.01(1)	10.16(1)	
$^{1}J(P_B,P_D)$	-187.04(8)	-181.54(2)	-177.38(1)	
$^{2}J(P_B,P_E)$	-92.75(8)	-99.47(3)	-107.58(1)	
$^{2}J(P_C,P_D)$	10.48(7)	10.06(2)	10.83(1)	
$^{1}J(P_C,P_E)$	-321.32(7)	-290.51(3)	-266.70(1)	
$^{1}J(P_D,P_E)$	-268.68(7)	-270.37(3)	-266.23(9)	
$^{1}J(P_A,W1)$			159	
$^{1}J(P_A,W2)$			144	
$^{1}J(P_C,W1)$			183	
$^{1}J(P_C,W2)$			132	
$^{1}J(P_B,W1)$			227	
$^{1}J(P_D,W2)$			170	
$^{2}J(P_E,W)$			20	

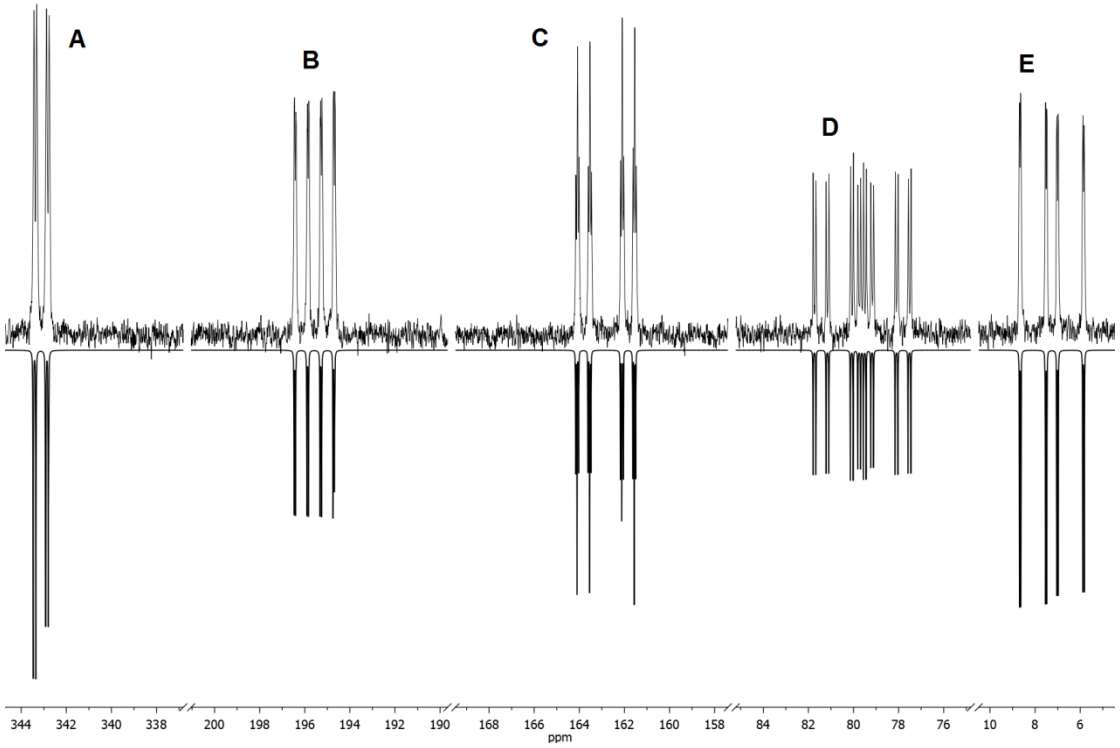


Figure S4. Experimental (top) and simulated (bottom) $^{31}P\{^{1}H\}$ NMR spectrum of complex **1a** in C_6D_6.

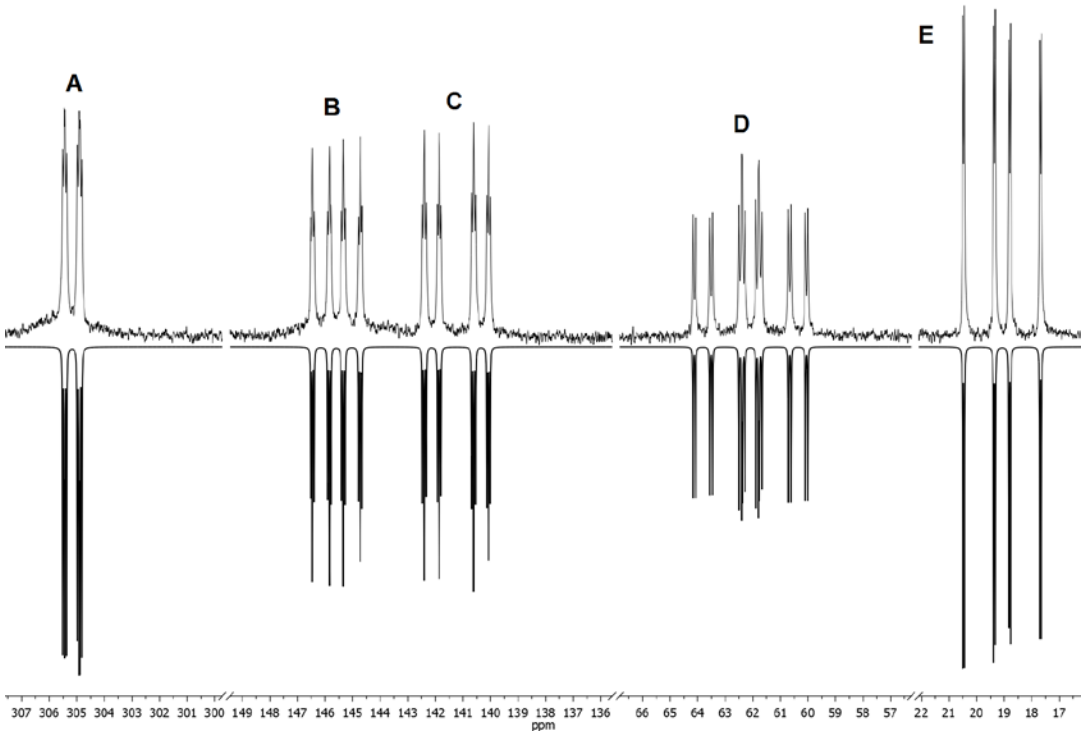


Figure S5. Experimental (top) and simulated (bottom) $^{31}P\{^{1}H\}$ NMR spectrum of complex **1b** in C_6D_6.

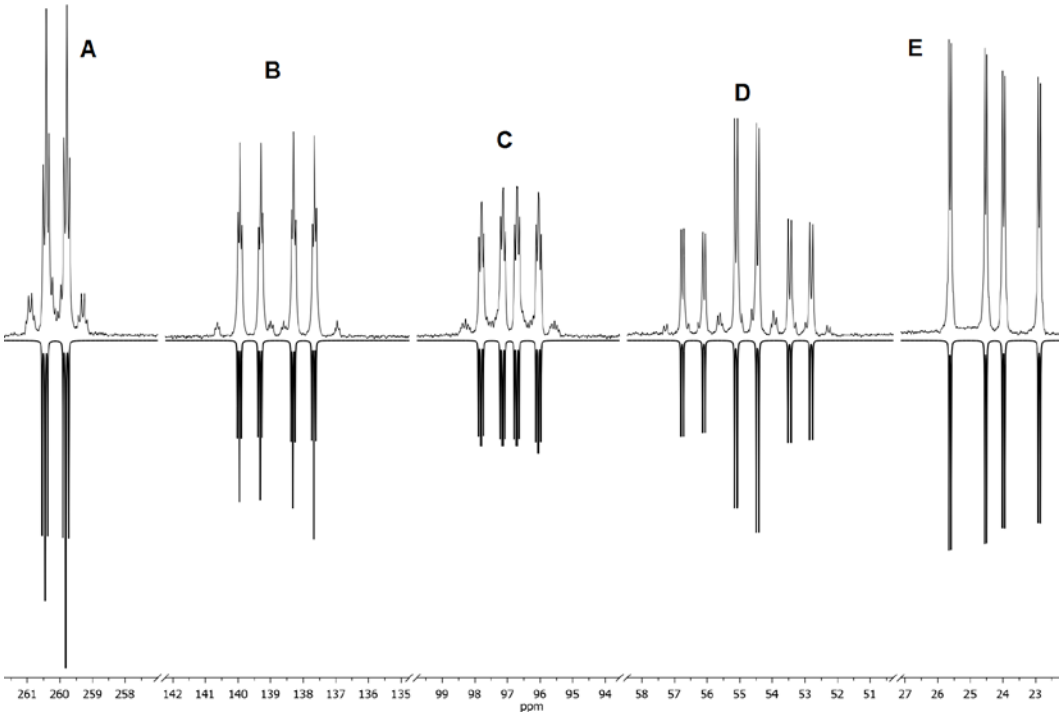


Figure S6. Experimental (top) and simulated (bottom) $^{31}P\{^{1}H\}$ NMR spectrum of complex **1c** in C_6D_6.

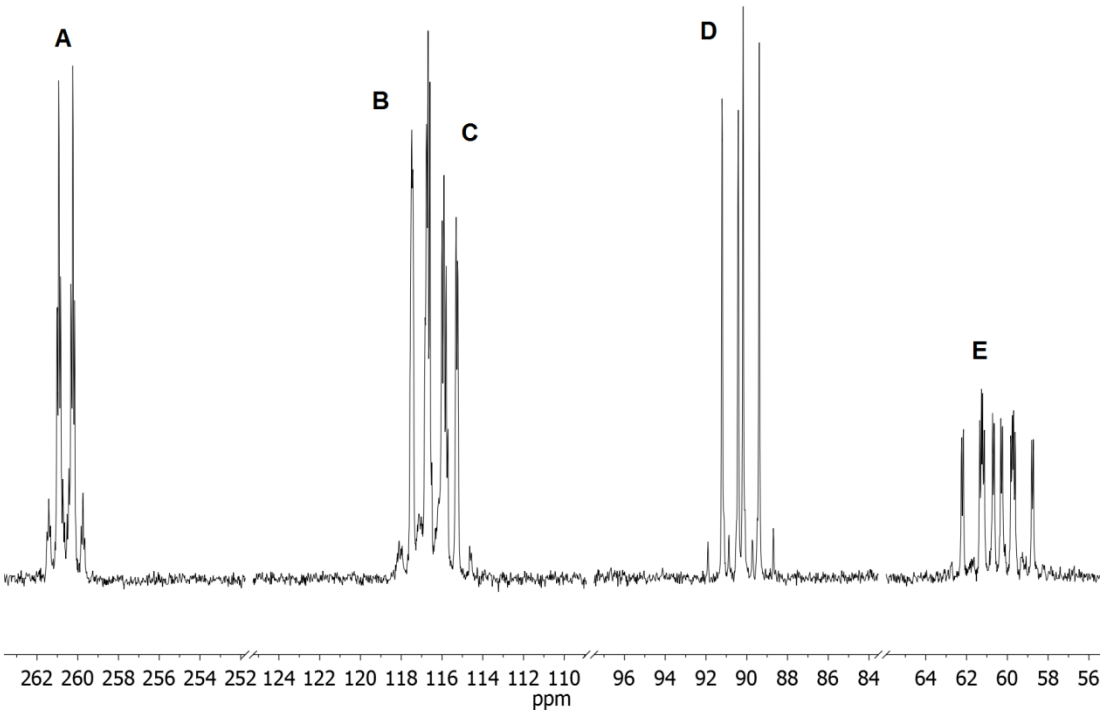


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of complex **2c** in C_6D_6.

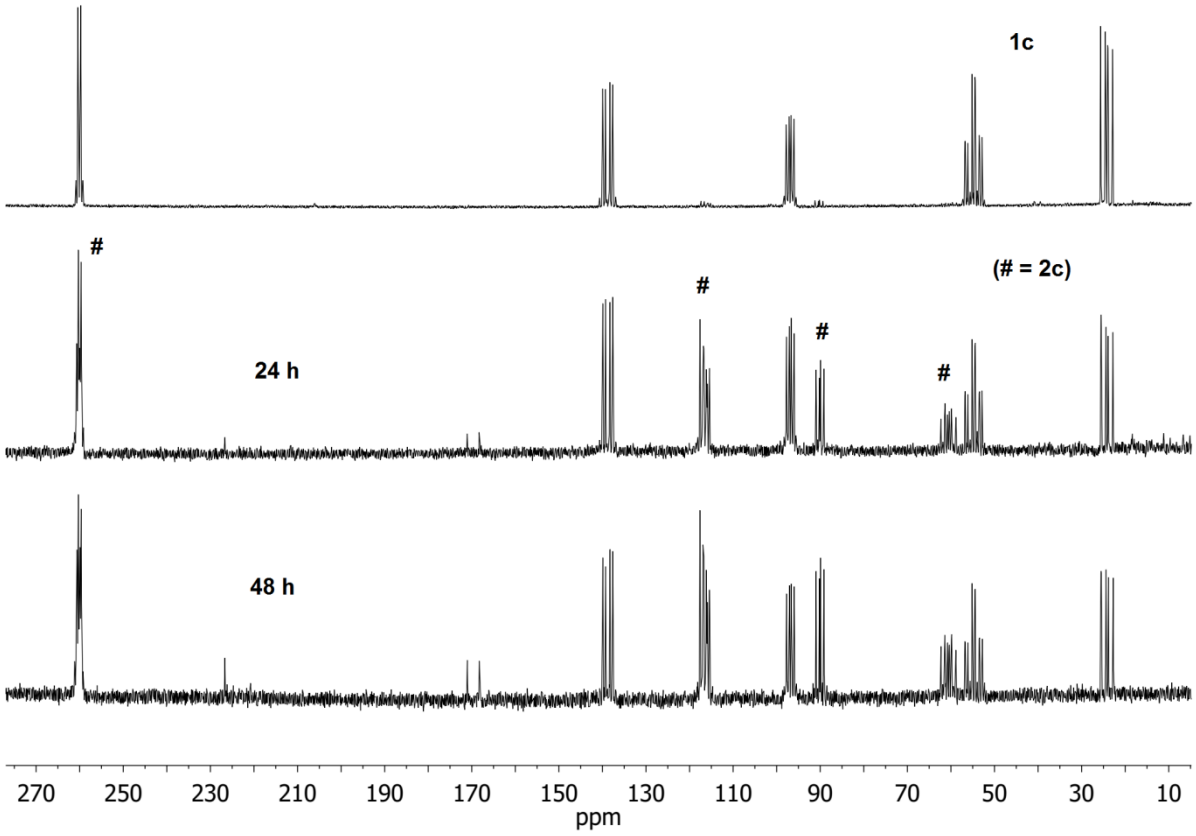


Figure S8. Time-dependent experimental $^{31}P\{^{1}H\}$ NMR spectra for the formation of complex **2c** compared to that of **1c** in C_6D_6.

Table S4. CO and C=N vibrations (cm^{-1}) of compounds **1a**–**c** and **2c**.

Complex	ν(CO)/cm^{-1}					ν(C=N)/cm^{-1}
1a	1991s	1953vs	1938vs	1906s	1880sh	1635w
1b	2009s	1969vs	1954vs	1920s	1890sh	1634w
1c	2005s	1964vs	1947vs	1903s	1881sh	1629w
2c	2073s	2005s	1976vs	1940vs	1923vs	1632w

s = strong; sh = shoulder; vs = very strong; w = weak

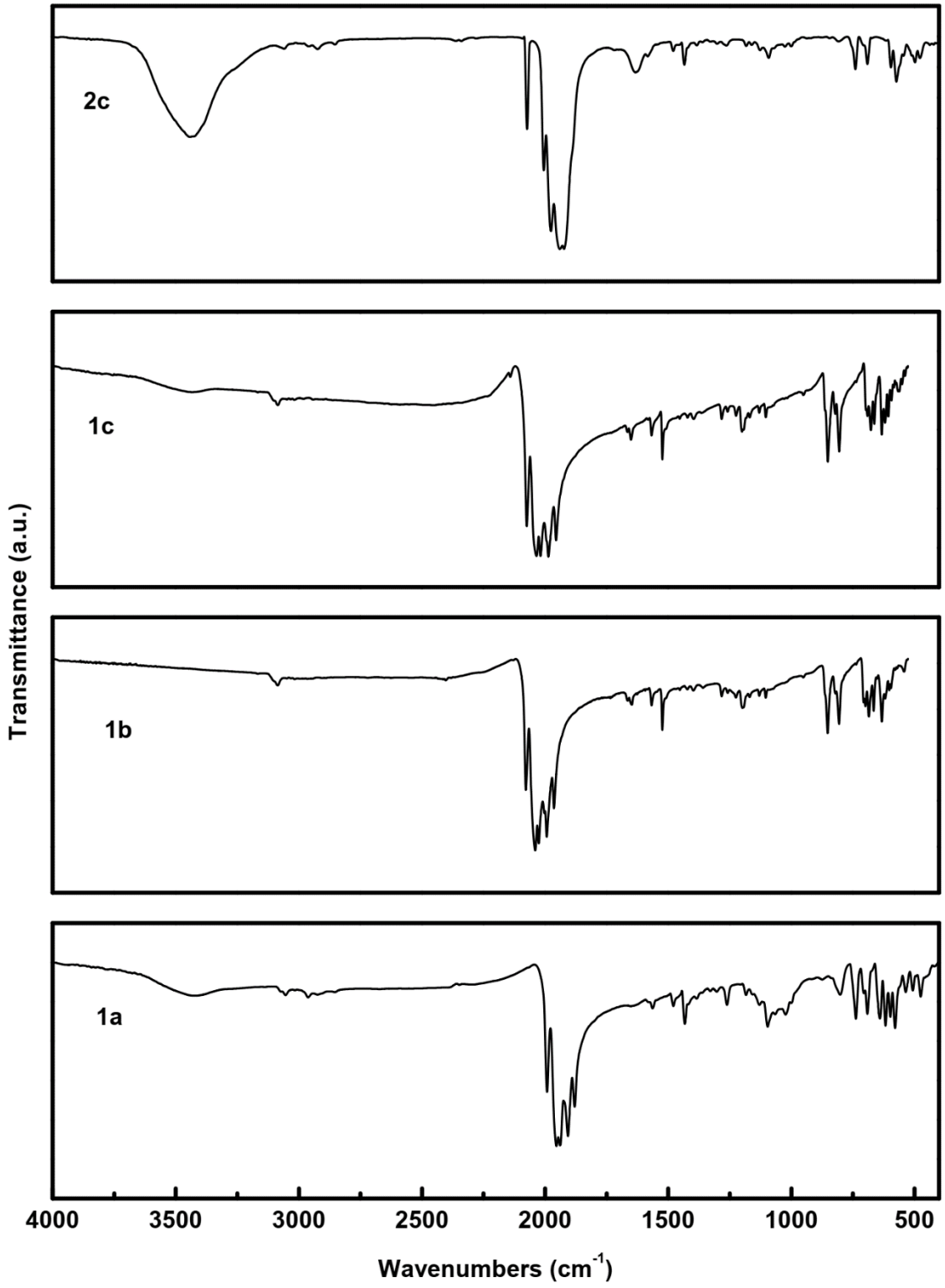


Figure S9. IR spectra of complexes compounds **1a**–**c** and **2c**.

The thermal properties of complexes **1b** and **1c** were studied by simultaneous TG/DTA/MS analyses in the temperature range 30–900 °C under an argon atmosphere (Fig. S10 and Table S5).

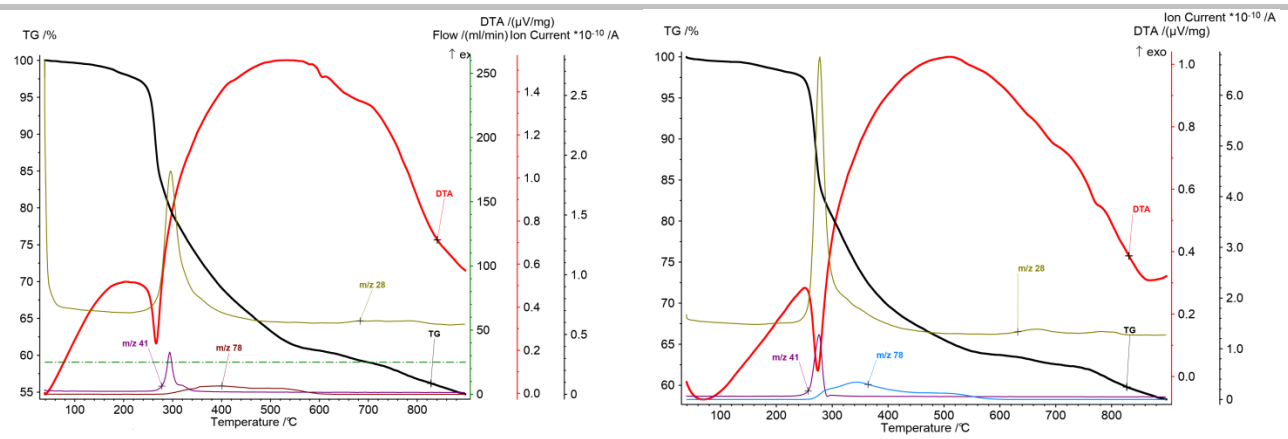


Figure S10. TG/DTA/MS plots for **1b** (left) and **1c** (right).

Table S5. Thermal decomposition data of **1b** and **1c** up to 900 °C.

Compound	Temperature Range (°)	Weight Loss (%)		Assignment
		Found	Calculated	
1b	200–290	21.53	22.20	6 CO + CH_3CN
(M = 941.34)	300–590	17.53	16.57	2 C_6H_6
	600–900	6.23	6.59	2 P
1c	170–290	18.34	18.71	6 CO + CH_3CN
(M = 1117.16)	290–540	17.42	16.74	1 P + 3 C_6H_6
	550–900	5.97	5.55	2 P

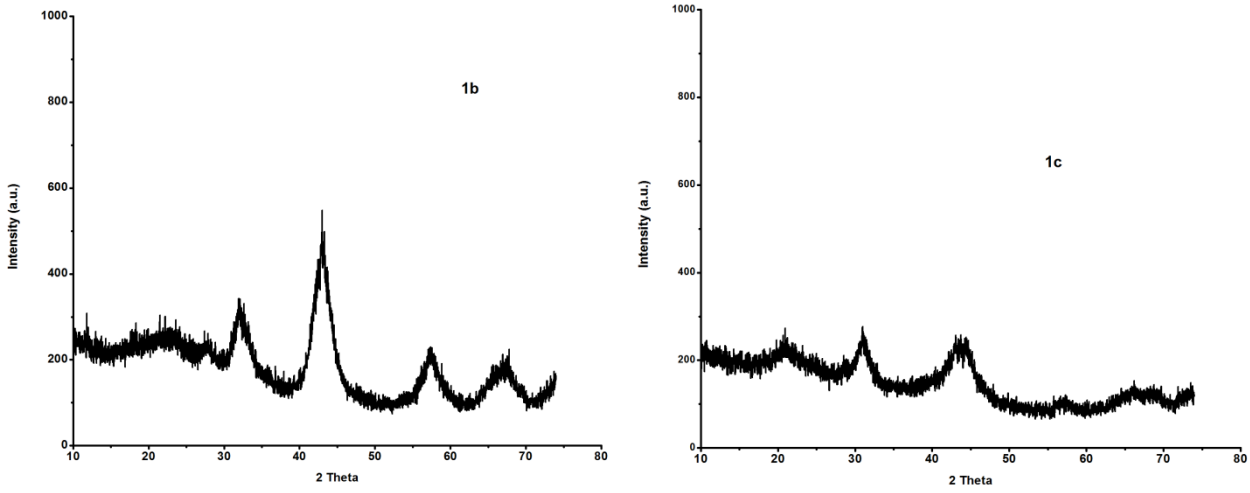


Figure S11. Powder XRD patterns of the thermal decomposition products of **1b** (left) and **1c** (right).

Powder XRD analyses were carried out on the residues of the samples from thermal decomposition. Measurements were performed with a STOE STADI-P powder diffractometer with a Cu-K_α (1.540598 Å) X-ray source; tube power: 40 KV/40 mA; scan mode: Debye-Scherrer) using a borosilicate glass capillary as sample holder during the measurement. The powder diffraction patterns were analysed with the STOE powder diffraction system software in combination with the ICDD (International Centre for Diffraction Data) powder diffraction database. The PXRD patterns of the residues (Fig. S11) indicate that they are poorly crystalline, and the very low intensity peaks could not be indexed to any phase.

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